Kinetics and mechanism of halogenation of aniline, p-toluidine and o-toluidine using N-chloro-p-toluene sulphonamide (CAT) under buffer conditions in ethanol – water mixtures.

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Abstract: *Kinetics of halogenation of aniline, p-toluidine and o-toluidine have been investigated by using N-chloro-p-toluene sulphonamide(CAT) under buffer conditions in ethanol – water mixtures. The kinetic orders are first order in chlorinating agent with all substrates. Dependence on substrate is fractional with aniline and p-toluidine but first order with o-toluidine. Increase in ethanol content decreases the rate in all the cases. Amis treatment has been applied and the molecular radii have been found to be reasonable with all substrates. Continuous pH profile has been investigated and the species at pH 1 and 6.85 is $RNHCl$ whereas between 2.5 and 3.5 it is $RNCl_2$ and the species at 4.5 is $HOCl$. The order of reactivity is p-toluidine > o-toluidine > aniline. Solvent parameters suggested by Grunwald – Winstein (Y), Dimroth (E_T) and Kosower (Z) have been applied and it is observed that all the treatments are useful in explaining the solvent behaviour.*

Keywords: *Halogenation , CAT , Amines , Reactivity of amines*

Aim:

The present work deals with the halogenation of aromatic amines (Aniline, o- toluidine and p-toluidine) in ethanol – water mixture by CAT.

Background:

A survey of literature indicates that there are number of reports on halogenation of aromatic amines by different chlorinating agents[1-25]. Almost all the chlorinating agents react with aromatic amines yielding monochloro derivatives. The observed kinetic studies are widely different and depend upon acidity, solvent nature and the nature of chlorinating agent.

Experimental:

The chemicals used in these investigations were of analytical reagent or guaranteed reagent grade. Sometimes further purification by way of recrystallisation or redistillation was undertaken, whenever necessary. The organic compounds were purified whenever necessary and the purity was checked from their reported physical constants.

Tap water was first distilled over potassium permanganate and then redistilled over sulphuric acid (BDH, AnalaR), followed by distillation in the presence of Na_2 EDTA (Ca 1 x 10^{-4}M) from an all glass vessel. This was followed by boiling off dissolved carbon dioxide. Doubly distilled water prepared in this manner was used throughout for all preparative and analytical procedures.

CAT

0.1M stock solution of chloramine-T was prepared using analytical grade BDH make as such and stored in a black coated bottle and was kept in dark. For every kinetic run 1ml of the stock solution was used to give 0.0005M of CAT.

All the experiments were carried out in duplicate and the velocity constants were reproducible with in $\pm$ 3% error. Solvent oxidation was routinely checked and proper correction was applied, where there was such oxidation. For fast reactions, each run was performed at least thrice and the mean value of these runs has been taken into record.

Results and conclusions:

CAT the sodium salt of N- chioro p- toluene sulphonamide is a two electron oxidant in both acidic and basic media. CAT oxidations of a number of systems both in the presence and absence of HCl have been well documented. There are several reports of oxidation of organic compounds using transition metal catalysts.CAT is quite stable in aqueous acidic solutions. It is interesting to recall that hypochlorite ion is unstable in acidic medium whereas CAT is quite stable in acidic medium.

Reactions are found to be first order with respect to chlorinating agent at pH 6.85. The first order nature with respect to chlorinating agent is confirmed from the constancy (Table-1) in the rate constants at different

initial concentrations of chlorinating agent. Moreover a plot of log(a-x) vs time is linear confirming the first order dependence on chlorinating agent.

TABLE – 1

[Substrate] = 0.0062M; [KH_2PO_4] = 0.01M; [Na_2HPO_4] = 0.01M; Temp. 35^0C; $C_2H_5OH – H_2O$ = 10% - 90%

Substrate	[CAT]M	$k_1 \times 10^2$ (min^{-1})
P-Toluidine	0.00025	3.809
	0.0005	3.518
	0.001	3.609

An increase in rate of reaction is observed with increase in the concentration of substrates p-toluidine, o-toluidine and aniline (Table-2).The plots of log k vs log S were linear unit slope indicating first order dependence in o-toluidine and fractional order dependence in p-toluidine and aniline. The effect of variation in the percentage of ethanol on the reaction rate has been studied and there is uniform retardation in all the cases (Table-3). A plot of log k vs 1/D is linear. The molecular radius has been calculated using Amis[26] equation and the values are reasonable for bimolecular reactions in all the three cases.

TABLE – 2
Effect of varying concentration of substrate on reaction rate

[CAT] = 5.0 x 10^{-4}M; [Na_2HPO_4] = 0.01M ; [KH_2PO_4] = 0.01M; Temp. 35^0C; $C_2H_5OH – H_2O$ = 10% - 90%

Substrate	[Substrate]M	$k_1 \times 10^2$ (min^{-1})
P-Toluidine	0.0015	1.265
	0.0031	2.542
	0.0062	3.518
	0.0125	7.030
o-Toluidine	0.0066	1.043
	0.0131	2.038
	0.0254	3.555
	0.0514	7.000
Aniline	0.0064	1.910
	0.0124	3.022
	0.0252	4.817
	0.0500	8.606

TABLE-3
Variation in dielectric constant at pH 6.85

[CAT] = 0.0005M; [KH_2PO_4] = 0.01M; [Na_2HPO_4] = 0.01M; Temp. = 35^0C

Substrate	$C_2H_5OH – H_2O$	$k_1 \times 10^2$(min^{-1})
[O-Toluidine] = 0.05M	10% - 90%	7.001
	15% - 85%	5.499
	20% - 80%	4.373
	25% - 75%	3.561
[p- Toluidine] = 0.0062M	10% - 90%	3.518
	15% - 85%	2.870
	20% - 80%	2.245
	25% - 75%	1.756
[Aniline] = 0.05M	10% - 90%	8.606
	15% - 85%	6.736
	20% - 80%	4.516
	25% - 75%	3.194

pH profile and nature of CAT species:

Experiments have been carried out at various pH values to determine the nature of CAT species in the present investigation. A continuous pH profile has been investigated in aqueous ethanol medium in order to throw light on the likely chlorinating species at various pH levels.

TABLE – 4

[o-Toluidine] = 0.05M   Temp. = 35^{0}C

pH	[CAT]M	$k_1 \times 10^2$ (min^{-1})	$k_2 \times 10^2$ (litre-mole^{-1}-min^{-1})
1	0.00025	8.31	–
	0.0005	8.40	–
	0.001	8.57	–
2.7	0.00025	–	1.221
	0.0005	–	1.194
	0.001	–	1.173
2.82	0.00025	–	1.072
	0.0005	–	1.093
	0.001	–	1.113
4.5	0.00025	37.90	–
	0.0005	40.81	–
	0.001	46.60	–
6.85	0.00025	6.936	–
	0.0005	7.001	–
	0.001	7.015	–

As the rate constant data in the Table-10 shows that the order on CAT is unity upto pH 2.5. The monomeric species RNHCl is important at this pH range which is quite in consonance with the earlier reports by Radhakrishnamurti and Prasada Rao[27] and Mahadevappa[28].

After pH 2.5 there is change of order on CAT to second order dependence , upto pH 3.5. Second order rate constants computed at pH 2.7 and at pH 2.82 are fairly constant over a four fold variation of CAT. Hence, it is reasonable to believe that the active species is dichloramine-T at this pH range and the equilibrium, becomes kinetically important. This has been confirmed by other investigators like Higuchi[29] and Radhakrishnamurti et.al[30].

2RNHCl ⟶ RNCl$_2$ + RNH$_2$
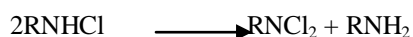
The order on CAT becomes unity at pH 4.5. The rate attains a maximum value at this pH and then decreases as one goes to higher pH. The species has been postulated to be as HOCl at pH 4.5 by Mushram and others[31] . The rate constant data at pH 6.85 also confirms first order kinetics on CAT. The species is RNHCl. Thus the rate profile indicates that the report of Kucsman[32] is reasonably valid regarding reactivity order.

HOCl > DCT > RNHCl

Thus in aqueous acid solutions the possible species are sodium salt of CAT, RNHCl, RNCl$_2$ and HOCl and the formation of each species is pH dependent. All these observations are quite in conformity with the work of Bishop and Jennings[33].

Application of Hammett[34] equation:

A number of empirical models have been employed for studying the effect of structure on rates of reactions of organic compounds. The most successful models are linear free energy relationships enunciated by Hammett for aromatic compounds and modified by Taft[35] for aliphatic compounds.

$$\frac{\log k}{\log k_0} = \rho\sigma$$

Where σ is substituent constant

ρ is reaction constant

An approximate discussion can be made regarding structure and reactivity of the three compounds studied viz., aniline, o-toluidine and p-toluidine. The reaction is mainly electrophilic substitution process yielding halogenated products. Aniline is essentially a system where ortho and para positions have high electron densities. Hence, for the purpose of comparison with ortho toluidine and p-toluidine partial rate for aniline is used by dividing the obtained rate constant by two, the reason being electron densities at ortho and para positions are equal. This approximation is necessary for comparing halogenated products obtained in three systems.

The information in Table-5 has been used for the purpose of discussion on structure and reactivity.

TABLE – 5
Structure on reactivity

Substrate	$k_1 \times 10^2$ (min^{-1})	σ_+
p-Toluidine	3.59	-0.31
o-Toluidine	1.043	-0.08**
Aniline	0.95*	0.00

* indicates partial rate constant for aniline.
** indicates σ_+ value corrected for ortho effect.

Plot of log k vs σ_+ has been found to be linear with a slope of -2. Thus the ρ value -2 indicates an ionic electrophilic halogenation process.

Thus the process of halogenation can be treated as follows:
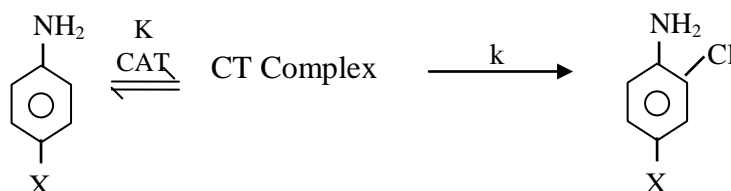
The following rate law can explain the observed kinetic orders.

RNHCl + S $\underset{}{\overset{K}{\rightleftharpoons}}$ Complex $\xrightarrow{\ \ k\ \ }$ Products

Rate = k[C] = k K[RNHCl] [S]

Replacing [RNHCl] by [RNHCl]$_T$

We get

Rate = k K[RNHCl]$_T$[S]/ 1+ k[S]

This equation explain the observed unit order with o-toluidine and fractional order observed with aniline and p-toluidine.

Application of Grunwald - Winstein treatment[36]

TABLE – 6

Substrate	Ethanol – Water	$k_1 \times 10^2$ (min^{-1})	Y
p-Toluidine	10% - 90%	3.518	+ 3.31
	15% - 85%	2.870	+ 3.19
	20% - 80%	2.245	+ 3.05
	25% - 75%	1.756	+ 2.91
o-Toluidine	10% - 90%	7.001	+ 3.31
	15% - 85%	5.499	+ 3.19
	20% - 80%	4.373	+ 3.05
	25% - 75%	3.561	+ 2.91
Aniline	10% - 90%	8.606	+ 3.31
	15% - 85%	6.736	+ 3.19
	20% - 80%	4.516	+ 3.05
	25% - 75%	3.194	+ 2.91

Plots of log k vs Y in all the cases are linear.

According to Grunwald and Winstein $\log k/k_0 = mY$,

where m is characteristic of substrate and is usually unity. Y denotes the ionizing power of the solvent. It is interesting that all the plots are linear indicating that decrease in ionizing power decreases the kinetic rate.

Application of Dimroth[37] parameter (E_T) and Kosower[38] factor:

TABLE – 7

Substrate	Ethanol – Water	$k_1 \times 10^2$ (min^{-1})	Z
p-Toluidine	10% - 90%	3.518	94.0
	15% - 85%	2.870	93.5
	20% - 80%	2.245	93.1
o-Toluidine	10% - 90%	7.001	94.0
	15% - 85%	5.499	93.5
	20% - 80%	4.373	93.1
Aniline	10% - 90%	8.606	94.0
	15% - 85%	6.736	93.5
	20% - 80%	4.516	93.1

TABLE – 8

Substrate	Ethanol – Water	$k_1 \times 10^2$ (min^{-1})	E_T
p-Toluidine	10% - 90%	3.518	61.9
	15% - 85%	2.870	61.3
	20% - 80%	2.245	60.8
o-Toluidine	10% - 90%	7.001	61.9
	15% - 85%	5.499	61.3
	20% - 80%	4.373	60.8
Aniline	10% - 90%	8.606	61.9
	15% - 85%	6.736	61.5
	20% - 80%	4.516	60.8

An attempt has been made to apply Dimroth parameter (E_T) and Kosower factor (Z) in the present investigation. A very sensitive measure of solvent polarity is Kosower factor (Z). Dimroth proposed another solvent parameter E_T. These values have been proposed basing on the theory that the solvent molecules have no time to adjust to the orientation. The solvent stabilization of the transition state is much less than that of the ground state. Sometimes it may lead to destabilization. Hence, solvent effects, are sensitive measures to know the electrostatic solvation of an ion pair or dipole and the transition energy is also effected by solvent effects.

Plots of $\log k$ vs Z and $\log k$ vs E_T have been found to be linear in all the systems. This confirms the applicability of above treatments in the present investigation.

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