Kinetics and Mechanism of the Selective Oxidation of Benzoic and Isonicotinic Acid Hydrazides to their Corresponding Acids by Thallium (III) in Aqueous 1, 4-Dioxane Medium

Dr. Amit Shrikant Varale

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

Abstract: *Kinetics of the oxidation of benzoic and isonicotinic acid hydrazides has been studied by Thallium (III) in a mixture of perchloric and hydrochloric acid media at a constant ionic strength in 1, 4-dioxane-water medium, iodometrically. The reaction showed pseudo-first order. The reaction was found to fractional with [Hydrazide] and unity with [oxidant]. The reaction failed to induce the polymerisation of added acrylonitrile and this rules out the involvement of any radical intermediate in the reaction. 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 15^0C to 30^0C. The order of reactivity among the studied hydrazides is isonicotinic acid hydrazide > Benzoic acid hydrazide. The Michealis - Menten plots of $1/k_{obs}$ versus $1/[Hydrazide]$ were linear with an intercept in support of the complex formation. Thermodynamic parameters were determined and a suitable mechanism is proposed in accordance with the obtained results.*

Keywords: Thallium (III), benzoic and isonicotinic acid hydrazides, Oxidation, Kinetics, Mechanism

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 results of this research are of immediate interest to Engineering and to study enzyme catalyzed reactions.

Applin and Zhao 1 were the first to describe chemical clogging with iron of 51 production wells. They considered the rate of oxidation of iron (II) as a three-52 stage process. The oxidation of dissolved Fe(II) from the groundwater to 53 insoluble Fe(III), which makes up the low-crystalline iron hydroxide 54 encrustations, tends to be gradual. Apart from the pH value of the 55 groundwater, the *Eh* value and the iron concentration, iron bacteria, which 56 catalyze oxidation 9, play a major role in this process [1, 2, 3.]

The hydrazides are pharmaceutically important compounds used as antitubercular[4] and antibacterial[5, 6] agents; some of them have been reported to possess anti-inflammatory[7] and diuretic[8] 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 examined[9].The oxidation of phenol by thallium(III) acetate in aqueous acetic acid leads to formation of dione as a major product[10]. It is clear that little information is available regarding the oxidation of benzoic and isonicotinic acid hydrazides by thallium (III).Hence, the present work deals with the kinetics and mechanism of oxidation benzoic and isonicotinic acid hydrazides by thallium (III) in acidic medium.

2. Experimental

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 isonicotinic acid hydrazides were prepared from reported procedure and characterized by determining their melting points. Stock solution of benzoic and salicylic acid hydrazides were prepared in 50 % v/v, 1, 4-dioxan. Ionic strength was kept constant.
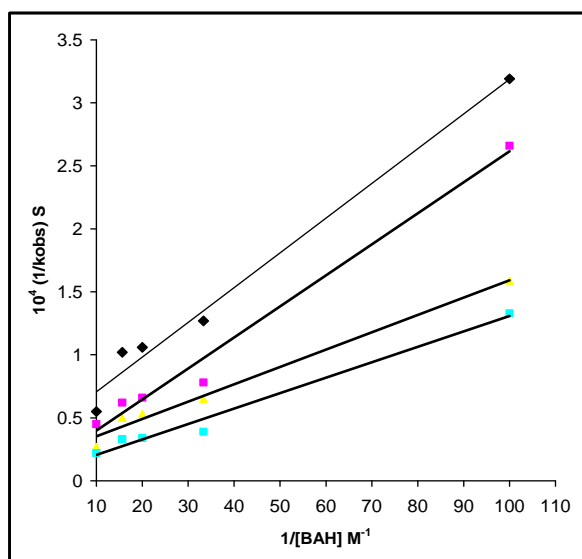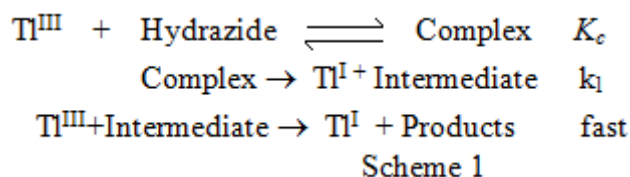
3. Results and Discussion

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 $6.4x10^{-4}$ to $6.4x10^{-3}$ mol dm^{-3} keeping the [hydrazide] constant at $1x10^{-1}$ mol dm^{-3}.Since,the pseudo first order rate constants were fairly constant($3.6 \pm 0.1x10^{-4}$ s^{-1} for benzoic acid hydrazide (BAH) at 25^0C and $8.30 \pm 0.1x10^{-4}$s^{-1} for isonicotinic acid hydrazide (ISNAH), the order with respect to [oxidant] is unity. The effect of [hydrazide] was studied between the concentration range from $1x10^{-2}$ to $1x10^{-1}$ mol dm^{-3} keeping the [oxidant] constant at $3.0x10^{-3}$ 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 $3.0x10^{-3}$,$1x10^{-1}$ 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 25^0C and

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6.2 to 0.045 x10^{-4} s^{-1} for ISNAH at 25^{0}C. Increase in [Cl$^-$] from 0.13 to 0.60 mol dm^{-3} decreases from 2.80 to 0.085 for BAH at 25^{0}C and 2.04 to 0.076 x10^{-4} s^{-1} for ISNAH. 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.

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

Scheme 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.

$$Rate = k_1 [Complex] = k_1 K_c [Hydrazide]_{free} [Tl^{III}]_{free} \quad (1)$$
$$[Tl^{III}]_{total} = [Tl^{III}]_{free} + [Complex] \quad (2)$$
$$[Tl^{III}] total = [Tl^{III}]_{free} + K_c [Hydrazide] [Tl^{III}]_{free} \quad (3)$$
$$[Tl^{III}]_{free} = [Tl^{III}]_{total}/(1 + K_c [Hydrazide]) \quad (4)$$
$$Rate = k_1 K_c [Hydrazide] [Tl^{III}]_{free} \quad (5)$$
$$k_{obs} = k_1 K_c [Hydrazide]/(1 + K_c [Hydrazide]) \quad (6)$$

Rate law 8 is verified by plotting 1/kobs 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.
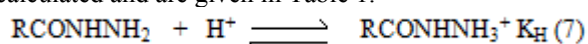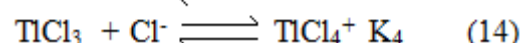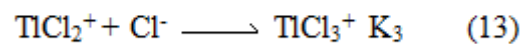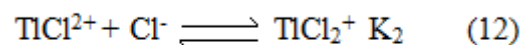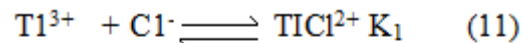
$$RCONHNH_2 + H^+ \rightleftharpoons RCONHNH_3^+ \quad K_H \quad (7)$$
$$[Hydrazide]_{total} = [Hydrazide]_{free} + [Hydrazide]_{protonated} \quad (8)$$
$$[Hydrazide]_{total} = [Hydrazide]_{free} + K_H [Hydrazide]_{free} \quad (9)$$
$$[Hydrazide]_{free} = [Hydrazide]_{total} / (1 + K_H [H^+]) \quad (10)$$

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 X 10^8, K_2 = 3.98 X 10^{13}, K_3 = 6.02 X 10^{15} and K_4 = 1.0 X 10^{18} mol^{-1}dm^3.

$$Tl^{3+} + Cl^- \rightleftharpoons TlCl^{2+} \quad K_1 \quad (11)$$
$$TlCl^{2+} + Cl^- \rightleftharpoons TlCl_2^+ \quad K_2 \quad (12)$$
$$TlCl_2^+ + Cl^- \rightleftharpoons TlCl_3^+ \quad K_3 \quad (13)$$
$$TlCl_3 + Cl^- \rightleftharpoons TlCl_4^+ \quad K_4 \quad (14)$$
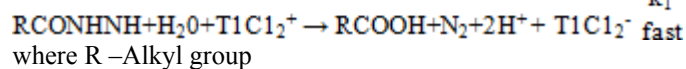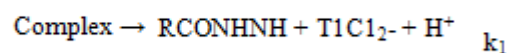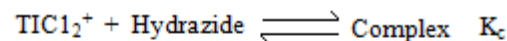
All the thallium (III) will exists as TlCl$_2^+$ and its concentration can be expressed by Equation 17. The [TlCl$_2$]$^+_{free}$ can now be given by eq. 19 where, $\beta_1 = K_3/K_2 = 151$ and $\beta_2 = K_4/K_3 = 166$, further, using Equations 18 and 19 the concentrations of [TlCl$_2$]$^+_{free}$, 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.

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

The concentration of both of [TlCl$_2^+$] $_{free}$ and TlCl$_3$ parallel the values of rate constants as [Cl$^-$] changes but the order [Cl$^-$] is $- 1.5$, which makes [TlCl$_2^+$] $_{free}$ as the only active species.

$$TlCl_2^+ + Hydrazide \rightleftharpoons Complex \quad K_c$$
$$Complex \rightarrow RCONHNH + TlCl_2^- + H^+ \quad k_1$$
$$RCONHNH + H_2O + TlCl_2^+ \rightarrow RCOOH + N_2 + 2H^+ + TlCl_2^- \quad fast$$

where R –Alkyl group

Scheme 2

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. 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 isonicotinic acid hydrazides respectively.
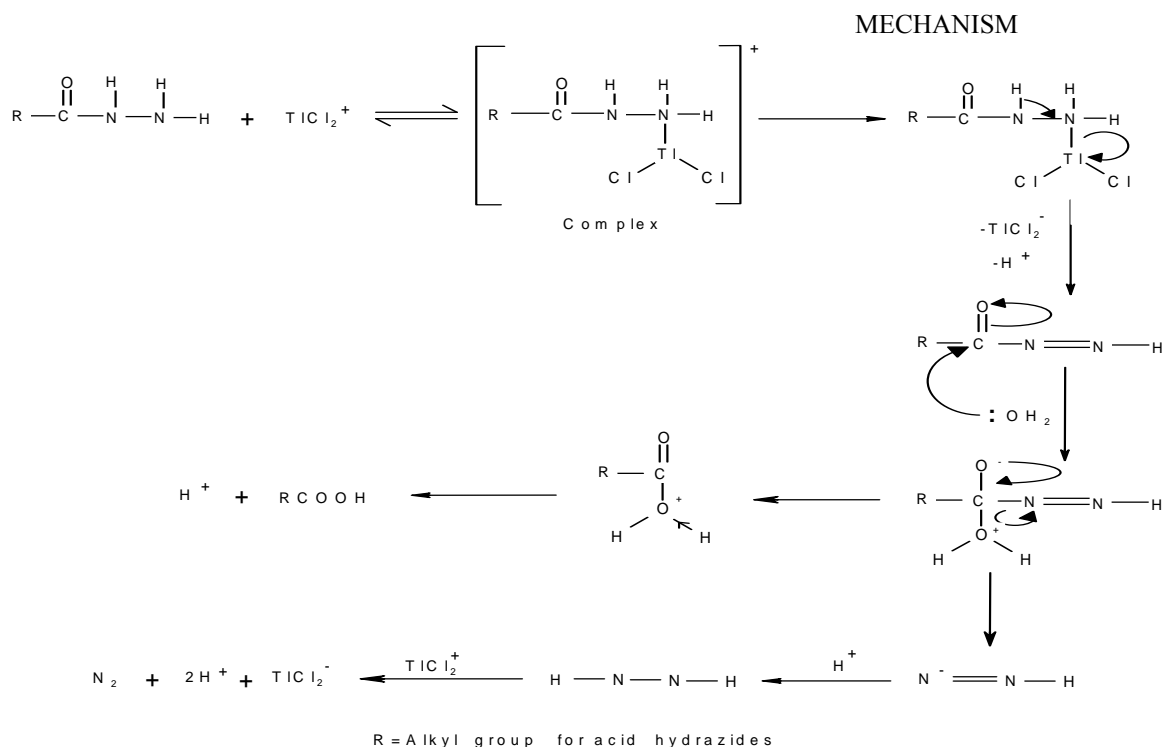
$$Rate = \frac{k_1 K_c [Hydrazide]_{total} [TlCl_2^+]_{total}}{(1 + K_c [Hydrazide]) (1 + K_H [H^+]) (1 + \beta_1 [Cl^-] + \beta_2 [Cl^-]^2)} \quad (18)$$

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

Table 1 – values of Kc and k_1
HCl] = 0.1 moldm^{-3}, [HClO$_4$] = 0.1 mol dm^{-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*
BAH	59.09	55.50	47.69	40.00	1.23	2.05	2.58	4.44
ISNAH	6.17	7.52	8.10	9.70	10.00	14.30	20.00	33.34

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MECHANISM

R = Alkyl group for acid hydrazides

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 permittivity[11-12].

Table 2: Activation Parameters

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
ISNAH	65.52	59.74	90.49	-103.19

4. Conclusion

The order of reactivities of Benzoic and isonicotinic acid hydrazides under investigation is -
 PAH < NAH < BAH < ISNAH.

In the case of heterocyclic hydrazides, nitrogen is electron withdrawal from ring carbon atoms hence, decrease in rate of oxidation of PAH and NAH as compared with benzoic acid hydrazide. In the case of ISNAH the electron withdrawing inductive effect is less as compared with PAH and NAH. But rate of oxidation is found to be faster than BAH. Its behavior is seen to be anomalous.

References

[1] Houben, G. *Ground Water.,* 42 78 312 (2004).
[2] David, E. R. Stevenson, J. M. *Water Res.,* **29** 365 313 (1995).
[3] Obradović, V. Majkić-Dursun, B. Petković, A Dimkić, M. *Water 2012,* in Proceeding *of* 314 *.the 41st Annual Conference of the Serbian Water Pollution Control Society*, 315, 359 316 (2012).
[4] Dimkić, M. Pušić, V. Obradović, S. Kovačević, *Water Sci. Tech.,* **65** 2206 317 (2012).
[5] de Vet, W. W. Dinkla, L. C. Rietveld, M. C. van Loosdrecht, M. *Water Res*., 45, 318 (2011).
[6] Werner, W. *J org chem.,* 18, 133, (1953).
[7] Madzhoyan, A.L *Arm Khim Zh.,* 19, 793, (1966).
[8] Winter stein, A. Hegedus, H. *Helv.Chem.Acta.,* 39, 229 (1956).
[9] Pfister, R. Soilman, A. *Chem. Abstract.,* 68, 492 (1968).
[10] Jucker F. and Linde A. *Nomann Helv chim Acta.,* 45, 2316 (1962).
[11] Varale, A.S. Hilage, N.P. Comparative Kinetic and Mechanistic Study of Oxidation of Benzoic, o-toluic Benzoic, p- Toluic Benzoicacid Hydrazides with Thallium (III) in Acidic Medium, Oriental Journal of Chemistry, 27(1), 113-118 (2011).
[12] Varale, A.S. Hilage, N.P. Comparative Kinetic and Mechanistic Study of Oxidation of Heterocyclic Acid Hydrazides by Thallium (III) in Acidic Medium, Oxidation Communications. 35(2),371-377 (2012).