



SYNTHESIS, MECHANISTIC INTERPRETATION AND KINETIC APPROACH OF BENZOIC, p-METHOXY, p-CHLORO BENZOIC ACID HYDRAZIDES BY THALLIUM (III) IN ACIDIC MEDIUM

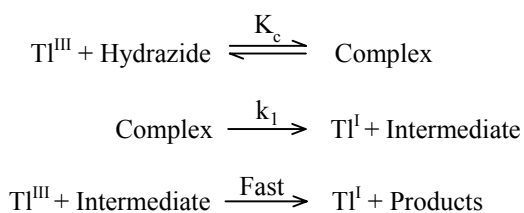
AMIT S. VARALE* and YASHODHARA S. VARALE^a

Department of Chemistry, Athalye-Sapre-Pitre College, DEVRUKH – 415804,
Dist-Ratnagiri (M.S.) INDIA

^aDepartment of EVS, Dr. Ambedkar College of Commerce and Economics, Wadala,
MUMBAI – 400031 (M.S.) INDIA

ABSTRACT

The kinetics of oxidation of benzoic p-methoxy and p-Chloro 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 increase in $[\text{H}^+]$ and $[\text{Cl}^-]$ decreases the rate of the reaction. The activation parameters were also determined and a mechanism is predicted.

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

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,

* Author for correspondence; E-mail: amitvarale @ gmail.com

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.

The study of oscillating chemical reactions has been dominated by the Belousov-Zhabotinskii (BZ) reaction. It is also called the chemical clock, which is similar to the biological clock. During the last 10 to 20 years, vitamin C, glucose, lactic acid, fructose, amino acid, lactose, maleic acid and ethanol have been reported^{1,2} to be very important reaction substrates in oscillation reactions; they also play an important role in the synthesis of cell substances in life.

Other investigations have included those of the oxidation of captive oxalate³, the reaction of phenyl Thallium dicarboxylate with tetramethyltin in methanol⁴, oxythallation of norbornene derivatives in aqueous solution and in methanol⁵, the oxidation of aryl dialkyl amines⁶, the Thallium (III) promoted hydrolysis of thiol esters⁷, and the Thallium (III) oxidation of catechol in chloride containing media⁸. An interesting study of oxidation of anilines by Thallium (III) acetate in aqueous acetic acid is also reported⁹.

The literature survey on oxidation of various organic compounds including hydrazides by Tl (III) revealed that oxidation of hydrazides appears not to have received much attention.

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

EXPERIMENTAL

The oxidation of carboxylic acid hydrazide by Thallium (III) is carried out in water 1,4-dioxan mixture (50% v/v). To ensure that the oxidation of 1,4-dioxan with Thallium (III) under these experimental conditions is carried out without taking hydrazide. Repeated experiments were performed. But it is confirmed that 1,4-dioxan does not undergo oxidation with Thallium (III). The oxidation by Thallium (III) ion takes place slowly but proceeds with a measurable velocity in HCl medium.

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 [HClO₄] of 0.1 mol dm⁻³ each and ionic strength of 0.6 mol dm⁻³. Concentration of oxidant was varied from 6.4 x 10⁻⁴ to 6.4 x 10⁻³ mol dm⁻³ keeping the [hydrazide] constant at 1 x 10⁻¹ mol dm⁻³. Since, the pseudo first order rate constants were fairly constant (3.6 ± 0.1 x 10⁻⁴ s⁻¹ for BAH at 25°C and 6.70 ± 0.1 x 10⁻⁴ s⁻¹ for p-Methoxy BAH at 25°C and 2.30 ± 0.1 x 10⁻⁴ s⁻¹ for p-Chloro BAH at 25°C, the order with respect to [oxidant] is unity. The effect of [hydrazide] was studied between the concentration range from 1 x 10⁻² to 1 x 10⁻¹ mol dm⁻³ keeping the [oxidant] constant at 3.0 x 10⁻³ 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 3.0 x 10⁻³, 1 x 10⁻¹ and 0.6 mol dm⁻³, respectively. To vary [H⁺] and [Cl⁻], HClO₄ 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°C and 74.20 to 1.05 for p-Methoxy BAH at 25°C and from 2.03 to 0.080 for p-Chloro BAH at 25°C. Increase in [Cl⁻] from 0.13 to 0.60 mol dm⁻³ decreases 10⁻⁴ k (S⁻¹) from 2.80 to 0.085 for BAH at 25°C and 7.35 to 1.05 for p-Methoxy BAH at 25°C and from 1.40 to 0.060 for for p-Chloro 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.^{10,11}

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 pseudo first order rate constants indicating absence of free radicals.^{12,13} 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 determined¹⁴⁻¹⁵.

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

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

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 p-Chloro benzoic acid hydrazides, respectively. The electrophilic character of TlCl_2^+ among the thallium (III) chlorocomplexes is highest thus making it the reactive species¹⁶⁻¹⁸.

Table 1: Values of K_c and k_1

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

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

Hydrazide	Kc. (mol dm^{-3})				$10^4 \times k_1$ (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
p-OCH ₃ BAH	7.42	8.00	7.00	7.57	0.10	0.12	0.16	0.22
p-Cl BAH	16.66	17.50	15.00	17.50	1.25	2.38	3.33	10.00

Activation parameters for selected hydrazides

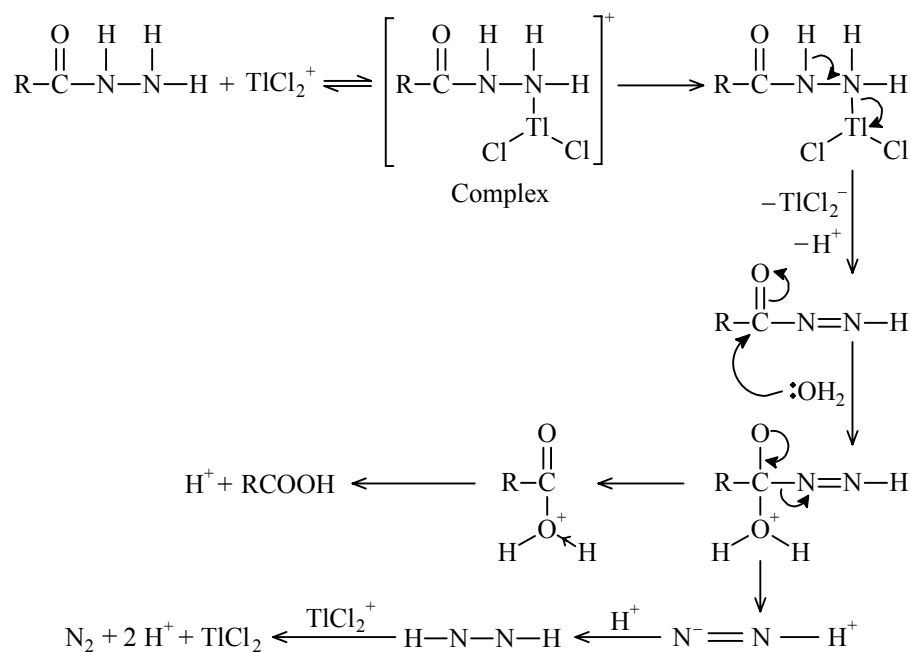
Hydrazide	Ea (KJ mol ⁻¹)	ΔH^\ddagger (KJ mol ⁻¹)	ΔG^\ddagger (KJ mol ⁻¹)	ΔS^\ddagger (KJ mol ⁻¹)
BAH	67.45	59.74	87.94	-94.64
p-OCH ₃ BAH	41.74	36.78	97.69	-204.38
p-Cl BAH	68.49	71.82	98.80	-90.54

Relative reactivities of hydrazides

The order of reactivities of Benzoic and substituted benzoic acid hydrazides under investigation is –



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

Mechanism

R = Alkyl group for acid hydrazides

ACKNOWLEDGEMENT

The authors are thankful to Dr. G. S. Gokavi for his keen interest and help during the course of work.

REFERENCES

1. J. G. Shen, J. H. San and G. S. Dang, J. Hebei University, **5**, 21 (1995).
2. C. L. Yuan, Z. X. Li and J. C. Wang, Acta Physico-Chimica Sinica, **10**, 87 (1994).
3. Farver, Ole and G. Nord, Acta. Chem. Scand A., **32**, 963 (1978).
4. I. F. Gunkin, K. P. Butin, I. P. Beletskaya, and O. A. Reutov, Bull Acad. Sci., U.S.S.R., **27**, 879 (1978).
5. S. Uemura, H. Mlyoshi, M. Okano Morshima and T. J. Inabushi, Organo Metal. Chem., **165**, 9 (1979).
6. G. Galliani and B. J. Rindone, Chem. Soc., (Perkin-Trans I), 828 (1980).

7. G. Patel and R. S. Satchell, *J. Chem. Soc.*, (Perkin-Trans II) 1403 (1980).
8. R. Menard and M. Zador, *Inorg. Chem. Acta. Letts.*, **45 L**, 217 (1980).
9. P. S. Radhakrishnamurthi and S. N. Patil, *Ind. J. Chem.*, **19A**, 980 (1980).
10. R. C. Weast, *Handbook of Chemistry and Physics*, Edited by, 50th Edn., (CRC) (1970).
11. (a) K. Kazo, T. Hirakazo, K. Hisashi and T. Zenzo, *Chem. Pharm. Bull.*, **11**, 797 (1963).
(b) P. V. Krishnarao, M. S. Frank and A. K. Ramaih, *React. Kinet. Cata. Lett.*, **9**, 59 (1978).
(c) P. V. Krishnarao, M. S. Frank and A. K. Ramaih, *Indian J. Chem.*, **16A**, 418 (1978).
(d) A. K. Ramaih, M. S. Frank, G. Baburao and P. V. Krishnarao, *Indian J. Chem.*, **18A**, 416 (1979).
12. A. G. Lee, *The Chemistry of Thallium*, Elsevier, London (1971) p. 48.
13. (a) A. Mckillop, J. D. Hunt, R. D. Naylor and E. C. Taylor, *J. Am. Chem.*, **93**, 4918 (1971).
(b) R. N. Buttler, G. J. Morris and A. M. O' Donohue, *J. Chem. Res. (s) Soc.*, 61 (1981).
14. A. S. Varale and N. P. Hilage, Oxidation of Nicotinic Acid Hydrazide by Thallium (III) in Acidic Medium: A Kinetic and Mechanistic Study, *Int. J. Chem. Sci.*, **7(3)**, 2173 (2009).
15. A. S. Varale and N. P. Hilage, Kinetic and Mechanistic Study of Oxidation of Salicylic Acid Hydrazide by Thallium (III) in Acidic Medium, *Int. J. Chem. Tech. Res.*, **3(1)**, 357 (2011).
16. A. S. Varale and 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 J. Chem.*, **27(1)**, 113 (2011).
17. A. S. Varale and N. P. Hilage, Comparative Kinetic and Mechanistic Study of Oxidation of Heterocyclic Acid Hydrazides by Thallium(III) in Acidic Medium, *Oxidation Communications*, **35(2)**, 371 (2012).
18. A. S. Varale and N. P. Hilage, Oxidation of o-toluic Acid Hydrazide by Thallium (III) in Acidic Medium: A Kinetic and Mechanistic, *Oriental J. Chem.*, **29(2)**, 667 (2013).

Revised : 11.06.2014

Accepted : 13.06.2014