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Kinetics and Mechanism of Oxidation of Aliphatic Primary Alcohols with 1-Chlorobenzimidazole in Aqueous Acetic Acid Medium

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Abstract: The kinetics of oxidation of a few aliphatic primary alcohols with 1-chlorobenzimidazole (CBI) was studied in aqueous acetic acid medium. The reactions were found to be first order each with respect to the concentrations of CBI and alcohol. The added $HClO_4$ increases the rate and the order in $HClO_4$ was found to be fractional. The reactions were catalyzed by NaCl and fractional order dependence was observed. The ionic strength had negligible influence on the rate. The reaction rates increase with decrease in dielectric constant of acetic acid. Addition of benzimidazole, one of the products does not affect the rate. Effect of temperature on the reaction rates was studied at different temperatures and the various activation and thermodynamic parameters were evaluated. The rate constants show good correlation with Taft–Pavelich Dual substituent parameter model (DSP). Product analysis shows the formation of aldehydes as major products of oxidation of aliphatic primary alcohols. $CBIH^+$ has been postulated as the reactive oxidizing species. A mechanism involving a proton transfer by water molecule has been proposed.

Keywords: Aliphatic Alcohols, 1-Chlorobenzimidazole, Oxidation, Kinetics.

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1 Introduction

Chemistry of N-halo compounds has received considerable attention of the researchers owing to their ability to act as a source of halogenonium cations, hypo halite species and nitrogen anions which act as both as bases and nucleophiles [1–7]. Much of kinetic works have been carried out for the oxidation of variety of organic substrates with N-halo compounds [8–14]. 1-Chlorobenzimidazole (CBI) has been widely used as an oxidant for the oxidation kinetics. The oxidation reactions of benzaldehydes [15], furfural [16] and cyclanols [17] with CBI in aqueous acetic acid medium have been studied.

Recent studies on the oxidation of aliphatic alcohols by 2,2,6,6-tetramethyl piperidine 1-oxychlorite [18], 2,2-bipyridyl chromium peroxide [19], 2,2-bipyridyl promoted chromic acid [20], BTPPD [21], TBATB [22], Pyridinium fluorochromate [23], Quniolinium fluorochromate [24], $KMnO_4$ [25], Quinolinium bromochromate [26], Isoquinolinium bromochromate [27], Benzyl triethyl ammonium chlorochromate [28], Benzyl triphenyl phosphonium chromate [29], N-bromosaccharin [30], N-chloronicotinamide [31, 32], N-chlorosuccnimide [33], N-bromosuccinimide [34–36], Bromamine-B [37], N-bromoisonicotinamide [38], N-bromoacetamide [39, 40] and 1-bromobenzimidazole [41] prompted the authors to undertake the present work on the kinetics and mechanism of oxidation of aliphatic primary alcohols with CBI in aqueous acetic acid medium.

2 Materials and methods

2.1 Materials

1-Chlorobenzimidazole was prepared by passing a slow stream of chlorine gas into a solution of 5 g of benzimidazole dissolved in 20 ml of glacial acetic acid (0.04 mole) at 305 K for half an hour. On dilution with water the product CBI was formed as dirty white precipitate. It was then filtered, washed with water, dried and recrystallized from ethanol. Its melting point was 497–499 K. Yield was about 3.8 g, 62.5% [42]. Acetic acid was purified by standard method and the fraction distilling at 391 K was collected. Analar grade (E-merck) methanol, ethanol, 1-propanol, 1-butanol, 1-pentanol, 1-hexanol, 1-heptanol were purchased and used as such. Benzimidazole (BDH, AnalaR) was used as such without purification. Analytically pure compounds such as sodium perchlorate (Global manufacturers, Germany), sodium chloride, perchloric acid (BDH, AnalaR), acrylonitrile and nickel chloride were used. Perchloric acid was standardized using standard sodium hydroxide solution.

2.2 Kinetic method

All the standard flasks and the reaction bottles were made up of pyrex glass with ground joint stoppers. The volumetric apparatus, pipettes, burettes and standard flasks were standardized by usual methods. An electrically operated thermostat with a jumo contact thermometer (Global Manufacturers, West Germany) working in conjunction with an electronic relay which maintained temperature accurately with fluctuations not more than 273.1 K was used. The bath liquid was water and it was covered with a layer of thermocole bits to minimize heat and water loss due to radiation.

2.2.1 Preparation of standard solutions

The standard solution of CBI was prepared by dissolving the required quantity in glacial acetic acid. The solution was then standardized by titrating it against standard sodium thiosulphate solution by iodometry method. This standard solution of CBI was found to be invariant in its strength over a period of three months. The solutions of aliphatic primary alcohols were prepared by dissolving the alcohols in 80% acetic acid and 20% water mixture (v/v).

2.2.2 Kinetic measurements

All the kinetic reactions were carried out under pseudo-first order conditions keeping [alcohol] $\gg$ [CBI] in solvent system 80% (v/v) acetic acid-water medium at 303 K. The courses the reactions were followed by potentiometry method [15].

The required quantities of alcohol solutions, perchloric acid, acetic acid-water mixture and sodium chloride solution were pipetted out in a double walled beaker provided with an inlet and outlet for circulating water from the thermostat set at the desired temperature. The reaction mixture was kept in the beaker for nearly half an hour to attain the desired temperature. The reaction was started by pipetting out the required quantity of CBI solution which had also been thermostated for nearly half an hour. The total volume of the reaction mixture was kept as 25 ml. A stop-watch was started when half the amount of oxidant was added.

The reaction was followed by setting up a cell

$$[\mathrm{Pt}|\mathrm{BI}^{(+)}\text{—}\mathrm{CBI}||^{(-)}\mathrm{SCE}]$$

made up of the reaction mixture into which the platinum electrode and saturated calomel electrode (SCE) were dipped. The electromotive force of the cell was measured periodically using Equip-Tronics Digital potentiometer while the reaction mixture was continuously stirred using a magnetic stirrer. The pseudo-first order rate constant, k_1, was computed from the linear ($r > 0.999$) plots of $\log(E_\mathrm{t} - E_\infty)$ vs time.

Where, E_t – potential at time ‘t’ and E_∞ – potential at infinity.

When the kinetic run was also done by iodometry method, the same results were obtained within ±2%. Preliminary experiments showed that the rate of oxidation is not sensitive to change in ionic strength and hence no attempt was made to keep it constant.

2.2.3 Product analysis and stoichiometry

Different ratio of alcohol and CBI were mixed together with $\mathrm{HClO_4}$(1 M) in 80% acetic acid (total volume 100 ml). The reaction mixture was kept aside for 48 h to ensure the completion of the reaction. The solution was extracted with ether, washed with water and the washings were collected. Formaldehyde was formed as the main product which was identified by the formation of semicarbazone derivative (m.p 437–438 K, lit: 440 K). The estimation of unreacted oxidant indicated that one mole of the oxidant was consumed by one mole of the alcohol. Further the product formaldehyde has also been confirmed by its IR (Figure 1) and NMR Spectral data.

$$\mathrm{R\text{-}CH_2OH + CBI \longrightarrow RCHO + BI + HCl} \qquad \text{(i)}$$

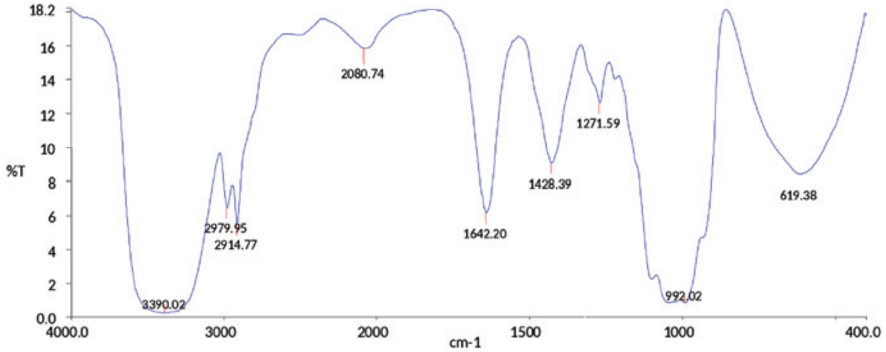


Figure 1: IR spectrum of product of oxidation of aliphatic alcohol (methanol) by CBI.

3 Results and discussion

Oxidation of methyl alcohol by 1-chlorobenzimidazole has been carried out in 80% (v/v) acetic acid – water medium in the presence of perchloric acid and sodium chloride at 303 K. In all the cases the corresponding aldehydes are the major products. The rates of the reactions were measured by following the disappearance of [CBI] potentiometrically. The reactions were followed under pseudo first order conditions where the concentrations of the substrates were in large excess compared to that of [CBI].

The reactions have first order dependence on [CBI] as revealed by the constancy of the rate constant values obtained from integrated first order equation, linearity of the $\log(E_t - E_\infty)$ vs time plot and invariance of k_{obs} values with varying initial [CBI] (Table 1 and Figure 2). The reaction is first order with respect to [substrate], k_{obs} is directly proportional to [methyl alcohol] as evident from the constant values of k_2. Plot of $\log k_{obs}$ vs log [methyl alcohol] is also linear with a slope of unity (Table 1).

Added perchloric acid increases the rate of the reaction (Table 1). A plot of $\log k_{obs}$ vs $\log[H^+]$ is linear with a slope of 0.51 ($r = 0.995$). This shows that the reaction is fractional order dependence with respect to $[H^+]$ indicating the participation of water molecule in the rate determining step [43]. This is further confirmed by Bunnett–Olsen's linear free energy relationship [44] by the plot of $(5 + \log k_{obs} + H_o)$ vs $(3 + \log C_{H^+} + H_o)$. The slope value (ϕ) of the above plot was found to be 1.15 (Figure 3).

The rates of oxidation increase with decreasing dielectric constant of the medium (Table 1). A plot of $\log k_2$ vs $1/D$ is linear with a positive slope. This is indicative of the fact that the reaction is of an ion-dipole type [45]. Increase in concentration of chloride ions increases the rate of the reaction (Table 1). A plot of $\log k_{obs}$ vs $\log[Cl^-]$ is linear with a slope of 0.79 ($r = 0.997$) shows that this reaction is fractional order dependence with respect to $[Cl^-]$.

Initial addition of one of the products, viz. benzimidazole, to the reaction mixture does not affect the rate. The reaction rate is not altered significantly with the addition of nickel chloride, a typical chlorine scavenger. Polymerization is not observed when acrylonitrite is added to the reaction mixture.

Table 1: Effect of varying [CBI], [alcohol], [$HClO_4$], [NaCl] and % acetic acid. Temperature = 303 K.

[CBI] × 10^3 mol dm^{-3}	[Alcohol] × 10^2 mol dm^{-3}	[H^+] × 10^2 mol dm^{-3}	[Cl^-] × 10^2 mol dm^{-3}	% acetic acid	k_{obs} s^{-1} × 10^4
1.50	3.00	3.25	6.00	80	1.90
2.25	3.00	3.25	6.00	80	1.85
3.00	3.00	3.25	6.00	80	1.82
3.75	3.00	3.25	6.00	80	1.89
4.50	3.00	3.25	6.00	80	1.79
3.00	1.50	3.25	6.00	80	1.07
3.00	3.00	3.25	6.00	80	1.82
3.00	4.50	3.25	6.00	80	2.88
3.00	6.00	3.25	6.00	80	3.98
3.00	7.50	3.25	6.00	80	5.13
3.00	3.00	1.30	6.00	80	1.20
3.00	3.00	3.25	6.00	80	1.82
3.00	3.00	5.20	6.00	80	2.29
3.00	3.00	7.80	6.00	80	2.81
3.00	3.00	9.75	6.00	80	3.54
3.00	3.00	3.25	3.60	80	1.31
3.00	3.00	3.25	6.00	80	1.82
3.00	3.00	3.25	9.60	80	2.88
3.00	3.00	3.25	14.40	80	3.80
3.00	3.00	3.25	18.00	80	4.67
3.00	3.00	3.25	6.00	60	1.11
3.00	3.00	3.25	6.00	70	1.40
3.00	3.00	3.25	6.00	80	1.82
3.00	3.00	3.25	6.00	90	3.60

The oxidation of other aliphatic alcohols viz. ethanol, 1-propanol, 1-butanol, 1-pentanol, 1-hexanol and 1-heptanol by CBI has been investigated under comparable conditions. All the other aliphatic primary alcohols exhibit similar kinetic trend (Table 2).

Activation and thermodynamic parameters have been calculated for all aliphatic alcohols (Table 3). The reaction rates are governed by the changes in both the enthalpy and entropy of activation. This is further supported by the lower values of Ea. The negative values of $\Delta S^{\#}$ imply the formation of an ionic transition state with an extensive charge separation with a high degree of solvation. Further, the constancy of $\Delta G^{\#}$ values also confirms the unified mechanism for the oxidation reactions of all the aliphatic alcohols.

A plot of $\log k(T_2)$ versus $\log k(T_1)$ is called Exner plot. It is found to be linear with the slope value of 1.095 ($r = 0.999$). The linearity of Exner plot is suggestive

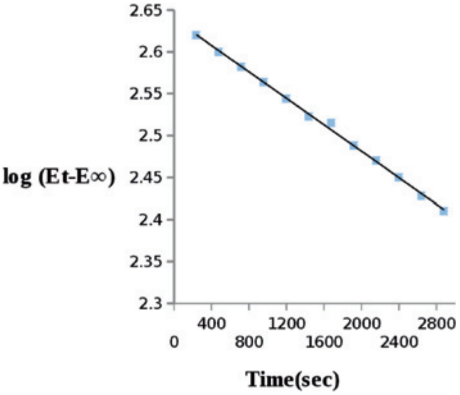


Figure 2: First order plot of CBI.

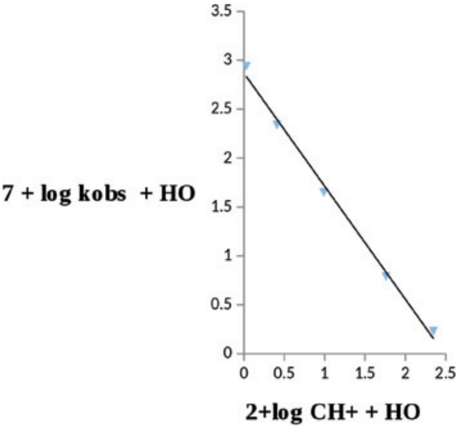


Figure 3: Bunnett–Olsen plot.

Table 2: Effect of alcohols.
[CBI] = 3.00×10^{-3} mol dm^{-3}, [NaCl] = 6.00×10^{-2} mol dm^{-3}
[$HClO_4$] = 3.25×10^{-2} mol dm^{-3}, Solvent = 80% CH_3COOH
[Alcohol] = 3.00×10^{-2} mol dm^{-3}, Temperature = 303 K

Alcohols	Methanol	Ethanol	1-Propanol	1-Butanol	1-Pentanol	1-Hexanol	1-Heptanol
$k_{obs} \times 10^4$ s^{-1}	1.82	2.18	2.83	3.75	4.35	5.20	6.10

of unified mechanism for the CBI oxidation of aliphatic alcohols (Figure 4). From the slope of the Exner plot the isokinetic temperature (β) is as 217.65 K. Since it is below the experimental temperature range (293–323 K), the observed effect of alcohols is real. The value of the slope ‘b’ of the Exner plot indicates nature of the reaction and selectivity (Table 4). Since the slope ‘b’ is greater than one and 217.65 is less than T_1 (293 K) the experimental data fit the type (3b) of Table 4.

Table 3: Arrhenius parameters for the oxidation of aliphatic alcohols by CBI.

Thermo dynamic parameters	Aliphatic Alcohols Methanol	Ethanol	1-Propanol	1-Butanol	1-Pentanol	1-Hexanol	1-Heptanol
E_a kJ mol^{-1}	33.37	31.18	30.18	31.51	31.64	29.70	30.71
$\Delta H^{\#}$ kJ mol^{-1}	30.85	28.66	27.66	28.99	29.12	27.18	28.19
$\Delta G^{\#}$ kJ mol^{-1}	95.94	95.49	94.84	94.08	93.70	93.28	92.85
$-\Delta S^{\#}$ kJ mol^{-1}	214.83	220.57	221.73	214.80	213.09	218.16	213.42
ln A	4.63	3.94	3.80	4.62	4.81	4.22	4.78

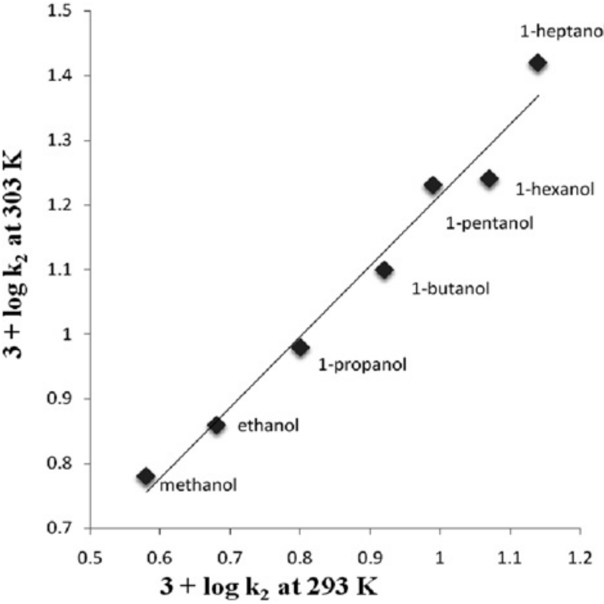


Figure 4: Exner plot.

These results indicate an increasing selectivity with an increase in temperature and the reaction series is characterized by compensation effect between $\Delta H^{\#}$ and $\Delta S^{\#}$.

The rates of oxidation of aliphatic alcohols failed to yield any significant correlation separately with Taft's [46] σ^* and Es values. The rates were therefore correlated in terms of Taft–Pavelich dual substituent parameters [47] (DSP) and presented in Table 5.

Table 4: Nature of reaction series and selectivity.

S. No.	Characterization	Slope		Selectivity
1	$\log A$ Constant	T_1/T_2	–	Decreases
2	Ea Constant	1	0	Unchanged
3a	Compensation effect	$< T_1/T_2$	$> T_2$	Decreases
3b	Compensation effect	> 1	$< T_1$	Increases
3c	Compensation effect	< 0	$< T_2 > T_1$	Increases

Table 5: Temperature dependence of reaction constants of aliphatic alcohols (Taft–Pavelich dual parameters).

Temp. (K)	Polar reaction constant (ρ^*)	Steric reaction constant (δ)	r^2	Standard deviation (sd)	ψ
293	$-1.23(\pm1.65)$	$-0.75(\pm0.64)$	0.569	0.13	0.08
303	$-1.25(\pm1.65)$	$-0.74(\pm0.64)$	0.690	0.13	0.09
313	$-1.56(\pm1.57)$	$-0.86(\pm0.61)$	0.712	0.12	0.08
323	$-1.50(\pm1.60)$	$-0.82(\pm0.62)$	0.687	0.13	0.09

The values of substituent constants were obtained from the compilation of Wiberg [46].

3.1 Mechanism and rate law: Scheme 1

CBI like other N-halo compounds may exist in various forms in acid medium as free CBI, $CBIH^+$, H_2O^+Cl, HOCl and Cl_2 etc. Molecular chlorine may not be the oxidizing species since the rate is not influenced by the initially added nickel chloride which is a well known chlorine scavenger. The H^+ ion dependence on the rate of oxidation of aliphatic alcohols cannot be rationalized if free CBI is considered to be active species. The observation that the reaction rate is not influenced by the added benzimidazole eliminates the possibility of HOCl or H_2O^+Cl being the reactive species [48, 49]. Hence the most probable oxidizing species is the protonated oxidant, $CBIH^+$ which is revealed by H^+ ion dependence on the reaction rate. The protonation of N-halo compounds as a pre-equilibrium step has already been proposed in the oxidation of benzyl alcohols by CBT [50] and BBI [51], aliphatic primary alcohols by NCN [32] and BBI [41], cyclanols by CBI [17] and BBI [52] and α-hydroxy acids by CBT [53].

The increase in reaction rate with the decrease in dielectric constant of the medium suggests that the interaction to be of positive ion–dipole type. The negligible electrolytic effect observed for the reaction substantiates the reaction between an ionic species and a neutral molecule in step 2. Further the participation of water molecule in the rate determining step is confirmed by Bunnet–Olsen plot giving a slope value $\phi = 1.15$ which is in good agreement with the slope value $\phi = 1.40$ for the oxidation of benzyl alcohols by CBT [50]. This clearly indicates that a proton transfer by water molecule occurs in the rate determining step leading to the formation of alkyl hypochlorite intermediate [54]. Hypohalites are known to decompose to carbonyl products [55, 56]. Therefore the following scheme has been proposed for the oxidation of aliphatic alcohols by CBI.

$$\text{CBI} + \text{H}_3\text{O}^+ \underset{}{\overset{K_1}{\rightleftharpoons}} \text{CBIH}^+ + \text{H}_2\text{O} \tag{1}$$

$$\text{CBIH}^+ + \text{R-CH}_2\text{-OH} + \text{H}_2\text{O} \underset{k_{-2}}{\overset{k_2\ \text{slow}}{\rightleftharpoons}} \text{R-CH}_2\text{O-Cl} + \text{BI} + \text{H}_3\text{O}^+ \tag{2}$$

$$\text{R-CH}_2\text{O-Cl} \xrightarrow{k_3\ \text{fast}} \text{R-CHO} + \text{H}^+ + \text{CL}^- \tag{3}$$

Applying equilibrium conditions for the formation of the oxidant species CBIH^+, one can write the equilibrium constant specifically for the formation of CBIH^+ as

$$K_1 = \frac{[\text{CBIH}^+]}{[\text{CBI}]_e[\text{H}_3\text{O}^+]} \tag{4}$$

Assuming $[\text{CBI}]_e = [\text{CBI}]_T - [\text{CBIH}^+]$ where

$[\text{CBI}]_e$ = equilibrium concentration of CBI
$[\text{CBI}]_T$ = total concentration of CBI

Therefore

$$K_1 = \frac{[\text{CBIH}^+]}{\{[\text{CBI}]_T - [\text{CBIH}^+]\}[\text{H}_3\text{O}^+]} \tag{5}$$

where from

$$[\text{CBIH}^+] = \frac{K_1[\text{CBI}]_T[\text{H}_3\text{O}^+]}{1 + K_1[\text{H}_3\text{O}^+]} \tag{6}$$

and Rate $= k_{\text{obs}}[\text{CBI}]_T$

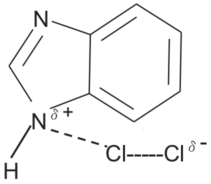
$$= k_2[\text{CBIH}^+][\text{AA}]$$

$$\text{Rate} = \frac{k_2K_1[\text{CBI}]_T[\text{H}_3\text{O}^+][\text{AA}]}{1 + K_1[\text{H}_3\text{O}^+]} \tag{7}$$

at constant $[\text{Cl}^-]$, where AA = Aliphatic alcohol.

3.2 Mechanism in presence of Cl^- ions: Scheme 2

The oxidant species in the presence of added chloride ions can be expected to be different from those oxidizing species already mentioned on account of the pronounced acceleration in the reaction rates observed in the presence of Cl^- ions. It has been well documented that chloride ions interact with N-chloro compounds and release molecular chlorine [32, 57] or species derived therefrom [53, 58]. Since the experimental observations clearly indicate the absence of any Cl_2 formation, it is inferred that the more likely oxidant in the presence of Cl^- ions would be coordinated species of the type (I) [53, 58].



(Type – 1)

The influence of added Cl^- ions on the rate and mechanism can also be accounted for by a small modification of the Scheme 1. It is assumed in Scheme 1 that the reactive species is essentially $CBIH^+$ and that CBI is relatively unimportant. However [CBI] may not be quite negligible at low acid concentrations employed in the experiments and so the reverse hydrolysis of $CBIH^+$ has to be taken into account. Also in presence of added Cl^- ions a coordinated complex of the type (I) would be envisaged. The true formation constant *K* for such a complex can be calculated as follows.

$$CBIH^+ + H_2O \overset{K_h}{\rightleftharpoons} CBI + H_3O^+ \tag{8}$$

$$CBIH^+ + Cl^- \overset{\bar{K}}{\rightleftharpoons} (\text{complex}) \tag{9}$$

$$\text{complex} + AA \xrightarrow[\text{fast}]{k_2} \text{products} \tag{10}$$

where AA = aliphatic alcohol.

$$\bar{K} = \frac{[\text{complex}]}{[CBIH^+][Cl^-]} \tag{11}$$

Assuming $$[\mathrm{CBI}]_{\mathrm{T}} = [\mathrm{CBI}]_{\mathrm{e}} + [\mathrm{CBIH}^{+}] + [\mathrm{complex}]$$

$$[\mathrm{Cl}^{-}]_{\mathrm{Total}} \gg [\mathrm{CBI}]_{\mathrm{Total}}$$

$$[\mathrm{Cl}^{-}]_{\mathrm{Total}} - [\mathrm{complex}] \approx [\mathrm{Cl}^{-}]_{\mathrm{Total}} \approx [\mathrm{Cl}^{-}]$$

and

$$K_{\mathrm{h}} = \frac{[\mathrm{CBI}]_{\mathrm{e}}[\mathrm{H}^{+}]}{[\mathrm{CBIH}^{+}]} \tag{12}$$

$$[\mathrm{complex}] = \frac{\bar{K}[\mathrm{CBI}]_{\mathrm{T}}[\mathrm{H}^{+}][\mathrm{Cl}^{-}]}{K_{\mathrm{h}} + [\mathrm{H}^{+}] + \bar{K}[\mathrm{H}^{+}][\mathrm{Cl}^{-}]} \tag{13}$$

$$\begin{aligned}\mathrm{Rate} &= k_{\mathrm{obs}}[CBI]_{\mathrm{T}} \\ &= k_{2}[\mathrm{complex}][\mathrm{AA}]\end{aligned} \tag{14}$$

Where $$k_{\mathrm{obs}} = \frac{k_{2}\bar{K}[\mathrm{H}^{+}][\mathrm{Cl}^{-}][\mathrm{AA}]}{K_{\mathrm{h}} + [\mathrm{H}^{+}] + \bar{K}[\mathrm{H}^{+}][\mathrm{Cl}^{-}]} \tag{15}$$

Reshuffling

$$\frac{[\mathrm{AA}]}{k_{\mathrm{obs}}} = \frac{1}{k_{2}} + \frac{1}{k_{2}\bar{K}[\mathrm{Cl}^{-}]} + \frac{K_{\mathrm{h}}}{k_{2}\bar{K}[\mathrm{Cl}^{-}][\mathrm{H}^{+}]} \tag{16}$$

Equation (16) predicts a linearity between $[\mathrm{AA}]/k_{\mathrm{obs}}$ and $1/[\mathrm{Cl}^{-}]$ at constant $[\mathrm{H}^{+}]$ and also between $[\mathrm{AA}]/k_{\mathrm{obs}}$ and $1/[\mathrm{H}^{+}]$ at constant $[\mathrm{Cl}^{-}]$. Plots of $1/k_{\mathrm{obs}}$ vs $1/[\mathrm{H}^{+}]$ and $1/k_{\mathrm{obs}}$ vs $1/[\mathrm{Cl}^{-}]$ are linear. From the slopes and intercepts of these plots, the hydrolytic constant (K_{h}) and the true formation constant ($\bar{K}$) of the oxidizing species are calculated to be 3.09 and 737 respectively. The corresponding values for NCSH^{+} equilibrium and for $[\mathrm{NCSH}^{+}\text{–}\mathrm{Cl}^{-}]$ complex and CBTH^{+} equilibrium and for $[\mathrm{CBTH}^{+}\text{–}\mathrm{Cl}^{-}]$ complex are also given in Table 6.

It is observed from Taft–Pavelich dual parameters that ρ^{*} values are negative indicating an electron deficient transition state of the reaction and support the suggested mechanism.

Table 6: Hydrolytic and true formation constants of NCSH^{+}, CBTH^{+} and CBIH^{+}.

S. NO	OXIDANT	K_{h}	$\bar{K}$
1	NCS [58]	0.46	78.4
2	CBT [53]	0.78	694
3	CBI	3.09	737

4 Conclusion

The kinetics of oxidation of aliphatic primary alcohols with 1-chlorobenzimidazole in aqueous acetic acid medium clearly shows that the order of the reaction with respect to [CBI] and [alcohol] is one. The reaction shows fractional order dependence with respect to $[H^+]$ and $[Cl^-]$. The decrease in dielectric constant of the solvent medium increases the rate of reaction significantly. The rate of reaction increases with increase in temperature and the various activation and thermodynamic parameters have been evaluated. The reaction rates show good correlation with Taft- Pavelich dual substituent parameter model. The mechanism proposed for oxidation kinetics is in accordance with the observed kinetic facts.

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