Mechanistic studies on the oxidation of Schiff's bases by trichloro-isocyanuric acid [TCICA] in non-aqueous medium

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ABSTRACT

The kinetics of oxidation of Schiff's bases by TCICA in 100./. methanol has been investigated. The fractional order dependence of rate on [substrate] was confirmed by MIchaelis-Menton plot. The order with respect to acid is also found to be fractional. The activation parameters for variously substituted Schiff's bases have been calculated by carrying out the reaction at various temperatures. A suitable mechanism has been proposed.

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INTRODUCTION

The N-halo compounds have proved to be an effective oxidizing agent in polar solvents for the oxidation of a variety of organic compounds. Recently, they have been widely used in the kinetics of oxidation of various organic substrates[1]Amongst the N-chloro compounds trichloroisocyanuric acid has wide synthetic utility as it has the most polar N-X bond among the series[2] TCICA, N,N-dichlorobarbital, N-chlorophthalimide, N-chlorosuccinimide (NCS) and N-bromosuccinimide (NBS). Kinetics and mechanistic studies involving TCICA with substituted phenol, anisole, and aniline derivatives[6] have been studied. The kinetics of acid catalysed chlorination of a number of substituted benzaldehyde[3], toluene[5], hydroxy acids[7,8]aliphatic, aryl and cyclic ketones[4], *o*-, *m*- and *p*-xylene have also been reported. Kinetic study on decarboxylation of mandelic acid[9] by TCICA is also reported, but there is no systematic kinetic reports on the oxidation of Schiff's bases and its substituted analogues by TCICA. So we planned to investigate extensively the reactionpathway for oxidation of Schiff's bases by TCICA through kinetic studies.
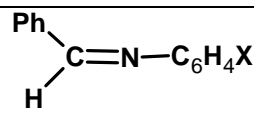
EXPEREMENTAL SECTION

General method for the preparation of Schiff's bases (anils)

$$\underset{H}{\overset{Ph}{\diagdown}}C = N - C_6H_4X$$
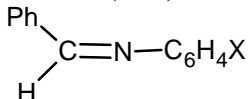
where X = H, *p*-OCH$_3$, *m*-OCH$_3$, *p*-NO$_2$, *m*-NO$_2$, *p*-CH$_3$, *m*-CH$_3$, *p*-Cl, *m*-Cl, *m*-Br, *p*-Br, *p*-COOH and *p*-F

The Schiff's bases (anil) were prepared [10] by refluxing equimolar quantities of benzaldehyde and aniline (or) substituted anilines in alcohol for about 2 to 3 hrs. The resulting solution was cooled and poured into the cold water. The precipitated anil was filtered, washed dried and recrystallized from alcohol. The purity of the anils was checked by determining their melting points (Table 1).

Table 1

S. No.	C_6H_4X (Ph–C=N–C_6H_4X, X)	Melting point (°C)	
		Observed	Literature
1.	H	54.3	54.0
2.	*p*-CH₃	34.2	35.0
3.	*p*-OCH₃	59.5	60.0
4.	*p*-Cl	60.8	62.0
5.	*p*-Br	56.0	57.0
6.	*p*-COOH	136.4	135.0
7.	*p*-NO₂	119.5	120.0
8.	*m*-Cl	58.0	58.0
9.	*m*-CH₃	114.6	115.0
10.	*m*-NO₂	65.2	66.0
11.	*m*-OCH₃	44.0	-
12.	*m*-Br	48.0	-
13.	*p*-F	53.0	-

Acetic acid

The procedure followed for the purification of acetic acid was essentially similar to that Weissberger[11] Glacial acetic acid (AR) (2 l) was partially frozen and about one litre of the liquid was removed. The residue was melted and refluxed with chromium trioxide (30g) and fractionally distilled. The portion distilling between 116-118°C was collected, partially frozen and about half of the acid was discarded as liquid. The remaining residue was melted and fractionated again after treating with chromium trioxide (30 g). The fraction boiling at 117-118°C was collected and kept in brown bottles.

Kinetic measurements

The reactions were carried out in 100% methanol medium. The reactions were carried out under pseudo first order condition at 308 K .The mixture was homogeneous throughout the course of the reaction. The reaction was followed titrimetrically. The rate constants were evaluated from log titre versus time plots.

Trichloroisocyanuric acid

The oxidant trichloroisocyanuric acid (TCICA) was of Fluka grade. Standard iodometric procedure was adopted in estimating TCICA.

Stoichiometry

A number of reaction mixtures containing excess of TCICA, at least twice the concentration of anil in the presence of *p*-toluene sulphonic acid were kept at room temperature for sufficient length of time. The estimation of unreacted TCICA showed that one mole of substrate consumed two mole of oxidant.

Product analysis

For identifying the product excess of oxidant was mixed with substrate under kinetic conditions. After the reaction was completed, the reaction mixture was washed with water and evaporated at reduced pressure to remove solvent after drying over anhydrous sodium sulfate. The liquid product benzaldehyde was confirmed by its semi- carbazone (m.p. 221°C, lit. 222°C) and 2,4-dinitrophenylhydrazone (m.p. 237°C, lit. 239°C) derivatives and the solid product nitrosobenzene was confirmed from it's IR spectrum.

RESULTS AND DISCUSSION

The kinetics of oxidation of anils by TCICA in the presence of *p*-toluenesulphonic acid was studied at 308 K. The results are summarized as follows.

Effect of varying the oxidant [TCICA] and anil

The kinetic study on the oxidation of anils by TCICA was made in methanol medium under pseudo-first order conditions. The reaction was found to be first order with respect to the oxidant [TCICA] as evidenced by the linear plot of log titre *versus* time (Fig. 1). The rate constants increased with increase in the concentration of anil and the plot of log *k versus* log [S] with slope 0.70 showing (Fig. 2) fractional order dependence on the [substrate] (Table 2). This is also verified by Michaelis-Menton plot (Fig. 3).

Table 2
[H⁺] = 5.0 ×10⁻³ mol dm⁻³
Solvent = 85% MeOH-H₂O
Temperature = 308 K

[Ox] 10^3 mol dm^{-3}	[S] 10^3 mol dm^{-3}	$k_I \times 10^4$ s^{-1}
0.50	1.50	7.35
1.00	1.50	6.62
1.50	1.50	5.47
2.00	1.50	3.82
2.50	1.50	3.19
1.00	0.50	1.15
1.00	1.00	4.24
1.00	1.50	6.62
1.00	2.00	8.21
1.00	2.50	11.71
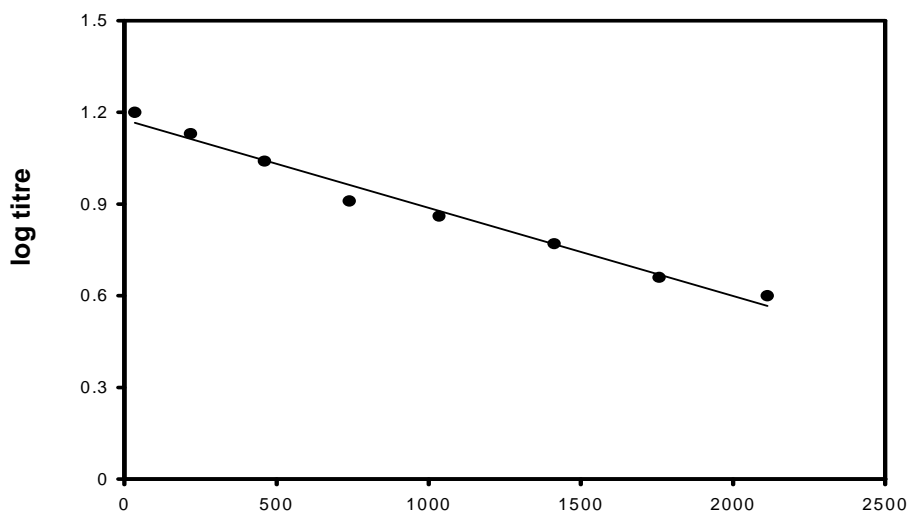
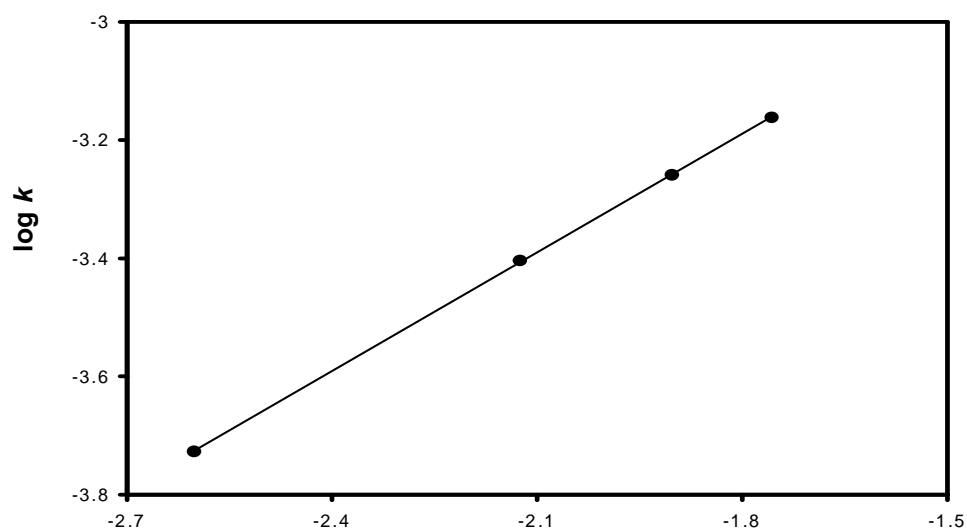**Fig. 1. The plot of log titre *versus* time (sec)**
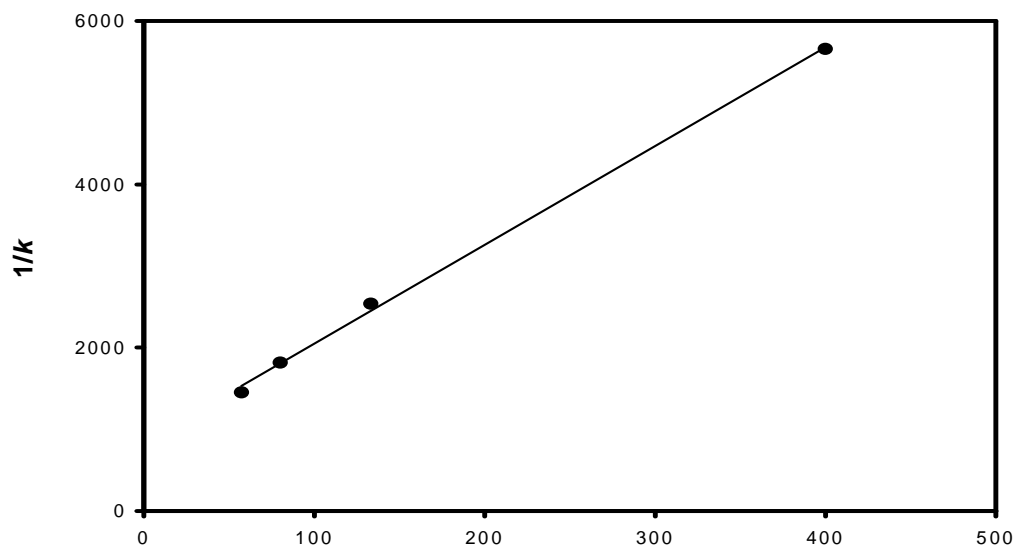

**Fig. 2. Plot of log *k versus* log [S]**

Fig. 3. Plot of 1/k versus 1/[S] (Michaelis-Menton Plot

Effect of varying [H$^+$] and the [ionic strength]

The rate constant increased with increase in the concentration of *p*-toluenesulphonic acid (Table 3). The plot of log k_1 *versus* log [H] gave a straight line with slope 0.40 indicating fractional order dependence on the [H] (Fig. 4). The rate of reaction is almost unaffected by changing the ionic strength of medium and the pseudo-first order rate constants were found to decrease with increase in the dielectric constant of the medium. This shows the involvement of ion-neutral molecules or molecular species in the rate-determining step of the reaction.

Table-3
[Ox] = 1.00 × 10^{-3} mol dm^{-3}
Temperature = 308 K
[S] = 1.5 × 10^{-2} mol dm^{-3}

[H$^+$] 10^3 mol dm^{-3}	[NaClO$_4$] 10^3 mol dm^{-3}	% MeOH-H$_2$O	Dielectric constant	$k_1 \times 10^4$ s^{-1}
2.50	-	85-15	39.83	5.18
5.00	-	85-15	39.83	6.62
7.50	-	85-15	39.83	7.58
10.00	-	85-15	39.83	8.54
12.50	-	85-15	39.83	9.62
5.00	5.00	85-15	39.83	7.12
5.00	10.00	85-15	39.83	7.82
5.00	15.00	85-15	39.83	6.89
5.00	25.00	85-15	39.83	7.52
5.00	-	70-30	46.95	11.64
5.00	-	75-25	44.57	10.04
5.00	-	80-20	42.20	8.92
5.00	-	85-15	39.83	6.62
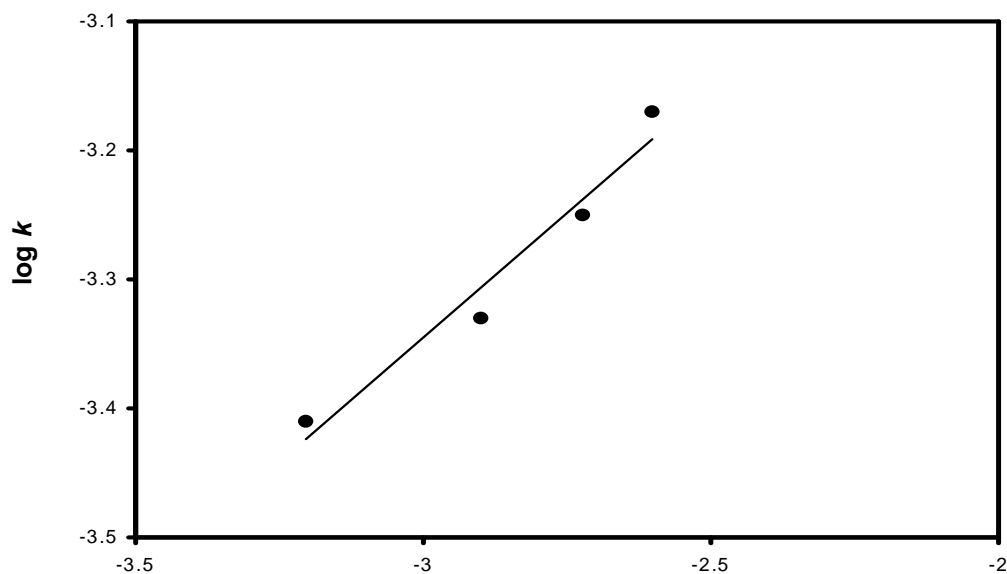
Fig. 4. Plot of log *k* versus log [H]

Effect of temperature
The reaction has been studied at four different temperatures keeping other factors constant (Table 4). The thermodynamic parameters have been computed from the linear plot of ln (k_2/T) *versus* (1/T) of Eyring's equation (Fig. 5)
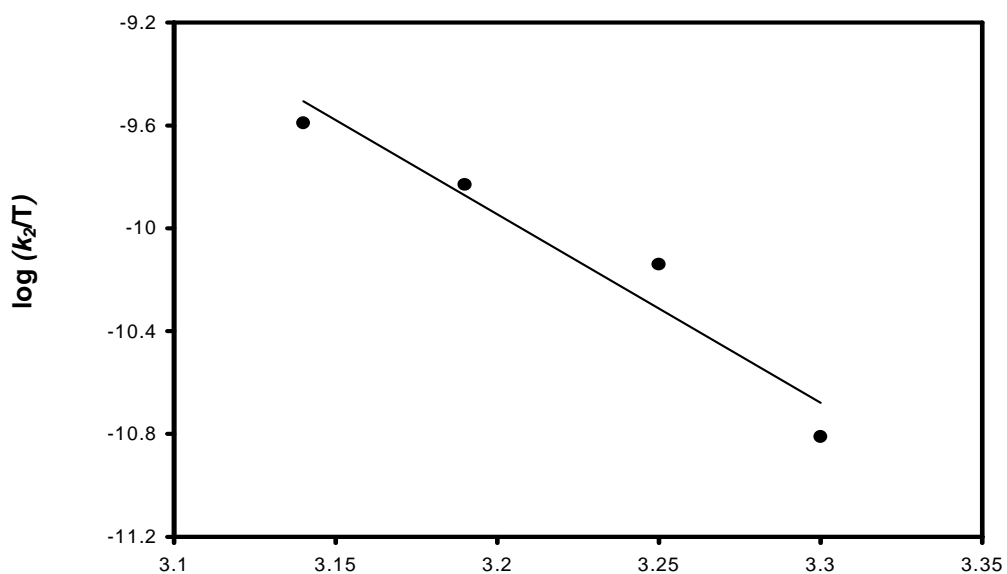
Table 4
[Ox] = 1.00 × 10⁻³ mol dm⁻³
[H] = 5 × 10⁻³ mol dm⁻³
[S] = 1.5 × 10⁻² mol dm⁻³
Solvent = 85% MeOH-H₂O (v/v)

Temperature (K)	$k_1 \times 10^4$ s⁻¹
298	2.28
303	3.93
308	6.62
313	8.75
318	11.12

Fig. 5. Plot of log (k_2/T) *versus* 1/T × 10⁻³

Rate constants and activation parameters for substituted **Schiff's bases**

The kinetics of oxidation of substituted anils like –CH_3, –OCH_3, -Cl, Br, -F, NO_2 and COOH were carried out employing the different initial concentrations of those Schiff's bases (Table 5). The pseudo-first order rate constants obtained for those substrates showed different order of dependence with respect to different substituted Schiff's bases. The variation in order of dependence with respect to different substituted Schiff's bases is explained by invoking different rate controlling steps in the proposed mechanism.

From a series of kinetic runs the rate constants k_1 were estimated for the above substituted Schiff's bases at four different temperatures *viz.,* 303, 308, 313 and 318 K in order to calculate the thermodynamic parameters. The thermodynamic parameters were calculated using the Eyring's plot and the values are given in (Table 5).

A plot of $\Delta H^{\#}$ against $\Delta S^{\#}$ gave a straight line with a correlation coefficient r = 0.980 (Fig. 15). The isokinetic temperatures obtained from the slope is 490 K. The linear correlation between $\Delta H^{\#}$ and $\Delta S^{\#}$ indicates that all the substituted Schiff's bases are following a common mechanism here.

The Exner [12,13]plot of log $k_{1\,(318\,K)}$ *versus* log $k_{1\,(308\,K)}$ (Fig. 6) gave straight line with r = 0.99. Such a good correlation indicates that all the substituents follow a common mechanism.

Table 5: Thermodynamic parameters for the oxidation of *m*- and *p*-substituted Schiff's bases by TCICA calculated from Eyring's plot

Substituent	$k_1 \times 10^4 s^{-1}$				$\Delta H^{\#}$ kJ mol^{-1}	$\Delta S^{\#}$ J K^{-1} mol^{-1}	$\Delta G^{\#}$ kJ mol^{-1}	E_a kJ mol^{-1}	r
	303 K	308 K	313 K	318 K					
H	1.98	3.94	5.46	7.04	66.40	- 71.31	88.72	68.88	0.980
m-Br	1.45	1.60	2.09	2.50	28.71	-183.60	86.18	31.19	0.981
m-Cl	0.39	1.87	2.17	3.05	39.10	-167.90	91.64	41.58	0.992
p-Br	1.67	2.89	4.06	5.62	63.48	-90.71	91.87	65.96	0.995
p-F	2.16	3.71	5.48	6.93	66.28	-60.48	85.21	68.76	0.982
p-OCH₃	0.17	0.40	0.46	0.69	70.11	-78.84	45.43	72.59	0.970
m-OCH₃	1.79	2.54	3.95	5.34	61.05	-97.09	91.44	63.13	0.996
p-CH₃	0.32	0.52	0.67	0.96	57.51	-118.88	94.72	59.99	0.996
m-CH₃	0.30	2.55	4.36	6.12	83.52	-21.63	90.29	86.00	0.992
p-Cl	1.93	3.79	4.79	6.02	58.58	-91.93	87.35	61.06	0.970
P-COOH	1.03	1.62	2.42	2.70	55.73	-111.08	90.49	58.21	0.982
m-NO₂	0.68	0.82	1.18	1.41	40.06	-174.14	94.52	42.14	0.984
p-NO₂	0.31	0.38	0.56	0.81	50.55	-138.28	93.83	53.03	0.980

$\Delta G^{\#}$ and E_a are calculated at 313 K
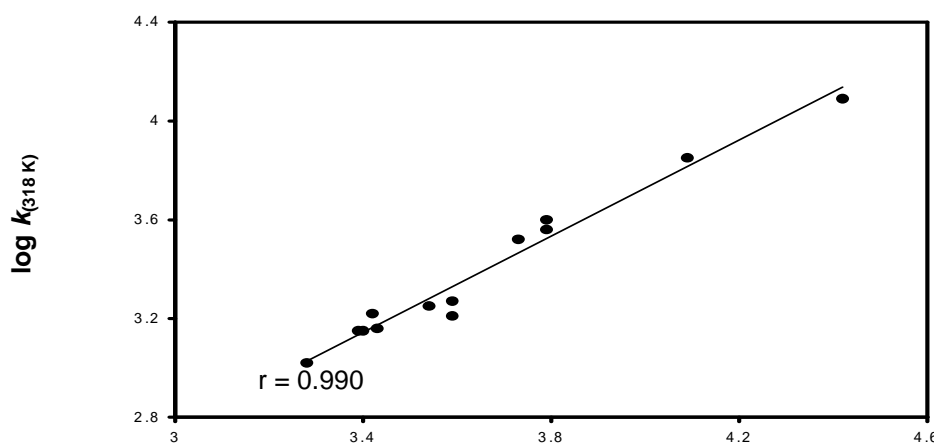
Fig. 6. Plot of log $k_{(318\,K)}$ *versus* log $k_{(308\,K)}$ (Exner plot)
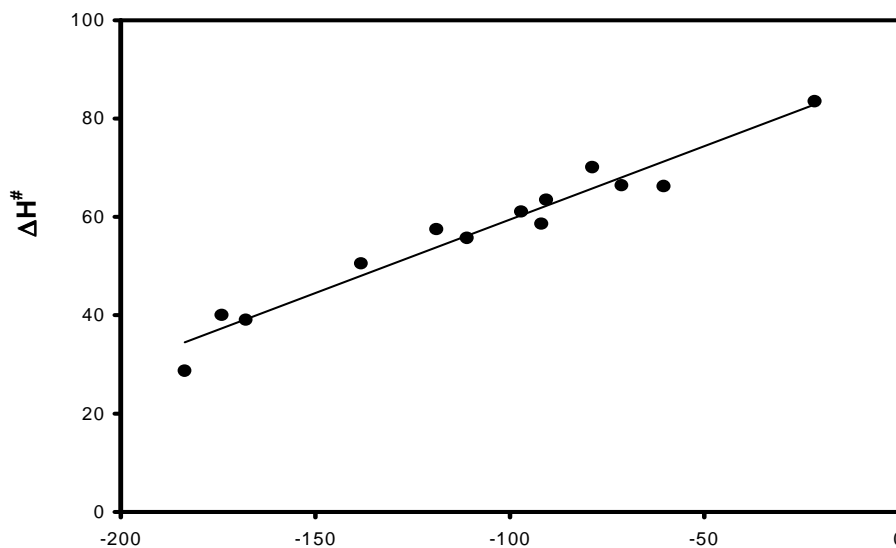
Fig. 7. Plot of $\Delta H^{\#}$ *versus* $\Delta S^{\#}$ (isokinetic plot)

Hammett equation

When the Hammett equation was applied to this reaction system with the usual substituent constants σ no linear correlation was obtained instead the curve concave downward was obtained (Fig. 8). An attempt was made to correlate the log k_1 values with substituent constants σ⁺and σ⁰ [14',15]. In both cases large deviations were noted in the Hammett plot. Hence the deviation from linearity in Hammett's plot is not due to change in σ.
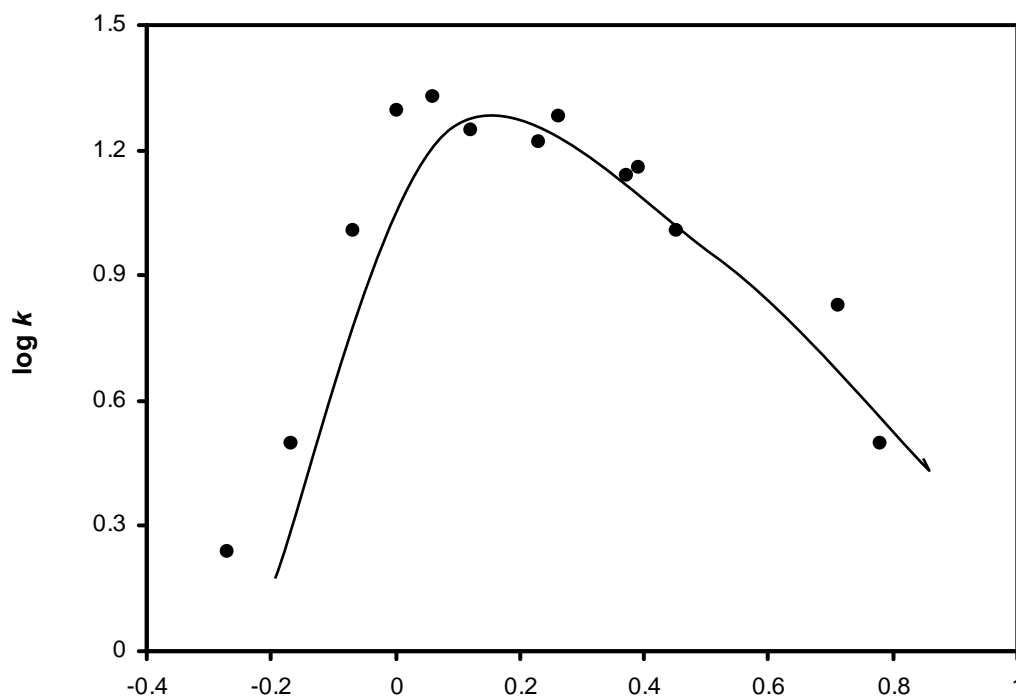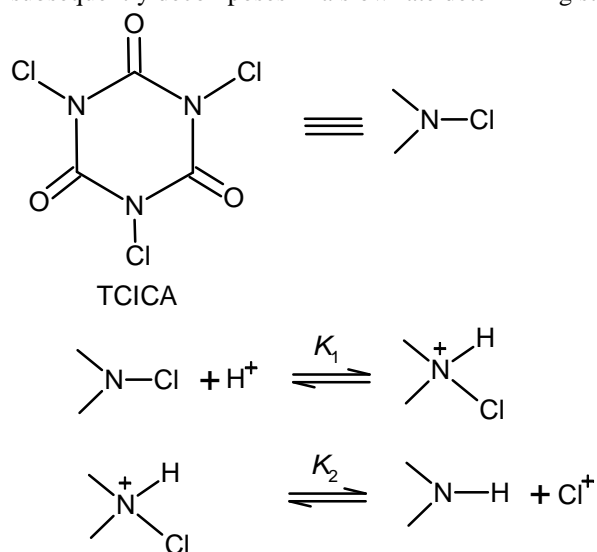

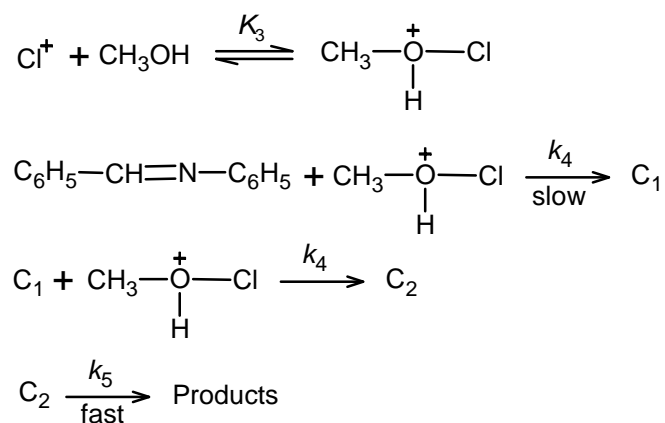**Fig. 8. Plot of log *k* *versus* σ[Hammett plot]**

The curvature may be due to either a gradual change in the reaction mechanism when one passes from electron-donating to electron-withdrawing substituents or change in the rate-determining step with change in the nature of substituents. The observed curvature in the Hammett's plot may be attributed to the change in rate determining step. Since Michaelis-Menton plots with some of the substrate yield some definite intercept confirming the complex formed which subsequently decomposes in a slow rate determining step to give the product. This is further confirmed by the shape (concave downward) of the Hammett curve, which indicates that the reaction series is following a common mechanism with the different rate-determining steps.

Mechanism

From the above observations it is clear that the reaction is showing first order dependence with respect to oxidant. In acid medium molecular TCICA, protonated TCICA $\left(\underset{H}{\overset{Cl}{N^+}}\right)$, HOCl and $CH_3\!-\!\overset{H}{\underset{+}{O}}\!-\!Cl$ cation are the possible reactive species. As the reaction is fractional order dependence on substrate, the molecular TCICA is not considered as the reactive species. The increase in rate with the increase in substrate concentration and Michaelis-Menton type of behaviour suggest the formation of a complex between the reactive species and the substrate. As the reaction is fractional order dependence on acid concentration, the protonated TCICA $\left(\underset{H}{\overset{Cl}{N^+}}\right)$ is not considered as the reactive species. Moreover the protonation is said to be fast, $\left(\underset{Cl}{\overset{H}{N^+}}\right)$ is less likely to be the reactive species. Methanol is found to be better nucleophile than water and hence abstraction of Cl from $\left(\underset{Cl}{\overset{H}{N^+}}\right)$ by methanol is considered.

Hence $CH_3\!-\!\overset{+}{\underset{H}{O}}\!-\!Cl$ cation is proposed to be the reactive species. The results are further confirmed by the fact that a plot of $1/k_1$ *versus* $1/[S]$ gave a straight line with an intercept confirming the complex (C_1) formed, which subsequently decomposes in a slow rate determining step to give the products.

$$Cl^+ + CH_3OH \xrightleftharpoons{K_3} CH_3{-}\overset{\overset{+}{|}}{\underset{|}{O}}{-}Cl$$

$$C_6H_5{-}CH{=}N{-}C_6H_5 + CH_3{-}\overset{\overset{+}{|}}{\underset{|}{O}}{-}Cl \xrightarrow[\text{slow}]{k_4} C_1$$

$$C_1 + CH_3{-}\overset{\overset{+}{|}}{\underset{|}{O}}{-}Cl \xrightarrow{k_4} C_2$$

$$C_2 \xrightarrow[\text{fast}]{k_5} \text{Products}$$

Rate law

$$\text{Rate} = \frac{K_1K_2K_3k_4\,[S]\,[H^+]\,[Ox]}{\{1 + k_4\,[S]\}\,\{1 + K_1\,[H^+]\}}$$

$$k_{obs} = \frac{K_1K_2K_3k_4\,[S]\,[H^+]}{\{1 + k_4\,[S]\}\,\{1 + K_1\,[H^+]\}}$$

CONCLUSION

The kinetics of oxidation of several *meta* and *para*-substituted Schiff' bases by trichloroisocyanuric acid have been studied in methanol medium, with a view to understand the substituent effects on the reaction rate. The effect of [substituent],[oxidant],[TsOH], ionic strength ,dielectric constant and temperature on the reaction rate is also studied. Based on these observations a suitable mechanism has been proposed and a suitable rate law is derived. The oxidation products are found to be nitrosobenzene and benzaldehyde.

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