CHAPTER – I V

DISCUSSION

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It has already been mentioned that the aim of the present study is not only to formulate the mechanism of the reaction under investigation but also to explain the relative reactivities of benzoic acid and 2-chloro benzoic acid hydrazides. Hence it is necessary to review the various mechanistic criteria usually employed in the determination of reaction mechanism and to suggest possible mechanism on the basis of experimental facts.
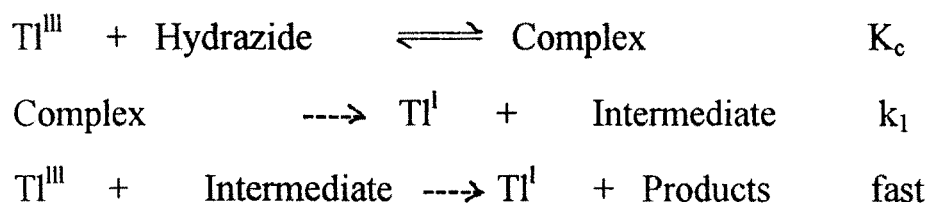
A 'mechanism of reaction' is a concept which explains the transformation of reactant (s) into product (s). Chemical reactions often occur in a number of relatively simple steps in which there is always a slowest of all other steps. The overall rate of reaction is governed by slowest step which is called the rate determining step. The species which occur in steps preceding the rate determining step appear in the rate law but those which react after the slowest step do not appear in the rate expression.

The most rational approach of Arrhenius[1] for explaining the chemical reaction is a placing the concept of molecular activation as a pre-requisite for chemical reaction. This concept of activation is now universally accepted and forms the basis of all subsequent theories of chemical reaction. Evans, Polanyl[2] and Eyring[3] have postulated that molecular collisions between energized molecules result in the formation of activated complex.

Oxidation of organic compounds by thallium(III) may involve either one-electron or two-electron transfer reactions. Generation of aromatic radical cations occur in one-electron transfer reactions which have been utilized for dehydrodimerization[4] and intramolecular[5] cyclizaions. While,

two-electron transfer reactions generally involve either oxythallation or electrophilic substitution or formation of complex and their subsequent decomposition without free radical intervention. In the present study since there was no effect of added acrylonitrile, a free radical scavenger, rules out the possibility of such free radical formation, therefore, the reaction proceeds with two electron transfer . The order in thallium (III) was found to be unity as evidenced by the linearity of the pseudo-first-order plots of log[Tl(III)] versus time for all the runs studied whereas, the order in the hydrazide were found to be fractional. Such fractional order in substrate concentration is due to the prior complex formation equilibrium between the reactants. The linearity of Michealis-Menten plot of $1/k_{obs}$ versus 1/[Hydrazide]. with an intercept is also 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.

The rate according to Scheme 1 is given by equation 1. Since, total $[Tl^{III}]$ exists in the form of free $[Tl^{III}]$ and the complex (Equation 2) the $[Tl^{III}]_{free}$ is given by equation 4. The overall rate law is now expressed by equation 5 and the pseudo-first-order rate constant, k_{obs}, by equation 6.

Tl^{III} + Hydrazide $\rightleftharpoons$ Complex K_c

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

Tl^{III} + Intermediate $\dashrightarrow$ Tl^{I} + Products fast

Scheme - 1

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

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

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

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

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

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

Rate law 6 is verified by plotting $1/k_{\text{obs}}$ against $1/[\text{Hydrazide}]$ at four different temperatures (Figures 1 & 2) and from the slopes and intercepts of these plots the values of k_1 and K_c were calculated and are given in Table-II.

The effect of hydrogen and chloride ion concentrations on the reaction is due to the protonation of hydrazide[6] and different chloro-complexes[7] of thallium(III) present in the solution. Hydrazides are known to be protonated in acid medium according to equation 7.

$$\text{RCONHNH}_2 \quad + \quad \text{H}^+ \rightleftharpoons \text{RCONHNH}_3^+ \quad K_H \qquad (7)$$
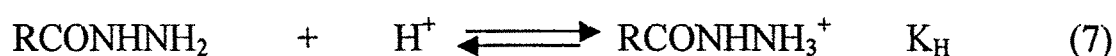
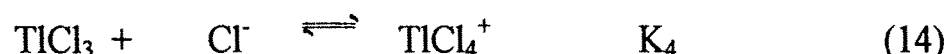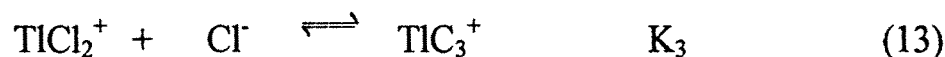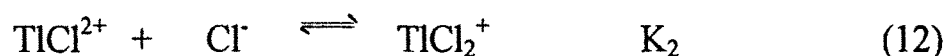Therefore, total [Hydrazide] can be expressed by equation 8 and the free [Hydrazide] by equation 10.
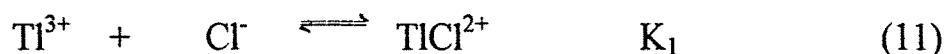
$$[\text{Hydrazide}]_{\text{total}} = [\text{Hydrazide}]_{\text{free}} + [\text{Hydrazide}]_{\text{protonated}} \qquad (8)$$

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

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

Since the rate of the reaction decreases as the $[\text{H}^+]$ increases (Table III), free hydrazide is the active species which is also supported by the fact that there was no effect of ionic strength on the reaction 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 complexed with thallium(III) as represented in equlibria 11 to 14. The values of respective stability constants[7] are $K_1 = 1.38 \times 10^8$, $K_2 + 3.98 \times 10^{13}$, $K_3 = 6.02 \times 10^{15}$ and $K_4 = 1.0 \times 10^{18}$ M^{-1}. In presence of 0.03 M chloride ion concentration all the thallium(III) will

$$Tl^{3+} + Cl^- \rightleftharpoons TlCl^{2+} \qquad K_1 \qquad (11)$$

$$TlCl^{2+} + Cl^- \rightleftharpoons TlCl_2^+ \qquad K_2 \qquad (12)$$

$$TlCl_2^+ + Cl^- \rightleftharpoons TlC_3^+ \qquad K_3 \qquad (13)$$

$$TlCl_3 + Cl^- \rightleftharpoons TlCl_4^+ \qquad K_4 \qquad (14)$$

exists as $TlCl_2^+$ and its concentration can be expressed by equation 15. The $[TlCl_2^+]$ can now be given by equation 17 where $\beta_1 = K_3/K_2 = 151$ and

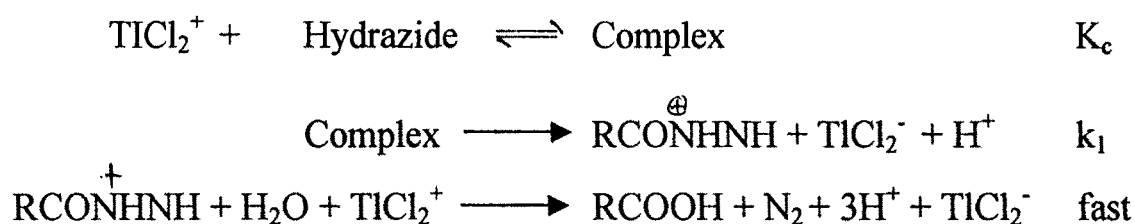$$[Tl (III)]_{total} = [TlCl_2^+]_{total} = [TlCl_2^+]_{free} + [TlCl_3] + [TlCl_4^-] \qquad (15)$$

$$[TlCl_2^+]_{total} = [TlCl_2^+]_{free} \ (1 + \beta_1[Cl^-] + \beta_2[Cl^-]^2) \qquad (16)$$

$$[TlCl_2^+]_{free} = [TlCl_2^+]_{total} \ / \ (1 + \beta_1[Cl^-] + \beta_2[Cl^-]^2) \qquad (17)$$

$\beta_2 = K_4/K_3 = 166$. Further, using equations 16 and 17 the concentrations of $[TlCl_2^+]_{free}$, $TlCl_3$ and $TlCl_4^-$ were calculated at different chloride ion concentrations (Table IV) and compared with the change in the rate constant as the chloride ion concentration varies. The concentrations of both $[TlCl_2^+]_{free}$ and $TlCl_3$ parallel the values of rate constants as the chloride ion concentration changes but the order in chloride ion concentration is -1.5 which makes $[TlCl_2^+]_{free}$ as the only active species. The data of Table-IV are also used to plot $[TlCl_2^+]_{free}$ and the values of rate constants as a function of chloride ion concentration (Fig. 3) which clearly indicate $[TlCl_2^+]_{free}$ as the reactive species of the oxidant.

The mechanism considering $TlCl_2^+$ of oxidant and free hydrazide of the substrate as the active species can now be represented by Scheme 2 with respective

$$TlCl_2^+ + \text{Hydrazide} \rightleftharpoons \text{Complex} \qquad K_c$$

$$\text{Complex} \longrightarrow R\overset{\oplus}{CONHNH} + TlCl_2^- + H^+ \qquad k_1$$

$$R\overset{+}{CONHNH} + H_2O + TlCl_2^+ \longrightarrow RCOOH + N_2 + 3H^+ + TlCl_2^- \qquad fast$$
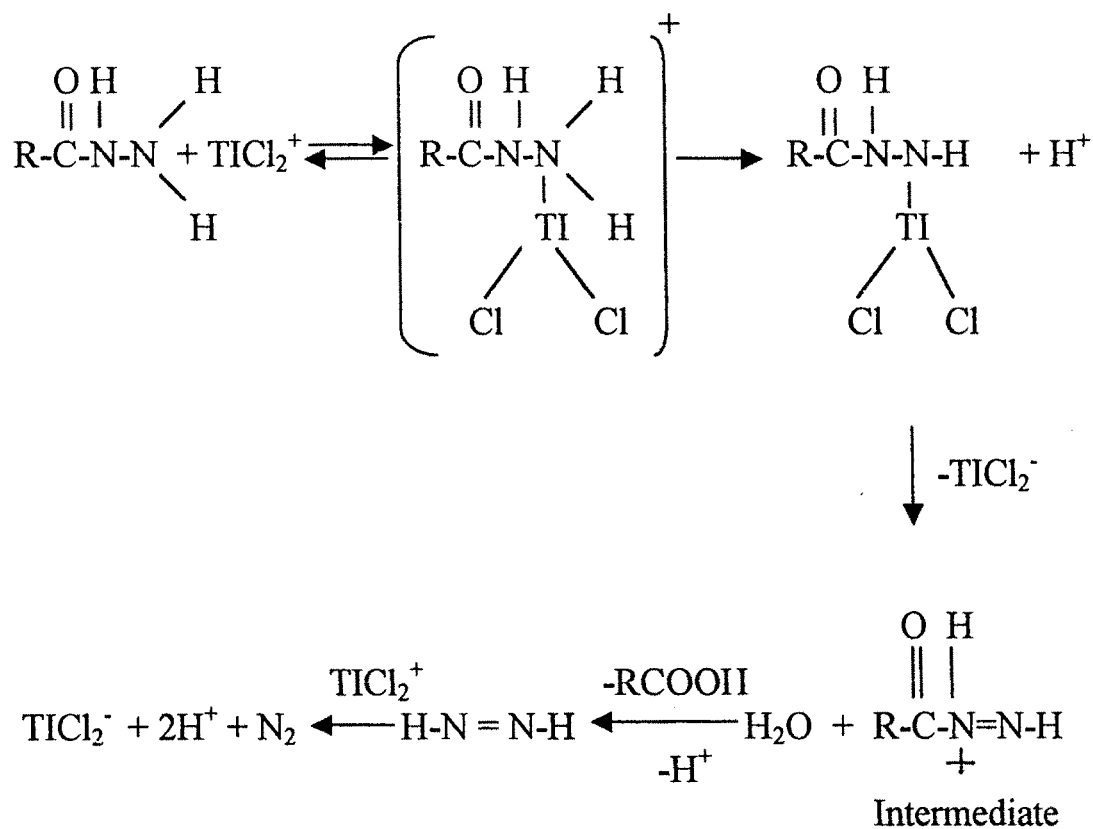
where $R = C_6H_5$ for benzoic acid hydrazide and

ClC_6H_4 for o-chlorobenzoic acid hydrazide

Scheme 2

$$\text{Rate} = \frac{k_1 K_c \,[\text{Hydrazide}]_{total}\,[TlCl_2^+]_{total}}{(1 + K_c\,[\text{Hydrazide}])\,(1 + K_H[H^+])\,(1 + \beta_1[Cl^-] + \beta_2\,[Cl^-]^2)} \qquad (18)$$

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

rate law and the expression for the pseudo-first-order rate constant by equations 18 and 19. The rate law 19 was verified by plotting $1/k_{obs}$ against $1/[\text{Hydrazide}]$ (Fig. 1 & 2) and $1/k_{obs}$ against $[H^+]$ (Fig. 4) 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-II and those of K_H were found to be 13 and 16 M^{-1} for benzoic and o-chlorobenzoic acid hydrazides respectively. the electrophilic character of thallium(III)-cholro complex increases as $TlCl_2^+ > TlCl_3 > TlCl_4$ thus making the

$$
\begin{array}{c}
\overset{\text{O}}{\underset{\parallel}{\text{R-C}}}\text{-}\overset{\text{H}}{\underset{\mid}{\text{N}}}\text{-N}\overset{\diagup \text{H}}{\underset{\diagdown \text{H}}{}} + \text{TlCl}_2^{+}
\end{array}
\rightleftharpoons
\left[
\begin{array}{c}
\overset{\text{O}}{\underset{\parallel}{\text{R-C}}}\text{-}\overset{\text{H}}{\underset{\mid}{\text{N}}}\text{-N}\overset{\diagup \text{H}}{\underset{\diagdown}{} } \\
\underset{\displaystyle \text{Tl}\ \text{H}}{} \\
\underset{\displaystyle \text{Cl} \quad \text{Cl}}{}
\end{array}
\right]^{+}
\longrightarrow
\begin{array}{c}
\overset{\text{O}}{\underset{\parallel}{\text{R-C}}}\text{-}\overset{\text{H}}{\underset{\mid}{\text{N}}}\text{-N-H} \quad + \text{H}^{+}\\
\underset{\displaystyle \text{Tl}}{} \\
\underset{\displaystyle \text{Cl} \quad \text{Cl}}{}
\end{array}
$$

$$\Big\downarrow\ -\text{TlCl}_2^{-}$$

$$
\text{TlCl}_2^{-} + 2\text{H}^{+} + \text{N}_2 \xleftarrow{\ \text{TlCl}_2^{+}\ } \text{H-N} = \text{N-H} \xleftarrow[-\text{H}^{+}]{\ -\text{RCOOH}\ } \text{H}_2\text{O} + \underset{\displaystyle +}{\overset{\text{O}\ \text{H}}{\underset{\parallel\ \mid}{\text{R-C-N}=\text{N-H}}}}
$$

Intermediate

where R = C_6H_5 for benzoic acid hydrazide and
ClC_6H_4 for o-chlorobenzoic acid hydrazide

Scheme 3

former species as the reactive ones. The detailed mechanism involves electrophilic substitution on the nitrogen of the hydrazide with the formation of N-Tl bond as shown in Scheme 3 which decomposes in the subsequent step with direct two electron transfer from hydrazide to thallium to give an intermediate followed by fast steps. The activation parameters with respect to slow step, k_1, were determined for benzoic acid and o-chlorobenzoic acid hydrazides and the values are given in the Table-V. Considerable decrease

in the entropy of activation is due to formation more ordered transition state as shown in Scheme 3. Chlorosubstitution in the ortho position retards the rate of oxidation of the hydrazide. Although, chloro group can withdraw electron density from saturated carbon chains by induction it is also capable of supplying π-electrons which retards the oxidation of o-chlorobenzoic acid hydrazide. The mechanism involves neutral hydrazide as the active substrate thus the reaction is unaffected by the change in the ionic strength. The increase in ethanol content in the reaction medium decreases the rate. Such an effect of the solvent is due to the stabilization of the complex formed between[8] reactants in a low relative permittivity.

Table I -   Effect of [hydrazide] on the oxidation of
hydrazides in 50% v/v ethanol.

10[Hydrazide]/M	$10^4 \times k_{obs}\ s^{-1}$							
	BAH				o-ClBAH			
	25°C	35°C	45°C	55°C	25°C	35°C	45°C	55°C
0.16	0.38	0.77	1.5	3.1	0.08	0.17	0.34	0.69
0.30	0.61	1.3	2.3	4.8	0.15	0.31	0.61	1.2
0.64	0.92	1.9	3.8	7.7	0.31	0.63	1.3	2.4
1.28	1.5	3.1	6.1	12.3	0.44	0.82	1.6	3.2
1.60	1.9	3.8	7.1	15.4	0.64	1.3	2.6	5.1

Table II - Values of K_c and k_1 (conditions as in Table I)

Temp.	BAH	ClBAH	BAH	ClBAH
25 °C	10.3	3.2	2.6	1.7
35 °C	10.7	4.5	5.3	2.5
45 °C	11.1	5.0	10	5.0
55 °C	11.6	6.8	20	6.7

Table III - Effect of [H^+] on the oxidation of hydrazides in 50% v/v ethanol.

[HCl] = 0.3 M; [T^{III}] = 3.0 x 10^{-3} M;

[Hydrazide] = 3.0 x 10^{-2} M; I = 0.3 M.

10[H^+] / M	10^5 x k_{obs} s^{-1}	
	BAH[a]	o-ClBAH[b]
0.2	6.4	5.1
0.7	3.8	3.1
1.7	2.4	1.7
2.7	1.7	1.1

[a] at 25°C

[b] at 35°C

Table IV - Effect of [Cl⁻] on the oxidation of hydrazides
in 50% v/v ethanol.

$[H^+] = 0.3$ M; $\qquad$ $[T^{III}] = 3.0 \times 10^{-3}$ M;

$[Hydrazide] = 3.0 \times 10^{-2}$ M; $\qquad$ $I = 0.3$ M.

				$10^5 \times k_{obs}$ s^{-1}	
$10[Cl^-]$/M	$10^5 \times [TlCl_2^+]$	$10^4 \times [TlCi_3]$	$10^3 \times [TlCi_4^-]$	BAH[a]	o-ClBAH[b]
0.3	10.7	4.87	2.40	25.6	15.4
0.5	4.22	3.18	2.65	6.9	3.83
1.0	1.13	1.70	2.85	2.8	1.70
2.0	0.29	0.87	2.93	0.73	0.67
3.0	0.13	0.59	2.93	0.73	0.67

[a] at 25°C

[b] at 35°C

Table V - Activation parameters with respect to
k$_1$ of Scheme 2 (Conditions as in Table I).

	BAH	o-ClBAH
$\Delta H^{\#}$ kJ mole^{-1}	57.8	52.9
$\Delta G^{\#}$ kJ mole^{-1}	116.8	111.7
$-\Delta S^{\#}$ JK^{-1} mole^{-1}	190.6	190.1

Figure 1. Plot of 1/ k_{obs} versus 1/[BAH] (Conditions as in Table I)
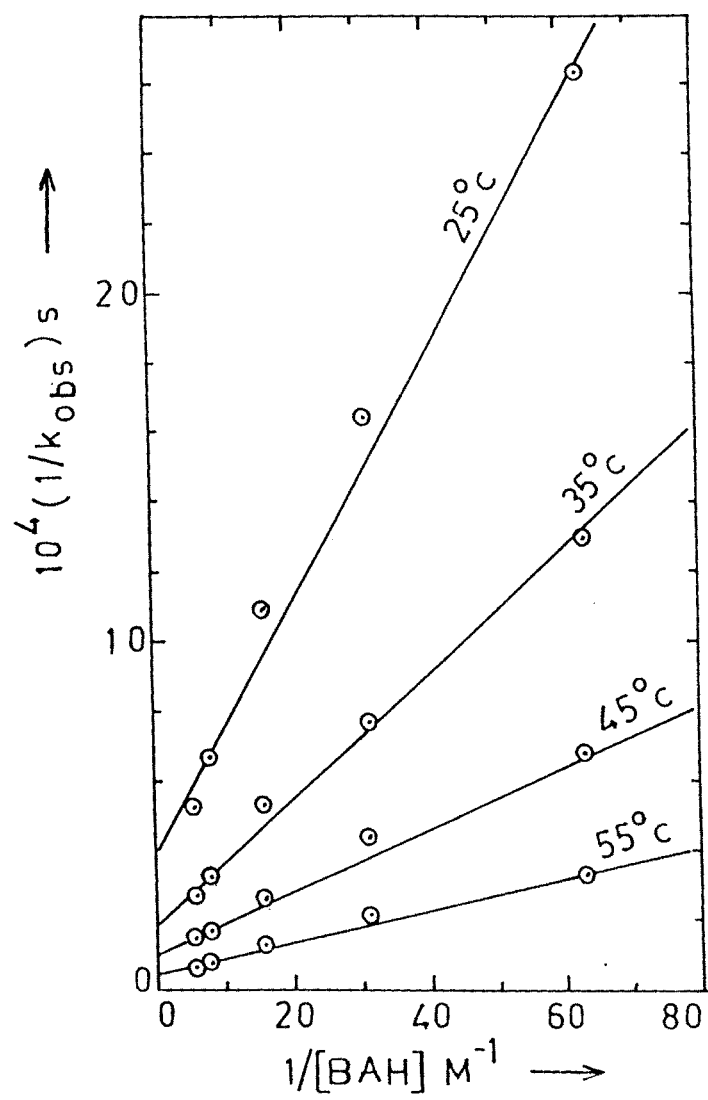
Figure 2. Plot of 1/ k_{obs} versus 1/[o-ClBAH] (Conditions as in Table I)
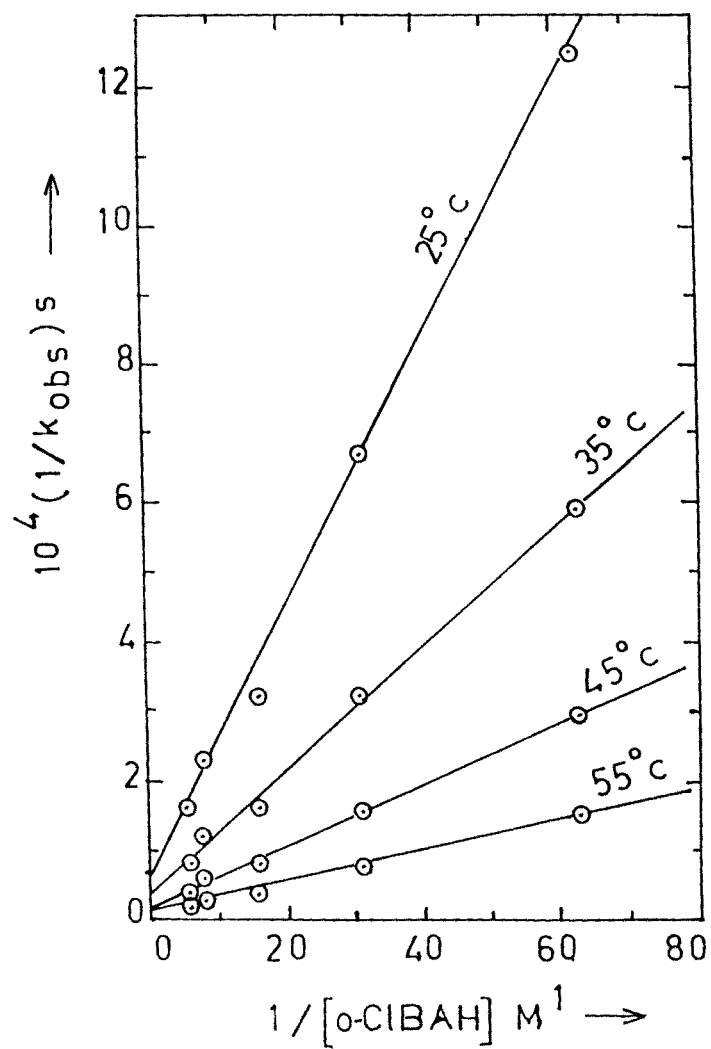
Figure 3. Plot of [TlCl$_2^+$] ($\bullet$) and k$_{obs}$ (o- BAH and $\circleddash$-o-ClBAH) as a function of
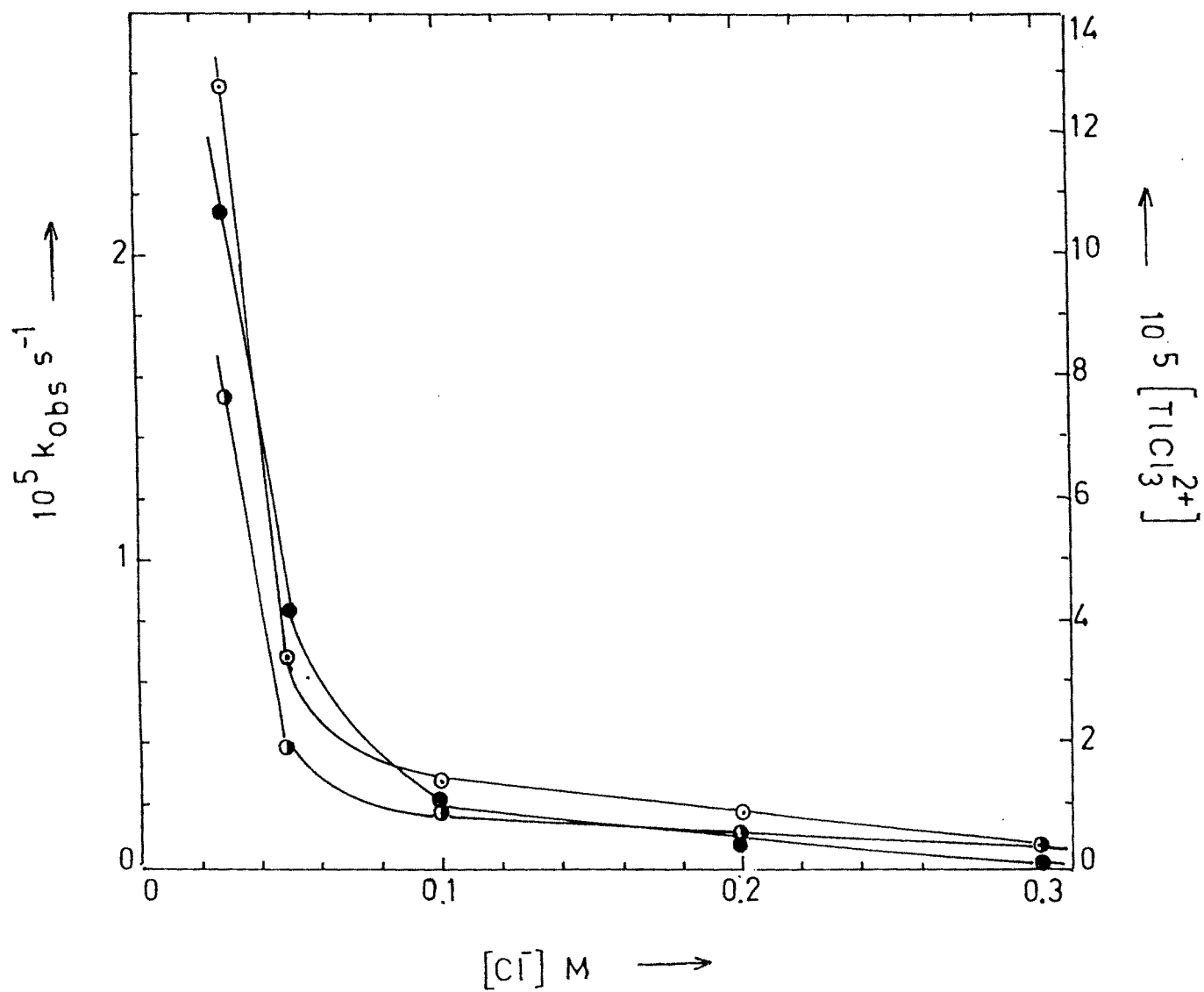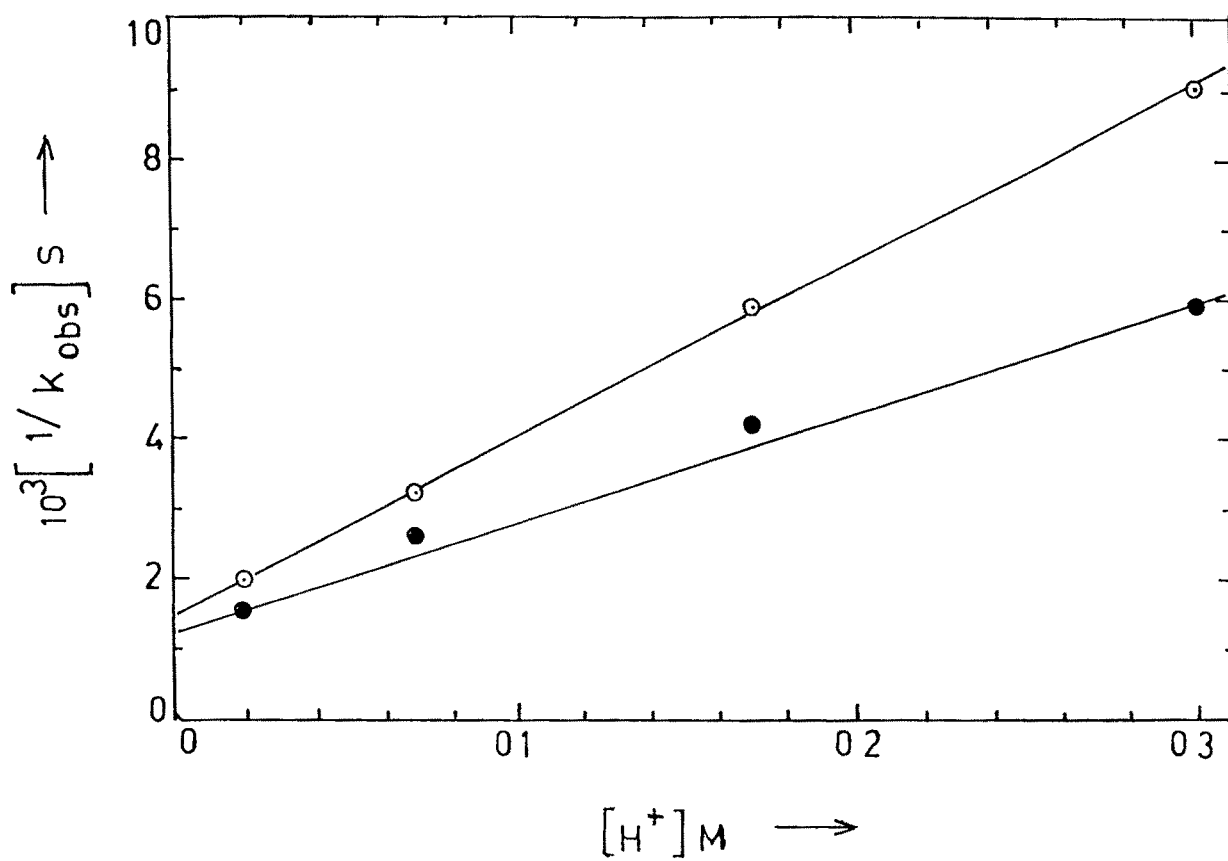
[Cl$^-$] (Conditions as in Table IV).

**Figure 4**. Plot of $1/k_{obs}$ versus $[H^+]$ (●-BAH and o-o-ClBAH) (Conditions as in TableIII)

From above results and discussion, it is observed that mesomeric, like inductive, effects are permanent polarizations in the ground state of a molecule, and are therefore, manifested in the physical properties of the compounds in which they occur. It appears that the –Cl substituent, although capable of withdrawing electron density from saturated carbon chains by induction, is capable also of supplying π-electron density to conjugated system. When such substituent is put on a conjugated system, resonance forms may be drawn for the resulting compound. Substituent Cl, present at ortho- position of hydrazide group, supplies π-electron density, deactivating carbonyl group of the hydrazide, which retards the rate of oxidation of 2-chlorobenzoic acid hydrazide as compared to benzoic acid hydrazide. The results embodied in Table - I are in agreement with the above justification.

I   II
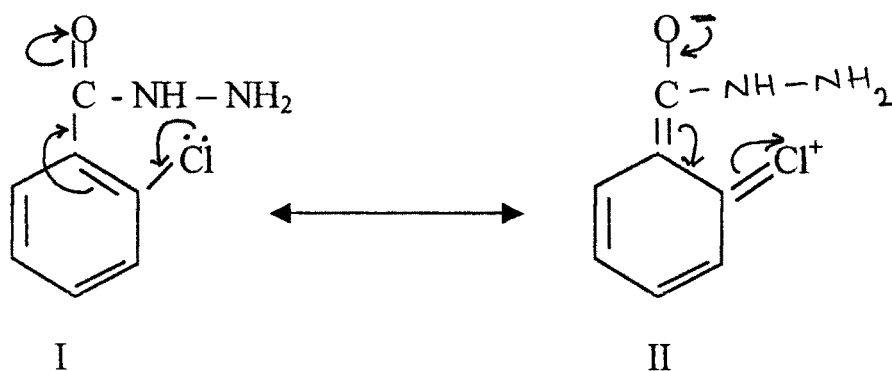
References

1. Arrhenius, S. : Z. Physik. Chem. 4, 226 (1889).

2. Evan, M.C.and Polanyl, M. : Trans. Far Soc. 31, 875 (1935), Ibid, 448 (1937).

3. Eyring, H. : J. Chem. Phys. 3, 107 (1935).

4. McKillop A., Taylor E.C., Comprehensive Organometallic Chemistry, Abel E.W. Ed., Pergomon, Oxoford, 1982, p 507.

5. Taylor E.C., Andrade J.G., Rall G.J.H., McKillop A., J. Am. Chem. Soc., 1980,102,6513.

6. (a) Kazo K., Hirakazo T., Hisashi K., Zenzo T., Chem. Pharm. Bull., 1963,11,797 (b) Krishna Rao P.V., Frank M.S., Ramaih A.K., React. Kinet. Cata. Lett., 1978,9,159 (c) Ramnaih A.K., Frank M.S., Babu Rao G., Krishna Rao P.V., Indian J.Chem., 1979,18A, 416.

7. Lee A.G. *The Chemistry of Thallium,* Elsevier, London, 1971, p48.

8. Amis E.S., Solvent Effects on Reaction Rates and Mechanisms, Academic Press, New York, 1966.

9. Gokavi G.S., Raju J.R., *Polythedron,* 1987, 6, 1721.

10. Volgel A.I., Textbook of Practical Organic Chemistry Including Qualitative Organic Analysis, ELBS & Longman Group, 3rd Edn., 1975, p.

11. Fritz Feigl, Spot Tests in Organic Analysis, 2nd ed. (Elsevier Publishing co., New York) 1972.