Research Article

Kinetics of oxidation of vanilin by 1-chlorobenzimidazole in acid medium

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Abstract

The kinetics of oxidation of vanillin by 1-Chlorobenzimidazole (CBI) had been studied in aqueous acetic acid medium. The reaction was followed potentiometrically at regular time intervals. The order of the reaction with respect to [CBI] and [H^+] are unity and the order in substrate was found to be zero. The rate of oxidation increases with decrease in dielectric constant of solvent medium indicating ion-dipole interaction. The rate of the reaction is not influenced by the addition of electrolyte like sodium perchlorate. Polymerization was not observed with acrylonitrile. The reactions were studied at different temperatures and the thermodynamic parameters have been calculated. Product analysis showed the formation of vanillic acid which was confirmed by physical constants and spectral analysis. $CBIH^+$ has been postulated as the reactive oxidizing species.

Introduction

The chemistry of N-halo compounds forms a separate branch which is of great synthetic importance [1]. In the recent development, N-halo compounds, the sources of positive halogens, have been extensively employed as oxidizing agents for a variety of organic substrates [2]. The nature of the oxidizing species and mechanism of the reactions depends on the nature of halogen atom, groups attached to the nitrogen atom and the reaction conditions [3].

Amino acids such as glycine, alanine, phenyl alanine, tryptophan, leucine and cysteine serve important functions in our biological system and also play a vital role in metabolism [4]. These amino acids are used in biochemical, microbiological, and nutritional investigation and are employed as dietary supplements [5]. Oxidation of amino acids by various N-halo compounds such as N-chlorosaccharin [6], N-bromonicotinamide [7], N-chloronictoinamide [8], N-bromosuccinimide [9], Chloramine – B [10], Bromamine-B [11], Chloramine-T [12] and N-bromophthalimide [13] have been reported.

The authors have already demonstrated the oxidative capacity of 1-Chlorobenzimidazole (CBI) for a good number of common reductants [14] and also utilized it for the oxidation of benzaldehydes [15] and furfural [16]. An extensive literature survey reveals that no systematic kinetic work hitherto has been done on the oxidation of vanilin using CBI. In the present investigation, the reaction kinetics of oxidation of vanilin with CBI has been studied in aqueous acetic acid medium.

Materials and methods

CBI was prepared and purified by literature method [17]. Acetic acid of AnalaR (Chennai, India) was purified by standard method and the fraction distilling at 118°C was collected and used [18]. Vanilin (B.D.H, AnalaR, Germany) was used as such after distilling at 162°C. All other chemicals are of Analytical grade samples from B.D.H brand obtained from Chennai, India and sodium perchlorate of E Merck brand was purchased from Trichy, India.

Kinetic measurements

All the kinetic reactions were carried out under pseudo-first order conditions, keeping [Vanilin] >> [CBI] in solvent system 80% (v/v) acetic acid-water medium at 303K and the courses the reactions were followed potentiometrically [8]. In a typical experiment, the required quantities of the vanilin solution, perchloric acid and acetic acid-water mixture 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 and the solution were 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 always 25 ml. A stop-watch was started when half the amount of oxidant was added.

The reaction in eq. (1) was followed by setting up a cell made up of the reaction mixture into which the platinum electrode and saturated calomel electrode (SCE) were dipped.

$$[Pt|BI^{(+)}—CBI||^{(-)}SCE]   (1)$$

The emf 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 $(E_t- E_\infty)$ Vs time. Where, E_t - potential at time 't' and E_∞ - potential at infinity. When the kinetic run was also done by iodometry, the same results were obtained within $\pm 2\%$. [6]. 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.

Stoichiometry and product anlaysis

The stoichiometry of the reaction was determined by equilibrating varying ratios of [CBI] Vs [Vanilin] at 303K for 48 hours under kinetic conditions. Estimation of unconsumed CBI revealed that 1 mole of CBI was required to oxidize 1 mole of the vanilin. The stoichiometry of the reaction is 1:1 and is indicated by the eq. (2).
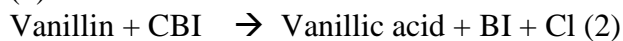
Vanillin + CBI $\rightarrow$ Vanillic acid + BI + Cl (2)
Where BI = Benzimidazole.

The reaction mixture from the actual kinetic run after sufficient time was then evaporated with ether. The layer was then separated and dried. Vanilic acid was formed as the major product which was physical constants and spectral data [19].

Result and discussion

The kinetics of oxidation of vanilin by CBI was investigated at several initial concentrations of vanilin. The oxidation of vanilin by CBI proceeds smoothly at 303K in aqueous acetic acid medium. The order of the reaction with respect to CBI (oxidant) was found to be unity as shown by the linearity of log $(E_t – E_\infty)$ Vs time plots, over 70% of the reaction. The reaction was found to be zero order dependent with respect to substrate as evidenced by the constancy of k_{obs} values at various substrate concentrations (Table 1).

Table 1. Effect of varying [substrate], [oxidant] and [H$^+$] on the reaction rate (Acetic acid= 80%; Temperature = 303K)

[CBI] X 10^3 mol/dm^3	[Vanilin] X 10^2 mol/dm^3	[HClO$_4$] X 10^2 mol/dm^3	k_{obs} X 10^4 (1/s)
1.50	3.00	3.25	6.34
2.25	3.00	3.25	6.29
3.00	3.00	3.25	6.36
3.75	3.00	3.25	6.40
4.50	3.00	3.25	6.32
3.00	1.50	3.25	6.29
3.00	3.00	3.25	6.35
3.00	4.50	3.25	6.28
3.00	6.00	3.25	6.51
3.00	7.50	3.25	6.67
3.00	3.00	1.30	4.51
3.00	3.00	3.25	6.29
3.00	3.00	5.20	8.51
3.00	3.00	7.80	11.67
3.00	3.00	9.75	13.82

Added perchloric acid increases the reaction rate (Table 1). A plot of log k_1 versus log [H$^+$] is linear with a slope of 0.96 indicating the first order dependence of the reaction on [H$^+$] as indicated in Table 1. The rate of the reaction increases with increase in percentage of acetic acid. The plot of log k_{obs} Vs 1/D was found to be linear with positive slope (Table 2). This is according to Amis [20], indicating a positive ion-dipole reaction.

The reaction mixture when allowed to stand with acrylonitrile does not induce polymerization suggesting the absence of free radical mechanism. Added nickel (II) chloride has no appreciable effect on the reaction rate. The rate constants were measured at three different temperatures (Table 3) and the activation parameters have been calculated from the linear Eyring's plot by least square method.

Table 2. Effect of varying [acetic acid] on the reaction rate ([CBI] = 3.0 X 10^{-3} mol/dm^3; [Vanilin] = 3.0 X 10^{-2} mol/dm^3; [HClO$_4$] = 3.25 X 10^{-2} mol/dm^3; Temperature = 303K)

Acetic acid (%)	D	1/D X 10^2	k_{obs} X 10^4 (s^{-1})
90	12.80	7.8	9.20
80	20.00	5.0	6.35
70	27.00	3.7	4.15
60	34.50	2.8	2.64

Table 3. Effect of varying temperature on the reaction rate ([CBI] = 3.0 X 10^{-3} mol/dm^3; [Vanilin] = 3.0 X 10^{-2} mol/dm^3; Acetic acid= 80%; [HClO$_4$] = 3.25 X 10^{-2} mol/dm^3)

Temperature (K)	k_{obs} X 10^4 (s^1)
293	4.73
303	6.30
313	8.76
323	12.23

$\Delta H^{\#}$ = 29.18 KJ/mol^1; $\Delta S^{\#}$ = -223.69 J/Kmol^1; $\Delta G^{\#}$ = 90.99 KJ/mol^1

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.

Oxidising species and rate law

CBI like other N-halo compounds may exist in various forms in acid medium as free CBI, CBIH$^+$, H$_2$O$^+$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$_2$O$^+$Cl being the reactive species [21,22]. Hence the most probable oxidizing species is the protonated oxidant, CBIH$^+$ which is revealed by H$^+$ ion dependence on the reaction rate.

The rate law of the reaction is given by the eq, (3).

$$\text{Rate} = k_{obs}\,[CBI][H^+] \quad (3)$$

Conclusions

The kinetics of oxidation of vanillin in perchloric acid medium was followed potentiometrically by using 1-chlorobenzimidazole (CBI) as an oxidant. The kinetic data reveal that CBI is an excellent oxidant for Vanilin. The detailed kinetic parameters were studied. The kinetic data clearly shows that the order of the reaction with respect to [CBI] and [H$^+$] are unity and zero order with respect to [Vanilin]. The product analysis also shows the formation of Vanilic acid as the major product. The predominant oxidizing species involved in the reaction mechanism has been identified. The suitable mechanism has been proposed.

Conflict of interest

Authors declared no conflict of interests.

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