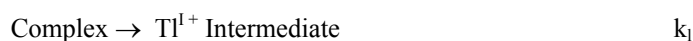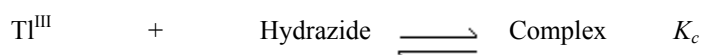# Thermodynamic Approach for Oxidation of P-Chloro Benzoic Acid Hydrazide by Thallium (III) in Acidic Medium- A Kinetic and Mechanistic Study

A. S. Varale[1], Y. S. Varale[2]

[1]Department of Chemistry, Athalye-Sapre-Pitre College, Devrukh-415804, Dist-Ratnagiri Maharashtra State, India

[2]Department of EVS, Dr. Ambedkar College of Commerce and Economics, Wadala Mumbai-400031 Maharashtra State, India

Abstract: *The kinetics of oxidation of benzoic and p-Chloro 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 K_c

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

Tl^{III}+Intermediate $\rightarrow$ Tl^I + Products 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, Thallium (III), Oxidation.

1. Introduction

Chemical kinetics is highly useful in chemical Engineering applications. It provides the most general method to determine the mechanism of reactions. Oxidation reaction is one of the most important types of organic reactions in solution in which the reagent atom (s) accepts electron from the organic molecule being oxidized. The complementary reaction between Tl^I and $AuCl_4$ was studied in 3.0 mol dm^{-3} HCl medium by Anna N Gidd and Gavisiddapa S Gokavi.

Other investigations have included those of the oxidation of captive oxalate [1] the reaction of phenyl Thallium dicarboxylate with tetramethyltin in methanol [2] oxythallation of norbornene derivatives in aqueous solution and in methanol [3] the oxidation of aryl dialkyl amines [4] the Thallium (III) promoted hydrolysis of thiol esters[5] and the Thallium (III) oxidation of catechol in chloride containing media[6]. An interesting study of oxidation of anilines by Thallium (III) acetate in aqueous acetic acid is also reported [7]. Dinesh kumar and Yugul Gupta studied oxidation of benzilic acid, phenyllactic and 2-Hydroxyisobutyric acids with Thallium(III) occurs via the formation of at least three complexes between the metal ion and organic acids.

Chromium compounds have been used in aqueous and non aqueous medium for the oxidation of a variety of organic compounds [8-9] Chromium especially Cr (VI) reagents have been proved to be versatile Reagents and capable of oxidizing almost all the oxidisible organic functional groups [10-11].The effect of varying solvent composition on the reaction rate was studied by varying the concentration of acetic acid 45% - 65%. The reaction rate increases with the increase in the proportion of acetic acid in the medium is suggesting the involvement of ion-dipole interaction [12, 13] The reaction does not induce polymerization of acrylonitrile indicating the absence of free radical pathway The reaction rate decreases with increasing the concentration of Al^{3+} ions confirming the involvement of three electron process in this 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 it'sMP.

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

... **(1)**
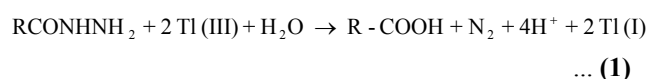
3. Results and Discussion

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 (2.30 +_ 0.1×10^{-4} S^{-1} for p-Cl 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 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 2.03 to 0.080 for p-Cl BAH at 25^{0}C.Increase in [Cl$^-$] from 7×10^{-2} to 5.4×10^{-1} mol dm^{-3} decreases 10^{-4} k(S^{-1}) from 1.4to 0.060 for p-Cl BAH at 25^{0}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. Since there is no formation of free radicals in the reaction, the reaction proceeds with two-electron transfer step.

Scheme 1: Michaelis-Menten plot for p-Chloro BAH
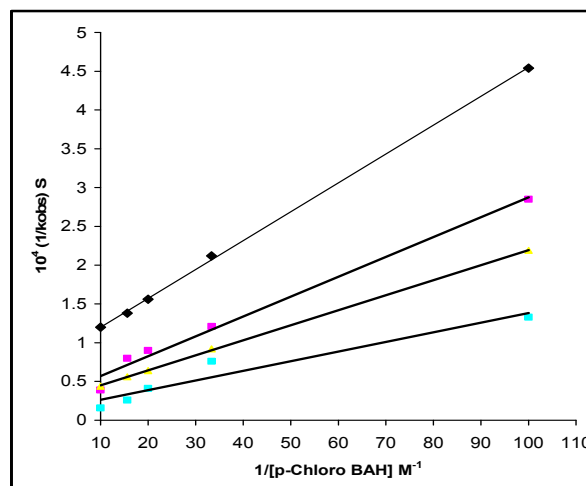
The Michealis - Menten plots of $1/k_{obs}$ versus 1/[Hydrazide] were linear with an intercept in support of the complex formation.

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 [14-16].

$$\text{Rate} = \frac{k_1 K_c \, [\text{Hydrazide}]_{total} \, [T1C1_2^+]_{total}}{(1+K_c\,[\text{Hydrazide}])\,(1+K_H[H^+])\,(1+\beta_1[Cl^-]+\beta_2\,[Cl^-]^2)} \quad (2)$$

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

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 [17-18].

Table 1: values of Kc and k$_1$ [HCl] = 0.1 moldm^{-3}, [HClO$_4$] = 0.1 moldm^{-3}[Tl^{III}] = 3.0 X 10^{-3} mol dm^{-3}, I = 0.6 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
p-Cl BAH	16.66	17.50	15.00	17.50	1.25	2.38	3.33	10.00

4. Mechanism

R=Alkyl group for acid hydrazides
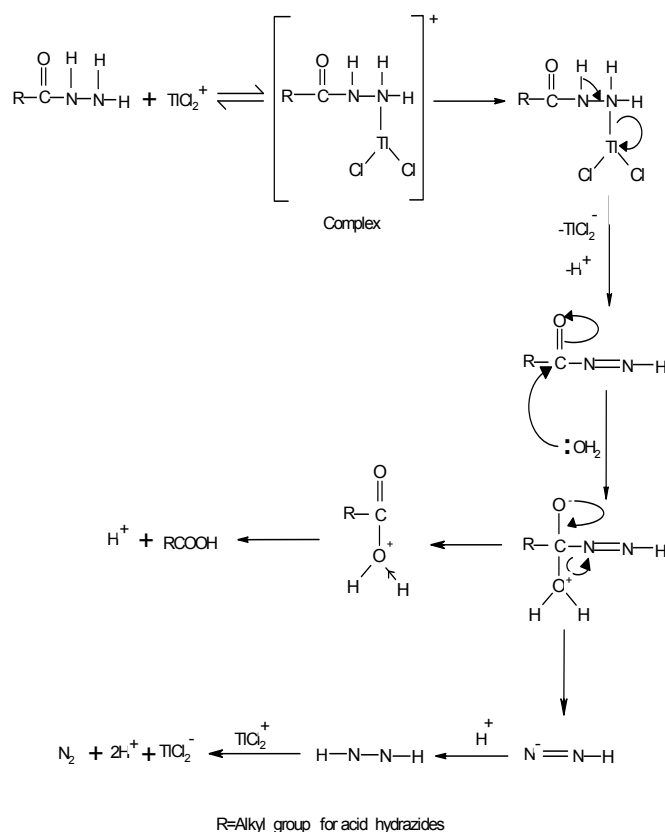
Hydrazide	Ea (KJ mol^{-1})	$\Delta H^{\#}$ (KJ mol^{-1})	$\Delta G^{\#}$ (KJ mol^{-1})	$\Delta S^{\#}$ (KJ mol^{-1})
BAH	67.45	59.74	87.94	-94.64
p-Cl BAH	68.49	71.82	98.80	-90.54

Relative Reactivities of Hydrazides

The order of reactivities of Benzoic and substituted benzoic acid hydrzides under investigation is:

p – Cl BAH < BAH < p-OCH$_3$ BAH

Chlorine has electron withdrawing inductive effect but an electron-donating mesomeric effect since it is in the para position.

Acknowledgement

References

[1] Farver, Ole and Nord G., Acta. Chem. Scand A., 32 (1978) 963.
[2] Gunkin, I.F. Butin, K.P. Beletskaya, I.P. and Reutov, O.A., Bull Acad. Sci., U.S.S.R. 27 (1978) 879.
[3] Uemura, S. Mlyoshi, H. Okano M. Morshima, I. and Inabushi T.J., Organo metal. Chem., 9 (1979) 165.
[4] Galliani, G. and Rindone, B., J. Chem. Soc., (Perkin-Trans I) 828 (1980).
[5] Patel, G. and Satchell, R.S., J. Chem. Soc., (Perkin-Trans II) 1403 (1980).
[6] Menard, R. and Zador, M., Inorg. Chem. Acta. Letts. 45 217 (1980).
[7] Radhakrishnamurthi, P.S. and Pati, S.N., *Ind. J. Chem.,* 19A 980 (1980).
[8] Sayyed Hussain, S.R. and Gour, Mazahar Farooqui, *Der Chemica Sincia.,* 2(1) (2011) 61.
[9] Sangita Sharma, Jayesh Ramani, Jasmin Bhalodia,Falguni Thakkar, *Der Chemica Sincia.,* 2(4) 140 (2011).
[10] Kothari, A Kothari S and Banerji K K, Indian J Chem., 44A, (2005) 2039.
[11] Chimatadar, S. A. Salunke, M. S. and Nandibewoor S. T. Indian J Chem., 45A (2006) 388.
[12] Parimala, S. Vaijayantyi, N. Der Chemica Sincia., 2(3) (2011) 41.
[13] Krantik Patil., *Der Chemica Sinica.,* 2(6) (2011) 245.
[14] A.S. Varale, N.P.Hilage : Kinetic and Mechanistic Study of Oxidation of Salicylic acid Hydrazide by Thallium (III) in Acidic Medium, International Journal of ChemTech Research., 3(1) (2011) 357-363.
[15] A.S. Varale, N.P.Hilage : Comparative Kinetic and Mechanistic Study of Oxidation of Benzoic, o-toluic Benzoic, p- Toluic Benzoic acid Hydrazides with Thallium (III) in Acidic Medium, Oriental Journal of Chemistry, 27(1) (2011) 113-118.
[16] A.S. Varale, N.P.Hilage : Comparative Kinetic andMechanistic Study of Oxidation of Heterocyclic Acid Hydrazides by Thallium(III) in Acidic Medium, Oxidation Communications., 35(2) (2012) 371–377.
[17] A.S. Varale, N.P.Hilage : Oxidation of o-toluic Acid Hydrazide by Thallium (III) inAcidic Medium (A Kinetic and Mechanistic, Oriental Journal of Chemistry, 29(2) (2013) 667-672.
[18] A.S. Varale, N.P.Hilage : Oxidation of p-methoxy Benzoic Acid Hydrazide by Thallium (III) in Acidic Medium (A Kinetic and Mechanistic Study) Oriental Journal of Chemistry 29(2) (2013) 519- 524