

Kinetics and Mechanism of Chlorination of Acetanilide and Substituted Acetanilides by Chloramine-T

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Kinetics of chlorination of acetanilide and substituted acetanilides in (20% HOAc - 80% H₂O) medium in presence of perchloric acid and hydrochloric acid are reported. The order with respect to CAT (0.00025 to 0.0025M) is unity. The reactions are found to be acid catalysed. The order with respect to substrate has been found to be fractional in the range (0.002 to 0.02M) studied. Added chloride ions (0.003 to 0.025M) have pronounced catalytic effect.

A mechanism involving the formation of N-chloro intermediate in an equilibrium step followed by intermolecular Orton rearrangement in rate determining step has been postulated. The rate laws consistent with the observations have been discussed.

Activation parameters at 60° have been computed and for acetanilide, *p*-methyl acetanilide, *p*-chloroacetanilide and *o*-chloroacetanilides the ΔE^\ddagger 's are 15.25 k cal/mole, 14.08 k cal/mole, 15.25 k cal/mole and 17.60 k cal/mole respectively and ΔS^\ddagger are -32.95 e.u., -36.69 e.u., -33.71 e.u. and -27.05 e.u. respectively.

N-CHLOROACETANILIDE is well known to undergo nuclear chlorination through intermolecular Orton rearrangement¹. But there appears to be few reports on the reaction of anilides with halogenating agents except molecular chlorine². We have, therefore, studied the kinetic aspects in the chlorination of acetanilide and substituted acetanilides by a mild halogenating agent like chloramine-T in aqueous acetic acid medium in presence of HClO₄ and HCl. Our object of study was mainly to investigate whether the halogenation process is through inter or intramolecular and whether the anilide reactions simulate the halogenation reactions of amines^{3,4} as studied earlier.

Experimental

Materials and Methods : Chloramine-T used for the purpose was of M and B make. Acetanilide, *p*-methylacetanilide, *p*-chloroacetanilide, *p*-bromoacetanilide and *o*-chloroacetanilide were prepared according to the method of Vogel⁵.

To initiate the reaction 50 ml of the solutions of each of the reactants at fixed known temperature and desired solvent composition and acidity were mixed and the progress of the reaction was monitored by estimating the unreacted chloramine-T at regular intervals of time iodometrically using starch as indicator. All the experiments have been carried out in duplicate and the results have been found to be reproducible within $\pm 3\%$ error. The pseudo first order rate constants have been computed by the integrated equation for a first order reaction.

Stoichiometry and product analysis : The stoichiometry of the reaction has been proven to be

as (1 : 2) acetanilide : halogenating agent as per the reaction

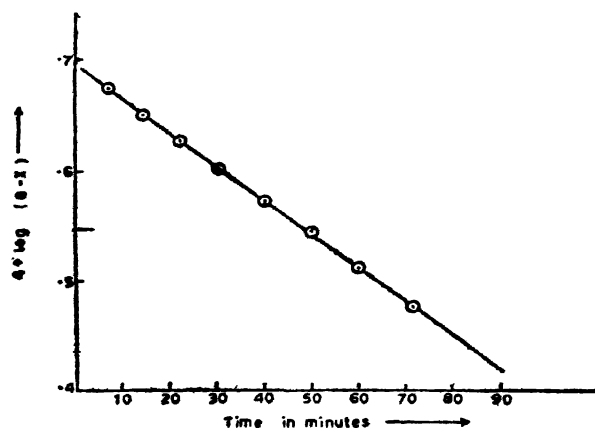


But in the experimental conditions the products isolated were exclusively the ortho-para isomers of chloroacetanilides with 50% yield in each case. Thus at higher concentration of halogenating agents the products isolated were the dichloro derivatives and at lower concentrations of the halogenating agent the products are ortho-para isomers. But in case of *p*-substituted anilides the products are only the ortho chloro derivatives with more than 95% yield.

Results and Discussion

The reaction has been found to be first order with respect to the disappearance of CAT as evidenced by a good linearity in the plot of $\log [\text{CAT}]$ vs time in an individual run (Fig.1). The pseudo first order rate constants ($k_1 \text{ min}^{-1}$) with respect to CAT are also fairly constant over a wide range in $[\text{CAT}]$ (Table 1).

Effect of varying the [Substrate] : The pseudo first order rate constants increase on increasing the substrate concentration (Table 2). The plots of $\log k_1$ vs $\log [S]$ for all the compounds studied have been found to be linear with slopes less than unity indicating fractional dependence on [substrate]. The double reciprocal plots of $1/k_1$ vs $1/[S]$ are linear with finite intercepts on the inverse rate axis

Fig. 1. Plot of $\log (a-x)$ vs time.

Acetanilide vs CAT
 $[\text{CAT}] = 0.0005 \text{ M}$; $[\text{S}] = 0.005 \text{ M}$; $[\text{HClO}_4] = 0.0125 \text{ M}$;
 $\text{HOAc} = 20\%$; $\text{Temp.} = 60^\circ$.

TABLE 1—EFFECT OF VARYING $[\text{CAT}]$ ON REACTION RATE

$[\text{Acetanilide}] = 4.814 \times 10^{-3} \text{ M}$, $\text{HOAc} = 20\% \text{ V/V}$		$[\text{HClO}_4] = 0.0125 \text{ M}$, $\text{Temp.} = 60^\circ$
$[\text{CAT}]_M$		$10^3 k_1, \text{ min}^{-1}$
0.00025		7.21
0.0005		7.11
0.00078		7.21
0.0011		6.94
0.00147		7.20
0.0025		7.18

indicating complex formation between CAT and substrate.

TABLE 2—EFFECT OF VARYING $[\text{SUBSTRATE}]$ ON THE REACTION RATE

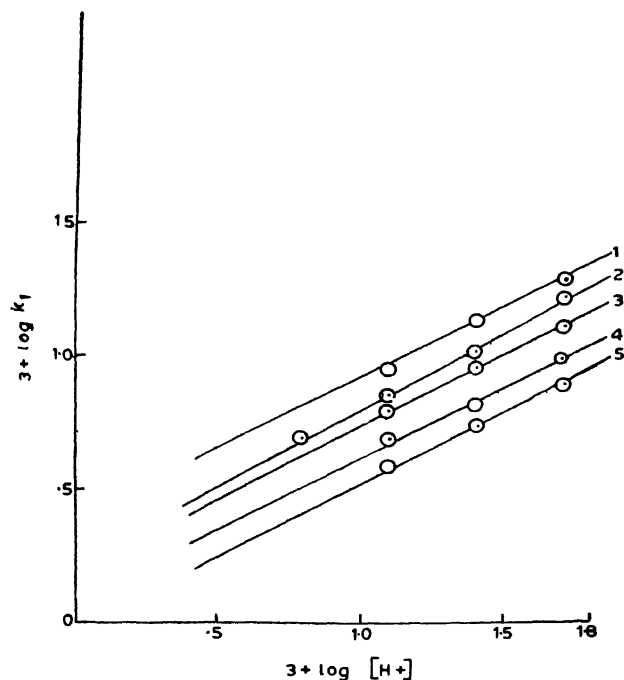
$[\text{CAT}] = 0.0005 \text{ M}$, $\text{HOAc} = 20\% \text{ V/V}$		$[\text{HClO}_4] = 0.0125 \text{ M}$, $\text{Temp.} = 60^\circ$	
Substrate	$10^3 [\text{Substrate}] \text{ M}$	$10^3 k_1, \text{ min}^{-1}$	Slope of plot of $\log k_1$ vs $\log [\text{S}]$
Acetanilide	2.444	4.48	0.50
	4.814	7.11	
	9.96	9.77	
	20.11	12.88	
<i>p</i> -CH ₃ acetanilide	5.20	6.37	0.50
	9.96	8.96	
	22.54	13.72	
<i>p</i> -Cl acetanilide	2.65	3.19	0.66
	5.04	4.86	
	9.88	8.31	
<i>p</i> -Br acetanilide	2.57	5.49	0.62
	5.04	8.93	
	10.05	13.46	
	20.30	19.06	
<i>o</i> -Cl acetanilide	4.912	8.97	0.66
	10.09	6.67	
	20.05	10.47	

Effect of acidity: The effects of acidity have been studied by varying the concentration of perchloric acid at a given substrate concentration (Table 3). Although the reaction rate is greatly

TABLE 3—EFFECT OF VARYING $[\text{HClO}_4]$ AND $[\text{HCl}]$ ON REACTION RATE

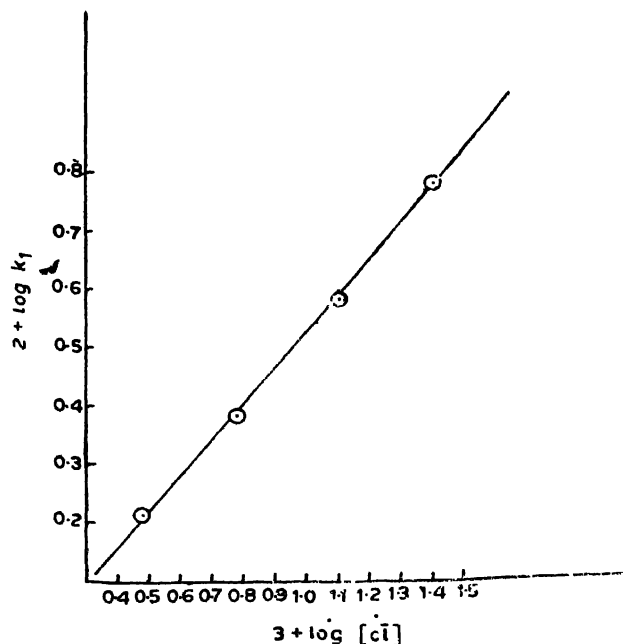
$[\text{Substrate}] = 0.005 \text{ M}$ $[\text{CAT}] = 0.0005 \text{ M}$		$\text{HOAc} = 20\% \text{ V/V}$ $\text{Temp.} = 60^\circ$	
Substrate	$[\text{HClO}_4] \text{ M}$	$[\text{HCl}] \text{ M}$	$10^3 k_1, \text{ min}^{-1}$
Acetanilide	0.00625	—	4.95
	0.0125	—	7.11
	0.025	—	10.51
	0.050	—	16.77
	—	0.003	22.67
	—	0.006	46.35
	—	0.0125	78.99
	—	0.025	151.70
<i>p</i> -CH ₃ acetanilide	0.0125	—	6.37
	0.025	—	9.25
	0.050	—	13.15
	—	0.003	12.77
	—	0.006	22.58
	—	0.0125	43.93
<i>p</i> -Cl acetanilide	—	0.025	87.10
	0.0125	—	4.86
	0.025	—	6.87
	0.050	—	9.91
	—	0.006	7.50
<i>p</i> -Br acetanilide	—	0.0125	13.09
	—	0.025	29.65
	0.0125	—	8.93
	0.025	—	13.79
	0.05	—	18.79
	—	0.006	21.78
<i>o</i> -Cl acetanilide	—	0.0125	41.66
	—	0.025	76.15
	0.0125	—	3.97
	0.025	—	5.53
	0.050	—	7.85
	—	0.006	2.31
	—	0.0125	4.15
	—	0.025	8.53

affected by an increase in acid concentration the plot of $\log k_1$ vs $\log [\text{H}^+]$ are linear with slopes 0.58, 0.52, 0.55, 0.55 and 0.55 for acetanilide, *p*-chloro acetanilide, *p*-bromo acetanilide, *p*-methyl acetanilide and *o*-chloroacetanilide respectively (Fig. 2). The plot of k_1 vs $[\text{H}^+]$ at a given substrate concentration is linear with an intercept on the rate axis. Thus it is highly probable that the reaction is proceeding through an acid dependent and an acid independent path. Addition of HCl (0.003M) in place of HClO_4 causes a drastic acceleration in the rate and further variation of $[\text{HCl}]$ between 0.003M–0.025M reveals that the order with respect to gross $[\text{HCl}]$ is nearly unity (Table 3). This might be due to the cumulative catalytic effects of both Cl^- ion and H^+ ion, operating in these reactions. This corroborates with the earlier findings⁶ where a second order dependence on HCl was postulated.

Fig. 2. Plot of $\log k_1$ vs $\log [H^+]$

- 1-*p*-Bromo Acetanilide
- 2-Acetanilide
- 3-*p*-Methyl Acetanilide
- 4-*p*-Chloro Acetanilide
- 5-*o*-Chloro Acetanilide

[CAT]=0.0005 *M*; [S]=0.005 *M*,
HOAc=20%; Temp.=60°

Fig. 3. Effect of varying Cl^- ions on the reaction rate at constant acidity.

Effect of Chloride ions : Addition of Cl^- ions at a given concentration of perchloric acid caused a marked acceleration in the rate (Table 4). The effect was studied at various $[Cl^-]$ and the plot of $\log k_1$ vs $\log [Cl^-]$ was found to be linear with a slope 0.6 for acetanilide (Fig. 3). The same effect was also observed (Table 4) in presence of HCl where the plot of $\log k_1$ vs $\log [Cl^-]$ was found to be linear with a slope 0.5. Hence the total order with respect to gross HCl is definitely due to both H^+ and Cl^- catalyses.

TABLE 4—EFFECT OF VARYING $[Cl^-]$ IN PRESENCE OF $HClO_4$ AND IN PRESENCE OF HCl

[Acetanilide]=0.005 <i>M</i> , [CAT]=0.0005 <i>M</i>		HOAc=20% V/V Temp.=60°	
[$HClO_4$] <i>M</i>	[HCl] <i>M</i>	[KCl] <i>M</i>	$10^3 k_1, \text{min}^{-1}$
0.0125	—	0.003	16.48
—	—	0.006	24.23
—	—	0.0125	38.28
—	—	0.025	61.32
—	—	0.006	54.24
—	0.0125	0.0125	75.58
—	—	0.025	94.79

Effect of temperature : In order to investigate the effect of temperature on the reaction rate, the reactions have been carried out at 50°, 60° and 70°. The rate constants at various temperatures are recorded in Tables (5a and b). The plots of $\log k_1$ vs $1/T$ are found to be linear. The activation parameters have been recorded in Tables (6a and b). A relative high negative entropy of activation indicates that intermediate transition state is rigid^{7,8}.

TABLE 5(a)—EFFECT OF TEMPERATURE ON REACTION RATE

[Substrate]=0.005 <i>M</i> , [CAT]=0.0005 <i>M</i> ,		HOAc=20% V/V [$HClO_4$]=0.0125 <i>M</i>	
Substrate		$10^3 k_1, \text{min}^{-1}$ at	
	50°	60°	70°
Acetanilide	3.72	7.11	13.48
<i>p</i> -CH ₃ acetanilide	3.83	6.37	12.76
<i>p</i> -Cl acetanilide	2.66	4.86	10.48
<i>o</i> -Cl acetanilide	1.87	3.97	7.57

TABLE 5(b)—EFFECT OF TEMPERATURE IN PRESENCE OF Cl^- AND HCl

[CAT]=0.0005 <i>M</i> , [HClO ₄]=0.0125 <i>M</i>		[Acetanilide]=0.005 HOAc =20% V/V	
[KCl]	[HCl]	10 ³ $\frac{k_1, \text{min}^{-1}}{60^\circ}$ at	
		50°	70°
0.0125	—	13.21	71.36
—	0.0125	35.68	119.00

TABLE 6(a)—ACTIVATION PARAMETERS AT 60°

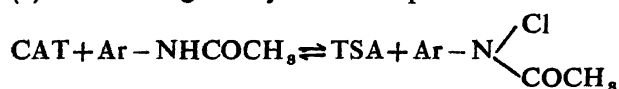
Substrate	E K cal/mole	ΔH^\ddagger K cal/mole	$\log_{10} A$	ΔS^\ddagger e.u.
Acetanilide	15.25	14.58	6.07	-32.95
<i>p</i> -CH ₃ acetanilide	14.08	13.41	5.26	-36.69
<i>p</i> -Cl acetanilide	15.25	14.58	5.90	-33.71
<i>o</i> -Cl acetanilide	17.60	16.93	7.37	-27.05

TABLE 6(b)—ACTIVATION PARAMETERS FOR ACETANILIDE AT 60° (IN PRESENCE OF Cl⁻ AND HCl)

	E K cal/mole	ΔH [‡] K cal/mole	log ₁₀ A	-ΔS [‡] e.u.
In presence of				
HCl	10.37	9.7	3.8	42.89
Cl ⁻	13.69	12.96	5.7	34.47

Mechanism and the rate law : A fractional dependence on substrate, a direct fractional dependence on acidity and first order dependence on the halogenating agent clearly indicate that the reaction might proceed through the formation of N-chloro intermediate in an equilibrium step, which then undergoes subsequent Orton rearrangement to nuclear chlorinated products in rate determining steps involving H⁺ catalysis and nucleophilic attack of water molecules.

The following facts are in support of the mechanism postulated : (a) The rearrangement can proceed in a dualistic pathway, acid catalysed and acid independent. (b) The rearrangement of N-chloro intermediate is the rate determining step is well established by the fact that chloride ions accelerate the reaction to a great extent. The chloride ions interact with the N-chloro compound to form molecular chlorine in a rate determining step which chlorinates the aromatic ring in a fast step. It is interesting to recall that in the CAT reactions of amines in acid medium, there was no chloride ion catalysis and hence the formation of N-chloro compound in a rate determining step followed by a fast isomerisation to nuclear products was postulated⁸. In the present study Cl⁻ catalysis is of prime importance indicating that the rearrangement of N-chloro acetanilide is the rate controlling step. (c) According to Pryde and Soper^{9,9} the reaction

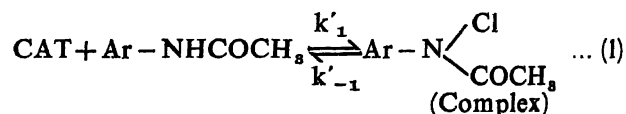


proceeds with great ease at lower pH and reverse reaction occurs at higher pH. In our study we have investigated the effect of pH on the reaction rate (Table 7). The reaction rate was found to decrease with an increase in the pH of the medium (Table 7). Hence the formation of the N-chloro intermediate in a fast equilibrium step followed by the rate determining rearrangement is the most plausible process under our experimental conditions.

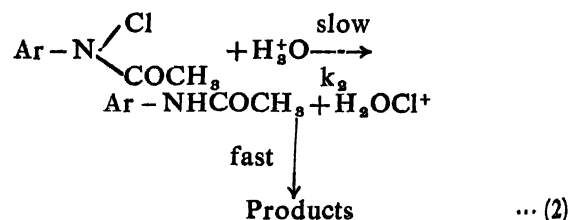
TABLE 7—EFFECT OF pH ON REACTION RATE IN AQUEOUS MEDIUM

[Acetanilide]=0.005M	[CAT]=0.0005M	Temp.=60°
Components	pH	10 ³ k ₁ min ⁻¹
0.0125 HClO ₄	1.90	5.89
0.008 HClO ₄	2.50	4.78
0.1M KH ₂ PO ₄	4.5	2.09

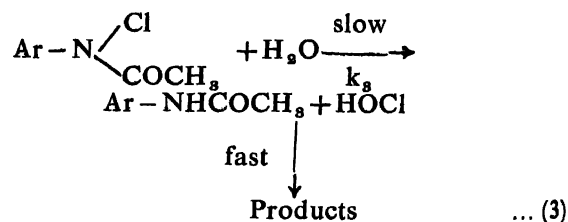
We, therefore, propose the following two mechanistic pathways, one involving H⁺ ion catalysis and the other involving nucleophilic attack of water molecules in removing the positive chlorinium species.



Scheme I



Scheme II



The rate law for scheme involving step (1) and (2) may be derived in the following manner.

Total CAT concentration is given by [CAT]_T = [CAT] + [Complex] ; Applying a steady state treatment to complex we get

$$k'_1[\text{CAT}][\text{S}] = k'_{-1}[\text{complex}] + k_2[\text{complex}][\text{H}^+]$$

$$[\text{Complex}] = \frac{k'_1[\text{CAT}][\text{S}]}{k'_{-1} + k_2[\text{H}^+]}$$

$$\begin{aligned} \text{Hence } [\text{CAT}]_T &= [\text{CAT}] + \frac{k'_1[\text{CAT}][\text{S}]}{k'_{-1} + k_2[\text{H}^+]} \\ &= \frac{k'_{-1} + k_2[\text{H}^+] + k'_1[\text{S}]}{k'_{-1} + k_2[\text{H}^+]} [\text{CAT}] \end{aligned}$$

$$[\text{CAT}] = \frac{\{k'_{-1} + k_2[\text{H}^+]\}[\text{CAT}]_T}{k'_{-1} + k_2[\text{H}^+] + k'_1[\text{S}]}$$

Now the rate

$$\begin{aligned} -\frac{d[\text{complex}]}{dt} &= k_2[\text{complex}][\text{H}^+] \\ &= \frac{k'_1 k_2 [\text{CAT}][\text{S}][\text{H}^+]}{k'_{-1} + k_2[\text{H}^+]} \\ &= \frac{k'_1 k_2 [\text{S}][\text{H}^+]\{k'_{-1} + k_2[\text{H}^+]\}[\text{CAT}]_T}{\{k'_{-1} + k_2[\text{H}^+]\}\{k'_{-1} + k_2[\text{H}^+] + k'_1[\text{S}]\}} \\ &= \frac{k'_1 k_2 [\text{CAT}]_T [\text{S}][\text{H}^+]}{k'_{-1} + k_2[\text{H}^+] + k'_1[\text{S}]} \end{aligned}$$

At lower acidity the term $k_2[H^+]$ may be neglected as k_2 is rate determining. Hence the rate law for the acid catalysed path takes the form

$$V_1 = \frac{k'_1 k_2 [\text{CAT}]_T [\text{S}] [\text{H}^+]}{k'_{-1} + k'_1 [\text{S}]}$$

$$\text{or, } V_1 = \frac{K k_2 [\text{CAT}]_T [\text{S}] [\text{H}^+]}{1 + K [\text{S}]} \quad \dots (4)$$

(where $K = k'_1/k'_{-1}$)

In the same way the rate law for the acid independent path involving step (1) and (3) only may be derived as

$$V_2 = \frac{K k_3 [\text{CAT}]_T [\text{S}]}{1 + K [\text{S}]} \quad \dots (5)$$

Hence, the observed rate law in terms of the total decrease in the concentration of active chlorine would be

$$\begin{aligned} V &= \frac{K k_2 [\text{S}] [\text{CAT}]_T [\text{H}^+]}{1 + K [\text{S}]} + \frac{K k_3 [\text{S}] [\text{CAT}]_T}{1 + K [\text{S}]} \\ &= \frac{K [\text{S}] [\text{CAT}]_T \{k_2 + k_3 [\text{H}^+]\}}{1 + K [\text{S}]} \quad \dots (6) \end{aligned}$$

This clearly indicates a fractional dependence on the substrate, fractional dependence on acidity and a unit dependence on total CAT.

To test the validity of the above rate law it may be arranged to the form

$$\begin{aligned} 1/k_1 &= \frac{1 + K [\text{S}]}{K [\text{S}] \{k_2 + k_3 [\text{H}^+]\}} \\ &= \frac{1}{K \{k_2 + k_3 [\text{H}^+]\}} \left(\frac{1}{[\text{S}]} + \frac{1}{k_2 + k_3 [\text{H}^+]} \right) \end{aligned}$$

where k_1 is the observed pseudo first order rate constant with respect to CAT.

The plot of $1/k_1$ vs $1/[\text{S}]$ for acetanilide was found to be perfectly linear (Fig. 4). The slope and intercept of this line correspond to $1/K \{k_2 + k_3 [\text{H}^+]\}$ and $1/\{k_2 + k_3 [\text{H}^+]\}$ respectively. From the slope and intercept of the line the value of equilibrium constant 'K' of the equation (1) was found out to be 162.5 lit. mole⁻¹ for acetanilide under our experimental condition. Again rearranging equation (6) we get,

$$\begin{aligned} k_1 &= \frac{K [\text{S}]}{1 + K [\text{S}]} \{k_2 + k_3 [\text{H}^+]\} \\ &= \frac{k_2 K [\text{S}]}{1 + K [\text{S}]} + \frac{k_3 K [\text{S}]}{1 + K [\text{S}]} [\text{H}^+] \end{aligned}$$

A plot of k_1 vs $[\text{H}^+]$ should thus be linear with a finite intercept on the rate axis. In the case of

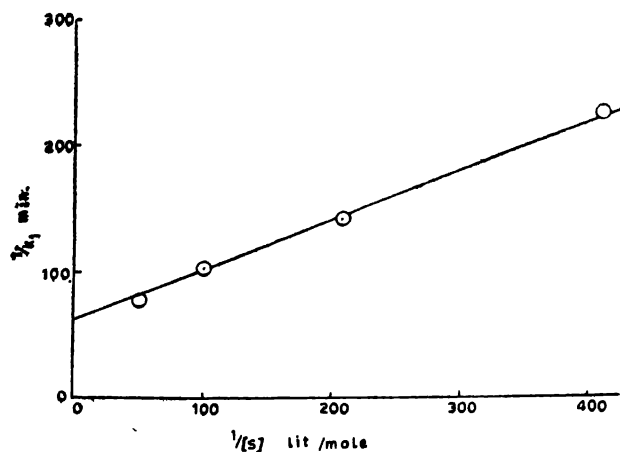


Fig. 4. Double reciprocal plot of $1/k_1$ vs $1/[\text{S}]$ for acetanilide. $[\text{CAT}] = 0.0005M$; $[\text{HClO}_4] = 0.0125M$; $\text{HOAc} = 20\% \text{ v/v}$; Temp. = 60° .

acetanilide the plot of k_1 vs $[\text{H}^+]$ for a particular [substrate] was linear (Fig. 5) with an intercept on the rate axis. From the intercept of the line the value of k_2 was found out utilising the value of K as obtained earlier. The average value of k_2 for three different substrate concentrations was found to be $7.803 \times 10^{-2} \text{ min}^{-1}$ under the experimental condition.

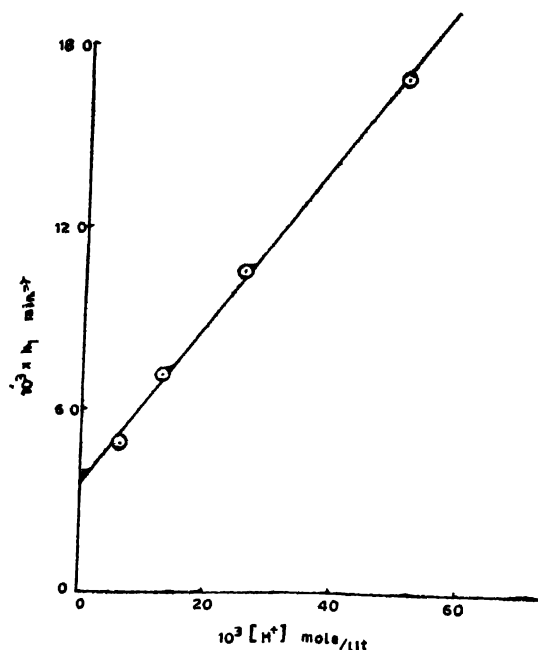
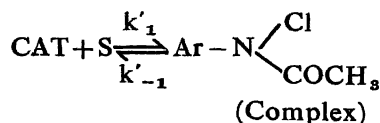


Fig. 5. Plot of k_1 vs $[\text{H}^+]$. $[\text{Acetanilide}] = 0.005M$; $[\text{CAT}] = 0.0005M$; $\text{HOAc} = 20\% \text{ v/v}$; Temp. = 60° .

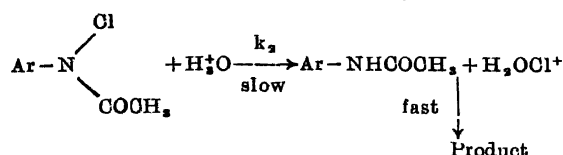
In the same way the average value of k_2 as obtained from three different substrate concentrations was evaluated from the slope of the lines to be $0.5944 \text{ lit mole}^{-1} \text{ min}^{-1}$.

Utilising these values of k_s , k_a and K in equation (6) the calculated rates have been found to be in excellent agreement with the observed rates in individual experiments. Thus the applicability of the above rate law in explaining the findings is justified.

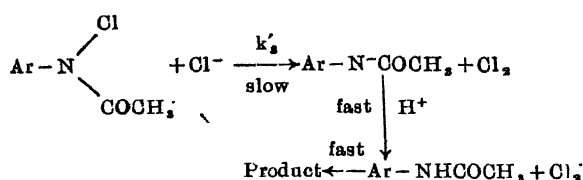
The enhanced acceleration in presence of HCl and the catalytic effect of Cl^- ions can also be rationalised in the following way, one involving the usual H^+ ion catalysis and the other involving attack of Cl^- on the positive chlorine of the N-chloro intermediate.



Scheme III



Scheme IV



Applying steady state treatment to the complex the combined rate law can be derived as

$$V = \frac{K[S][\text{CAT}]_T}{1 + K[S]} \{k_2[\text{H}^+] + k'_2[\text{Cl}^-]\} \quad \dots (7)$$

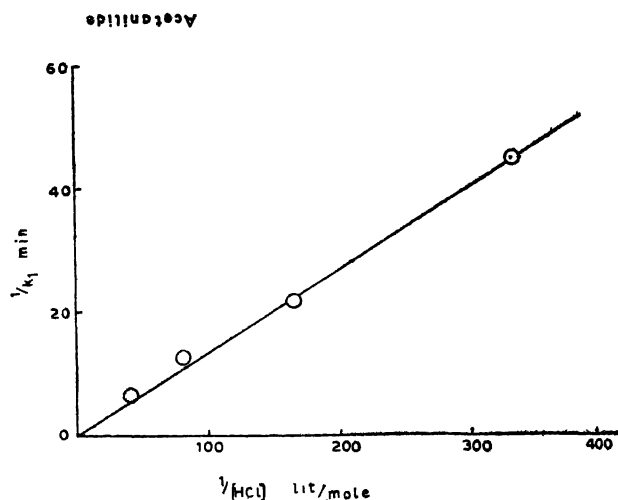
In the case of HCl alone $[\text{H}^+] = [\text{Cl}^-] = [\text{HCl}]$ Hence the rate law takes the form

$$V = \frac{K'K[S][\text{CAT}]_T[\text{HCl}]}{1 + K[S]} \quad (\text{where } K' = k_2 + k'_2)$$

This indicates a unit dependence on the gross $[\text{HCl}]$ which is the cumulative effect of both H^+ and Cl^- catalyses. The applicability of this rate law can also be tested by putting it in the form

$$1/k_1 = \frac{1 + K[S]}{K'K[S]} \times \frac{1}{[\text{HCl}]} \quad \dots (8)$$

For acetanilide a plot of $1/k_1$ vs $1/[\text{HCl}]$ was found to be linear (Fig. 6) passing through origin. From the slope of the line the value of K' was found to be $16.72 \text{ lit. mole}^{-1} \text{ min}^{-1}$ utilising the K value as derived earlier. The reproducibility of K'

Fig. 6. Plot of $1/k_1$ vs $1/[\text{HCl}]$.

Acetanilide = $0.005M$; $[\text{CAT}] = 0.0005M$;
HOAc = 20% v/v; Temp. = 60° .

was checked at three different concentrations of the substrate by varying HCl. Inserting the values of K , and K' in equation (8), the calculated rate constants in presence of HCl are found to be in excellent agreement with the observed values in individual experiments.

Structure reactivity: It is seen that there is marked effect due to variation of structure in these anilides as fractional dependence on each substrate is observed due to prior complex formation between substrate and CAT. As the order with respect to substrate is fractional, the double reciprocal plots of $1/k_1$ vs $1/[\text{Substrate}]$ have been plotted and from the finite intercepts on the inverse rate axis, the decomposition constants for different substrates studied have been computed and recorded in Table 8. A glance into the decomposition constants of Table 8 indicates that the order of reactivity among the different acetanilides studied is *p*-bromo acetanilide > *p*-methyl acetanilide > *o*-chloro

TABLE 8

Substrate	$10^4 k_{\text{dec}} \text{ min}^{-1}$
Acetanilide	16.69(8.94)*
<i>p</i> -Methyl acetanilide	22.22
<i>p</i> -Chloro acetanilide	15.38
<i>o</i> -Chloro acetanilide	20.00
<i>p</i> -Bromo acetanilide	27.03

* Rate constants for ortho isomer.

acetanilide > *p*-chloro acetanilide > acetanilide and $\rho\sigma$ plot of $\log k_{\text{dec}}$ vs σ is sigmoid indicating the complexation of different substrates with chlorinating agent are different. Such sigmoid curve has been also obtained in the chlorination of anilines by chloramine- T^{10}

References

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