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Kinetics and Mechanism of Chlorination of Some Ketones by Chloramine-B

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The kinetics of chlorination of acetone (AC), ethyl methyl ketone (EMK), ethyl phenyl ketone (EPK), methyl isobutyl ketone (MIK), diethyl ketone (DEK), acetophenone (A), 3′,4′-dimethoxy acetophenone (DMA) and *p*-hydroxy acetophenone (HA) by sodium N-chlorobenzenesulphonamide (Chloramine-B or CAB) in hydrochloric and perchloric acid media has been carried out at 30°C. The effect of $[H^+]$ and $[Cl^-]$, variation of ionic strength and dielectric constant to the medium on the rate of reaction has been studied. Addition of the reaction product, benzenesulphonamide had no effect on the rate of chlorination. Thermodynamic parameters have been evaluated by studying the kinetics at various temperatures. Suitable mechanisms have been proposed in consistency with the kinetic results.

INTRODUCTION

The chemistry of N-halo-N-metallo aromatic sulphonamides has attracted the attention of many investigators on account of their diverse behaviour. They are the sources of halonium cations and hypohalite species.[1–3] The kinetic investigations of the oxidation of ketones by several oxidants have been reported,[4–15] except with chloramine-B (CAS). As part of our mechanistic investigations of organic compounds[16–20] with chloramine-B, we report herein the detailed investigation of chlorination of ketones by chloramine-B in acid media.

EXPERIMETAL

Triply distilled water was used in preparing the solutions. An aqueous solution of CAB (0.1 M) was prepared and standardized by the iodometric method The ketones acetone (AC), ethyl methyl ketone (EMK), methyl isobutyl ketone (MIK), acetophenone (A), 3′,4′-dimethoxy acetophenone (DMA), *p*-hydroxy acetophenone (HA) (all BDH), diethyl ketone (DEK) and ethyl phenyl ketone (EPK) (both Fluka) were purified before use. Solutions of AC and EMK were prepared in water, while the other ketones in ethanol. All other chemicals used were of AnalaR grade. Heavy water (99.4%) supplied by Bhabha Atomic Research Centre, Bombay was used for studying the solvent isotopic effect. IR and ^1H NMR spectra of the products were recorded on a Perkin-Elmer model 781 spectrophotometer and on a Jeol FX 90/Bruker-WH 270 spectrometer respectively.

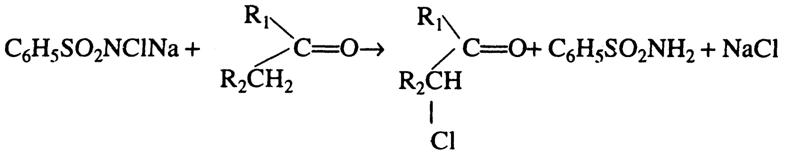
The reaction was carried out in a glass stoppered pyrex boiling tube. Requisite amounts of ketone, acid, $NaClO_4$ and H_2O/ethanol-water to maintain the total volume constant for all runs were taken in the tube and thermostated at 30°C. A measured volume of CAB solution thermostated at the same temperature was added to the mixture in the boiling tube. Aliquots of the reaction mixture containing AC, EMK, MIK, DEK and EPK were pipetted out into a known quenching of 5 mL ascorbic acid (0.005 M) and 10 mL HCl (4 N). The excess ascorbic acid was back titrated against a standard solution of CAB using starch-KI indicator. In the case of A, DMA and HA, the progress of the reaction was monitored by iodometric determination of unreacted CAB in a measured aliquot of the reaction mixture at different intervals of time.

The reactions were studied under pseudo first order conditions by keeping excess of ketone over CAB. The reactions were followed up to two half lives and pseudo first order rate constants were calculated from the linear plots of log [CAB] against time.

Regression analysis of the experimental data to obtain regression coefficient 'r' and standard deviations of the points from regression line 's' was carried out on a PC-XT.

Stoichiometry and Product Analysis

Reaction mixtures containing an excess of CAB over ketone (S) were kept at 30°C in presence of HCl or $HClO_4$ (overall concentration of 0.5 M) for 24 h. Iodometric estimation of unconsumed CAB revealed that one mole of ketone (S) consumed one mole of CAB. The reaction can be represented as,



$$C_6H_5SO_2NClNa + (R_1)(R_2CH_2)C{=}O \rightarrow (R_1)(R_2CHCl)C{=}O + C_6H_5SO_2NH_2 + NaCl \quad (1)$$

$$C_6H_5SO_2NClNa + C_6H_3R_3R_4COCH_3 \rightarrow C_6H_3R_3R_4COCH_2Cl + C_6H_5SO_2NH_2 + NaCl \quad (2)$$

where $R_1 = -CH_3$ or $-C_2H_5$ or $-CH_2-\underset{\underset{CH_3}{|}}{CH}-CH_3$ or $-C_6H_5$

$R_2 = -H$ or $-CH_3$

$R_3 = R_4 = -H$ in A

$R_3 = R_4 = -OCH_3$ in DMA

$R_3 = -H$ and $R_4 = -OH$ in HA

The reaction mixture was extracted into chloroform and benzenesulphonamide, among the reaction products, was detected by TLC. A mixture of petroleum ether, chloroform and *n*-butanol (2 : 2 : 1 v/v) was used as the solvent and iodine as the developing reagent ($R_f = 0.88$). The chloroketones formed were identified by preparing the dinitrophenyl hydrazine (DNP) derivatives. Further, the chloroketones were purified by passing through a silica gel column using chloroform as the eluent and the structures confirmed by recording IR and ^{1}H-NMR spectra.

RESULTS AND DISCUSSION

The chlorination of ketones were carried out at several initial concentrations of the reactants. At constant [HCl] or [$HClO_4$] and [S] in excess, plots of log $[CAB]_T$ *vs.* time were found to be linear, indicating first order dependence on $[CAB]_0$ (Table-1). The rate constant increased with increase in concentration of the substrate [S] and a plot of log k *vs.* log [S] was linear with a slope less than unity indicating fractional order depencence on the [S] (Table-2). The effect of [H^+] and [Cl^-] on the rate was studied in both the media. A fractional order dependence on [H^+] was observed in both the media for AC, EMK, EPK, MIK and DEK. First order dependence on [H^+] was noticed for A, DMA and HA in HCl medium, while no effect of [H^+] on the rate was observed in $HClO_4$ medium. Addition of chloride ion in the form of NaCl by keeping [H^+] constant had no effect on the rate for all the ketones in both the media except DMA and HA where

TABLE-1
EFFECT OF VARYING [OXIDANT] ON THE RATE OF CHLORINATION OF KETONES WITH CAB AT 30°C

M [CAB] 10^3	HCl medium 10^4 k (s^{-1})							
	AC	EMK	EPK	MIK	DEK	A	DMA	HA
3.0	1.06 (1.18)	1.24 (1.13)	0.37 (0.15)	0.39 (0.26)	0.41 (0.25)	0.70 (0.44)	0.72 (0.39)	1.88 (0.62)
4.0	1.03 (1.16)	1,21 (1.13)	0.37 (0.14)	0.38 (0.26)	0.40 (0.25)	0.74 (0.48)	0.72 (0.40)	1.90 (0.63)
5.0	1.05 (1.18)	1.23 (1.12)	0.36 (0.15)	0.39 (0.26)	0.40 (0.25)	0.71 (0.48)	0.72 (0.40)	1.90 (0.63)
6.0	1.04 (1.15)	1.24 (1.14)	0.37 (0.15)	0.39 (0.26)	0.41 (0.25)	0.72 (0.47)	0.72 (0.40)	1.90 (0.63)
7.0	1.07 (1.14)	1.24 (1.12)	0.36 (0.15)	0.39 (0.26)	0.40 (0.25)	0.71 (0.47)	0.72 (0.38)	1.87 (0.63)
5.0*	1.05 (1.16)	1.24 (1.12)	0.37 (0.15)	0.37 (0.26)	0.38 (0.22)	0.71 (0.44)	0.71 (0.40)	1.83 (0.63)
5.0†	1.08 (1.18)	1.26 (1.13)	0.37 (0.15)	0.39 (0.24)	0.41 (0.23)	0.71 (0.46)	0.72 (0.40)	1.86 (0.63)

[S] = 0.1 M; [HCl] or [$HClO_4$] = 0.2; μ = 0.5 M; % EtOH = 50 in EPK, MIK and DEK
[S] = 0.05 M; [HCl] or [$HClO_4$] = 0.1 M; μ = 0.5 M; EtOH = 30 in HA and 40 in A and DMA.
Values in parentheses are for $HClO_4$ medium.
*At ionic strength 1.0 M
†In presence of excess benzenesulphonamide.

a first order dependence was observed. Addition of the reaction product benzenesulphonamide (0.005 M) or variation of the ionic strength of the medium had no effect on the reaction (Table-1). Further, the addition of acrylamide to the reaction mixture did not initiate polymerization showing the absence of free radical species. The solvent composition was varied by adding ethanol to the reaction mixture. The rate decreased with the increase in the ethanol content and a plot of log k *vs.* 1/D, where D is the dielectric constant of the medium gave a negative slope in both the media for AC, EMK, EPK, MIK and DEK and only in $HClO_4$ medium for A and DMA. A straight line with a positive slope was observed in A, DMA and HA in HCl medium while no effect was observed in the case of HA in $HClO_4$ medium. Blank experiments performed showed that ethanol was not oxidized by CAB under the present experimental conditions. The reactions were studied at various temperatures and the kinetic and thermodynamic parameters evaluated. The results are given in Tables 3 and 4.

TABLE-2
EFFECT OF VARYING THE [S] ON THE RATE OF THE REACTION AT 30°C

10^2 [S] M	HCl medium 10^4 k (s^{-1})							
	AC	EMK	EPK	MIK	DEK	A	DMK	HA
2.0	—	—	—	—	—	0.39	0.50	1.56
	—	—	—	—	—	(0.35)	(0.29)	(0.53)
5.0	0.87	1.07	0.28	0.34	0.31	0.71	0.72	1.90
	(0.93)	(0.90)	(0.12)	(0.21)	(0.20)	(0.48)	(0.40)	(0.63)
8.0	—	—	—	—	—	1.11	0.80	2.00
	—	—	—	—	—	(0.53)	(0.42)	(0.69)
10.0	1.05	1.23	0.36	0.39	0.40	—	—	—
	(1.18)	(1.12)	(0.15)	(0.26)	(0.25)	—	—	—
12.0	—	—	—	—	—	1.56	0.86	2..10
	—	—	—	—	—	(0.60)	(0.45)	(0.72)
15.0	1.16	1.33	0.43	0.42	0.46	1.72	0.89	2.15
	(1.38)	(1.22)	(0.17)	(0.28)	(0.29)	(0.63)	(0.47)	(0.75)
20.0	1.23	1.48	0.49	0.47	0.51	—	—	—
	(1.51)	(1.40)	(0.19)	(0.32)	(0.32)	—	—	—
25.0	1.34	1.55	—	0.49	0.53	—	—	—
	(1.59)	(1.49)	—	(0.34)	(0.33)	—	—	—

[CAB] = 0.005 M; [HCl] or $[HClO_4]$ = 0.2 M; μ = 0.5 M; % EtOH = 50 in EPK, MIK, DEK.
[CAB] = 0.005 M; [HCl] or $[HClO_4]$ = 0.1 M; μ = 0.5 M; % EtOH = 30 in HA and 40 in A and DMA.

Values in parentheses are for $HClO_4$ medium.

TABLE-3
THEMODYNAMIC AND KINETIC PARAMETERS FOR THE CHLORINATION OF KETONES

Parameters	HCl medium				
	AC	EMK	EPK	MIK	DEK
E_a (kJ mol^{-1})	35.9	52.7	40.7	85.0	33.5
	(26.9)	(41.1)	(69.0)	(56.7)	(47.6)
log A	2.85 ± 0.02	5.86 ± 0.1	3.25 ± 0.01	10.87 ± 0.01	2.01 ± 0.01
	(1.89 ± 0.01)	(3.73 ± 0.01)	(7.75 ± 0.01)	(5.79 ± 0.01)	(4.35 ± 0.01)
$-\Delta S^{\#}$ (JK mol^{-1})	211.0 ± 0.3	154 ± 0.2	204.3 ± 0.3	37.3 ± 0.3	205.9 ± 0.4
	(239.2 ± 0.4)	(194.4 ± 0.2)	(99..2 ± 0.3)	(133 ± 0.4)	(31.3 ± 0.7)
$-\Delta H^{\#}$ (kJ mol^{-1})	33.3 ± 0.04	50.1 ± 0.05	38.1 ± 0.06	82.1 ± 0.05	31.3 ± 0.04
	(24.3 ± 0.02)	(38.5 ± 0.02)	(66.4 ± 0.04)	(54.2 ± 0.01)	(45.0 ± 0.03)
$-\Delta G^{\#}$ (kJ mol^{-1})	98.5 ± 1.1	97.9 ± 0.8	101.3 ± 1.03	93.6 ± 0.9	94.4 ± 1.0
	(98.3 ± 0.9)	(98.6 ± 0.8)	(97.1 ± 1.1)	(95 ± 1.0)	(95.3 ± 1.1)

Values in parentheses are for $HClO_4$ medium.

TABLE-4
THERMODYNAMIC AND KINETIC PARAMETERS FOR THE CHLORINATION OF KETONES

Parameters	HCL Medium		
	A	DMA	HA
E_a (kJ mol^{-1})	113.6	85.8	62.4
	(47.9)	(65.9)	(57.5)
log A	17.9 ± 0.04	13.2 ± 0.02	9.3 ± 0.01
	(5.3 ± 0.01)	(8.3 ± 0.01)	(7.1 ± 0.01)
$-\Delta S^{\#}$ (JK mol^{-1})	—52.8 ± 0.9	27.4 ± 0.04	98.2 ± 0.2
	(155.7 ± 0.3)	(99.4 ± 0.2)	(123.2 ± 0.3)
$-\Delta H^{\#}$ (kJ mol^{-1})	110.0 ± 0.04	83.3 ± 0.04	59.9 ± 0.02
	(45.3 ± 0.08)	(63.3 ± 0.08)	(59.9 ± 0.08)
$-\Delta G^{\#}$ (kJ mol^{-1})	94.0 ± 0.2	91.7 ± 0.2	90..1 ± 0.5
	(94.0 ± 1.5)	(94.4 ± 1.0)	(93.5 ± 1.2)

Values in parentheses are for $HClO_4$ medium.

Solvent isotopic studies were made in D_2O medium with acetone as the probe. It was found that $K_{H_2O}/K_{D_2O} = 0.5$.

The conductometric and pH metric titrations of CAB with HCl reveal the existence of the following equilibria.[17]

$$ArNClNa \rightleftharpoons ArN^{-}Cl + Na^{+} \quad (a)$$

$$ArN^{-}Cl + H^{+} \rightleftharpoons ArNHCl \quad (b)$$

$$ArNHCl + H^{+} \rightleftharpoons ArN^{+}H_2Cl \quad (c)$$

$$2ArNHCl \rightleftharpoons ArNH_2 + ArNCl_2 \quad (d)$$

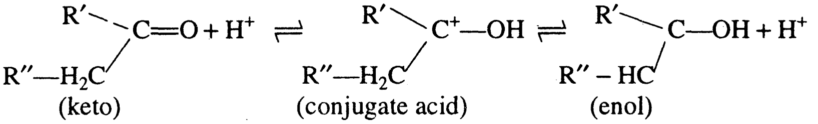
$$ArNCl_2 + H_2O \rightleftharpoons ArNHCl + HOCl \tag{e}$$

$$ArNHCl + H_2O \rightleftharpoons ArNH_2 + HOCl \tag{f}$$

where Ar = $C_6H_5SO_2$

The possible oxidizing species in an acidified solution of CAB are ArNHCl, $ArNCl_2$, ArN^+H_2Cl and HOCl. If $ArNCl_2$ were to be the reactive species, a second order dependence of rate on [CAB] would have been observed and if HOCl were to be the active species, a first order retardation of the rate by the added benzenesulphonamide would be expected and no such effects were noticed. Therefore, the influence of $ArNCl_2$ and HOCl on the chlorination of ketones can be ignored.

Enolisation of ketones could be catalysed both by acids and bases. In general it can be represented as;



(3)

The kinetics will be discussed by taking the above factors into consideration.

Kinetics of AC, EMK, EPK, MIK and DEK in HCl and $HClO_4$ media

The kinetics of chlorination of AC, EMK, EPK, MIK and DEK will be discussed first because of their similar behaviour in HCl and $HClO_4$ media. The following scheme involving ArNHCl as the reactive species is proposed:

$$ArN^-Cl + H^+ \overset{K_1}{\rightleftharpoons} ArNHCl \qquad \text{fast} \tag{g}$$

$$Ar{\cdot}NHCl + S \overset{K_2}{\rightleftharpoons} X \qquad \text{fast} \tag{h}$$

$$X \xrightarrow{K_3} X' \qquad \text{slow and r.d.s} \tag{i}$$

$$X' \xrightarrow{k_4} \text{products} \qquad \text{fast} \tag{j}$$

If $[CAB]_T = [ArN^-Cl] + [ArNHCl] + [X]$, then the rate law would be

$$-\frac{d[CAB]}{dt} = \frac{k_3K_1K_2[CAB]_T[S]}{1 + K_1[H^+] + K_1K_2[H^+][S]} \tag{4}$$

Equation (4) can be transformed into

$$\frac{1}{k_{obs}} = \frac{1 + K_1[H^+]}{k_3K_1K_2[S][H^+]} + \frac{1}{k_3} \tag{5}$$

A plot of $1/k_{obs}$ against $1/[S]$ at constant $[H^+]$ gave a straight line with an intercept equal to $1/k_3$ from which the values of k_3, the rate constant of the rate limiting step, can be evaluated. The values are presented in Table-5.

TABLE-5
VALUES OF k_3, THE RATE CONSTANT OF THE RATE LIMITING STEP DETERMINED FROM THE PLOTS OF $1/k_{obs}$ *vs.* $1/[S]$

Ketone (S)	$10^5\ k_3\ (s^{-1})$	
	HCl	$HClO_4$
AC	15.87	18.20
EMK	17.86	20.00
EPK	7.69	2.50
MIK	5.71	4.35
DEK	6.45	4.17

The above scheme is supported by the negligible influence of ionic strength, addition of benzenesulphonamide and chloride ion on the reaction rate. The proposed mechanism is also supported by the magnitude of the solvent isotopic effect. The moderate values of $\Delta H^\#$ and the negative $\Delta S^\#$ values support a rigid transition state.[3] The constancy in $\Delta G^\#$ values however indicate that a similar mechanism is operative in the chlorination of ketones by CAB in HCl and $HClO_4$ media. Amis and Jaffe[21] have shown that the slope of the line for a plot of log k *vs.* 1/D should be negative for a reaction between a dipole and a dipole while a positive slope is obtained for a positive ion-dipole reactions. In the present investigations, plot of log k *vs.* 1/D is linear with a negative slope, thus supporting participation of a dipole and a dipole in the rate determining step.

The kinetics of A, DMA and HA in HCl and $HClO_4$ media are discussed below.

In HCl medium

The following scheme accounts for the experimental results.

$$ArNHCl + H^+ \overset{K_5}{\rightleftharpoons} ArN^+H_2Cl \qquad \text{fast} \qquad (k)$$

$$ArN^+H_2Cl + S \overset{K_6}{\rightleftharpoons} Y \qquad \text{slow and r.d.s} \qquad (l)$$

$$Y' \xrightarrow{k_7} \text{products} \qquad \text{fast} \qquad (m)$$

Applying steady state conditions to $[ArN^+H_2Cl]$, the rate law would be;

$$-\frac{d[CAB]}{dt} = \frac{k_5 k_6 [CAB][S][H^+]}{k_{-5} + k_6[S]} \tag{6}$$

Equation (6) can be transformed into

$$\frac{1}{k_{obs}} = \frac{1}{k_5[H^+]} + \frac{k_{-5}}{k_5 k_6 [S][H^+]} \tag{7}$$

The values of k_5 were calculated by plotting $1/k_{obs}$ *vs.* $1/[S]$ at constant $[H^+]$. From the slope, the rate constant k_6 of the rate limiting step could be calculated if the values of k_{-5} were known at different temperatures. Table-6 gives the values of k_5 and k_{-5}/k_6 for the three substrates at different temperatures.

TABLE-6

VALUES OF k_5 AND k_{-5} / k_6 AT DIFFERENT TEMPERATURES IN HCl MEDIUM

Temp. K	A		DMA		HA	
	$10^4 k_5$ (s^{-1})	k_{-5}/k_6	$10^4 k_5$ (s^{-1})	k_{-5}/k_6	$10^4 k_5$ (s^{-1})	k_{-5}/k_6
303	2.70	0.127	0.80	0.019	22.22	8.69
308	5.88	0.164	18.87	0.014	33.90	5.37
313	10.00	0.030	30.30	0.013	48.78	9 .85

The rate law (6) is in agreement with the observed stoichiometry and kinetic orders. The positive dielectric effect indicates a charge dispersal in the transition state pointing towards an ion-dipole reaction and is also in general agreement about its influence.[22]

Addition of chloride ion increased the rate and a first order dependence on $[Cl^-]$ was observed in DMA and HA.

The proposed scheme explains the experimental observations.

$$ArNHCl + H^+ + Cl^- \overset{K_8}{\rightleftharpoons} ArN^+H_2Cl \ldots Cl^- \quad \text{fast} \qquad (n)$$

$$ArN^+H_2Cl \ldots Cl^- + S \xrightarrow{k_9} Z \quad \text{slow and r.d.s} \qquad (o)$$

$$Z \xrightarrow{k_{10}} \text{Products} \quad \text{fast} \qquad (p)$$

Applying steady state conditions to $[ArN^+H_2Cl \ldots Cl^-]$, the rate law would be

$$-\frac{d[CAB]}{dt} = \frac{k_8 k_9 [CAB][S][H^+]Cl^-}{k_{-8} + k_9[S]} \qquad (8)$$

The reaction is characterized by a moderate energy of activation. The activation parameters $\Delta H^{\#}$ and $\Delta S^{\#}$ decrease in the order HA < DMA < A.

In $HClO_4$ medium

The following scheme accounts for the experimental observations in the chlorination of A, DMA and HA in $HClO_4$ medium.

$$ArNHCl + S \overset{K_{11}}{\rightleftharpoons} P \quad \text{fast} \qquad (q)$$

$$P \xrightarrow{k_{12}} P' \quad \text{slow and r.d.s.} \qquad (r)$$

$$P' \xrightarrow{k_{13}} \text{products} \quad \text{fast} \qquad (s)$$

If $[CAB]_T = [ArNHCl] + [P]$, then the rate law would be

$$-\frac{d[CAB]}{dt} = \frac{k_{12}K_{11}[CAB]_T[S]}{1 + K_{11}[S]} \qquad (9)$$

or

$$\frac{1}{k_{obs}} = \frac{1}{k_{12}K_{11}[S]} + \frac{1}{k_{12}} \qquad (10)$$

A plot of $1/k_{obs}$ vs. $1/[S]$ gave a straight line with slope equal to $1/k_{12}K_{11}$ and intercept equal to $1/k_{12}$. The values of K_{11} and k_{12} were calculated and are given in Table-7.

TABLE-7

VALUES OF K_{11} AND k_{12} AT DIFFERENT TEMPERATURES IN $HClO_4$ MEDIUM

Temp. K	A		DMA		HA	
	K_{11}	$10^5 k_{12}$	K_{11}	$10^5 k_{12}$ (s^{-1})	K_{11}	$10^5 k_{12}$ (s^{-1})
303	35.17	7.35	37.09	4.90	109.42	7.69
313	88.39	13.16	100.63	11.90	121.83	16.95
323	165.00	23.81	78.57	25.00	168.95	32.26

The rate law (9) is in agreement with the observed stoichiometry and kinetic orders.

The following scheme is proposed for the effect of chloride ion in the case of DMA and HA in $HClO_4$ medium.

$$ArNHCl + S \overset{K_{11}}{\rightleftharpoons} P \qquad \text{fast} \qquad (q)$$

$$P + Cl^- \xrightarrow{k_{14}} Q \qquad \text{slow and r.d.s.} \qquad (t)$$

$$Q \xrightarrow{k_{15}} \text{products} \qquad \text{fast} \qquad (u)$$

If $[CAB]_T = [ArNHCl] + [P]$, then the rate law would be

$$-\frac{d[CAB]}{dt} = \frac{k_{14}K_{11}[CAB]_T[S][Cl^-]}{1 + K_{11}[S]} \qquad (11)$$

The rate law (11) is in agreement with the first order noted with respect to $[Cl^-]$. The observed decrease of rate with the decrease in dielectric constant of the medium is in conformity with the theories proposed.[23, 24] This concept agrees with the present observations and suggested reaction schemes which involves mostly dipoles in the rate limiting step. The large negative $\Delta S^{\#}$ and the near constancy of $\Delta G^{\#}$ values support the proposed mechanism. The latter indicates a solvated activated state[3] and the operation of a similar mechanism for the chlorination of A, DMA and HA in $HClO_4$ medium. The rates of chlorination decrease in the order A < HA < DMA.

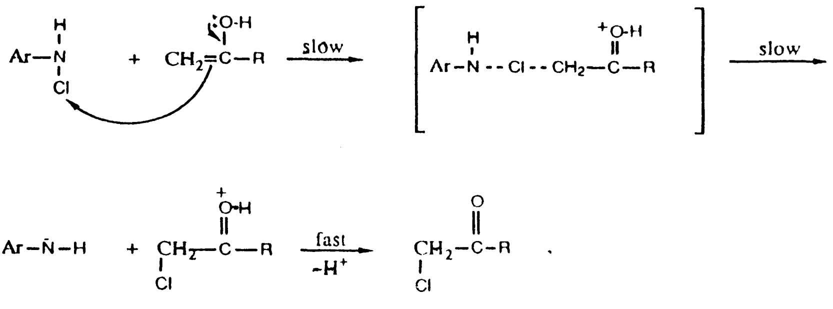
Similar rate laws have been observed in the chlorination of phenols.[25] This may be attributed to the fact that the rate had a first-order dependence on [H^+]. By analogy, a similar mechanism, wherein the enol-form of the ketone reacting with the positive chlorine species is proposed. This is in agreement with the positive dielectric effect observed, indicating charge dispersal in the transition state.

In the case of *p*-hydroxy acetophenone (HA) and in 3′,4′-dimethoxy acetophenone (DMA), the stability of the complex is likely to be enhanced by a strong electron-releasing effect of the *p*-substituent.[6] This is possibly the reason for the fractional-order dependence.

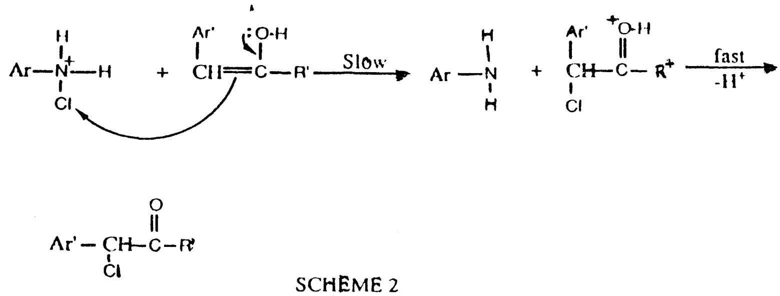
The isokinetic relation was tested by plotting $\Delta H^{\#}$ *vs.* $\Delta S^{\#}$ which was linear in all the cases. From the slope, the isokinetic temperature β was found to be higher than the experimental temperature (303 K) indicating enthalpy as the controlling factor. The relationship was found to be genuine through the Exner criterion[26] by plotting log k_{303K} *vs.* log k_{313K}. Current views[27] do not attach much significance to the concept of isokinetic temperature, as the Exner criterion is a necessary follow up factor of the isokinetic relation.

Substantial deuterium isotopic effect is in excellent agreement with carbonium ion character in the transition state (Eq. 3) and indicates a pre-equilibrium fast proton transfer with specified acid catalysed reaction,[28, 29] which establishes **the involvement of enol form and not the keto form in the above studied ketones.**

The detailed mechanism for the chlorination of ketones with chloramine-B in hydrochloric and perchloric acid media are given in Schemes 1 and 2.



SCHEME 1



SCHEME 2

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