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KINETICS OF OXIDATION OF SUBSTITUTED γ–KETOACID BY N–CHLOROSACCHARIN IN AQUEOUS ACETIC ACID MEDIUM

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ABSTRACT

The kinetics of oxidation of a γ–ketoacid namely, 4–oxo–4–(3'–4'–dimethylphenyl)butanoic acid by N–chlorosaccharin in aqueous acetic acid medium in the presence of perchloric acid have been investigated potentiometrically. The observed rate of oxidation is first order each in [KA], [NCSA] and [H^+]. The main product of the oxidation is 3,4–dimethylbenzoic acid. The rate decreases with the addition of saccharin, one of the products of the reaction. Variation in ionic strength of the reaction medium has no significant effect on the rate of oxidation, but the rate of the reaction is enhanced by lowering the dielectric constant of the reaction medium. Hypochlorous acidium ion (H_2O^+Cl), has been postulated as the reactive oxidizing species. A suitable mechanism consistent with the experimental results has been proposed. The activation parameters have been computed with respect to slow step of the mechanism.

Key word : Kinetics, Oxidation, γ–Ketoacids, N–Chlorosaccharin

INTRODUCTION

The chemistry of reactions of N–halo compounds form a separate branch, which is of great synthetic importance.[1] N–Halo compounds have been extensively employed as oxidizing agents for organic substrates[2,3]. N–halo compounds are the sources of positive halogen and have been exploited as oxidant for a variety of substrates in both acidic and alkaline media. The nature of active oxidizing species and mechanism depends on the nature of the halogen atom, the groups attached to the nitrogen and the reaction conditions. Although a lot of work has been reported on the oxidation of organic compounds by N–halo compounds,[4–7] it is to be noted that no systematic kinetic investigation on the oxidation of substituted γ–ketoacids by N–chlorosaccharin has yet been reported in the literature. Here we report the results of the kinetics of the oxidation of 4–oxo–4–(3'–4'–dimethyphenyl) butanoic acid (KA) with N–chlorosaccharin (NCSA) in aqueous acetic acid medium in the presence of perchloric acid.

EXPERIMENTAL

4–Oxo–4–(3'–4'–dimethylphenyl) butanoc acid[8] and N–chlorosaccharin[9] were prepared using reported procedures. Doubly distilled water and purified acetic acid were used. Perchloric acid (AnalaR) was used as source of hydrogen ions. Sodium perchlorate (Merck) was used to keep the ionic strength constant.

The reaction was carried out under pseudo–first order condition ([KA] >> [NCSA]). The reaction was followed potentiometrically by setting up a cell made up of the reaction mixture into which a platinum electrode and a reference electrode (SCE) were dipped. The emf of the cell was measured periodically using an Equip–Tronic potentiometer, while the reaction mixture was continuously stirred. The pseudo–first order rate constants computed from the plots of log (E_t–E_∞) against time were reproducible within ± 5%.

RESULTS AND DISCUSSION

Stoichiometry and reaction products : Different sets of reaction mixtures containing different quantities of NCSA and KA at constant concentrations of perchloric acid and sodium perchlorate were allowed to react for 24 h at 30°C and then analyzed. The remaining NCSA was estimated. The oxidation products were identified as 3,4–dimethylbenzoic acid and saccharin. The products were identified by noting the melting point, chemical tests and TLC. The results are in good agreement with 1 : 1 stoichiometry.

$$(CH_3)_2\,C_6H_3COCH_2CH_2COOH + C_6H_4\,SO_2\,CONCl + 5\,H_2O \xrightarrow{H^+} (CH_3)_2\,C_6H_3COOH + C_6H_4SO_2CONH + 3\,CO_2 + 6\,H_2 + HCl \quad ...(1)$$

Reaction order : The reaction orders were determined from the slopes of the double logarithmic plots by varying the concentrations of substrate (KA) and perchloric acid in turn while keeping others constant. The plot of log k_1 against log [KA] is linear (r = 0.991) with a slope value of 0.998 and the plot of log k_1 against log [H^+] is also linear (r = 0.993) with a unit slope. This is further supported by the fact that the plots of k_1 *versus* [KA] and k_1 *versus* [H^+] give straight lines passing through the origin. The linearity of the plots of log [NCSA] *versus* time indicates the order in [NCSA] as unity, which is also confirmed by the constant k_1 values at varying [NSCA] (Table 1). These results indicate clearly that the reaction is first order each with respect to [KA], [NCSA] and [H^+].

Effect of added saccharin : The effect of adding saccharin to the reaction mixture on the reaction rate has been studied in the concentration range 0.02–0.1 mol dm^{-3}. The addition of saccharin reduced the rate of oxidation of ketoacid.

Effect of ionic strength and dielectric constant : The effect of changing dielectric constant of the reaction medium on reaction rate has been studied by carrying out the reactions

at different solvent compositions. The reaction rate increased remarkably with the increase in the proportion of acetic acid in the solvent medium. The effect of ionic strength has also been studied by varying the concentration of $NaClO_4$ in the reaction medium. It was found that the rate of reaction is independent of ionic strength of the medium. The reactions were also carried out in the presence of acrylonitrile, a free radical scavenger and it was confirmed that no free radicals were involved in the reaction.

Table 1. Rate constants for the oxidation of 4–oxo–4–(3'–4'–dimethylphenyl) butanoic acid by NCSA in aqueous acetic acid medium at 30°C[a].

10^2 [KA] mol dm^{-3}	10^3 [NCSA] mol dm^{-3}	[H$^+$] mol dm^{-3}	10^4 k_1b s^{-1}	10^3 k_2c dm^3 mol^{-1} s^{-1}
2.0	2.0	0.5	5.35 ± 0.13	26.7 ± 0.7
4.0	2.0	0.5	9.73 ± 0.53	24.3 ± 1.3
6.0	2.0	0.5	15.5 ± 0.1	25.8 ± 0.2
8.0	2.0	0.5	21.0 ± 1.4	26.3 ± 1.8
2.0	2.0	0.8	7.70 ± 0.37	0.96 ± 0.05
2.0	2.0	1.2	12.0 ± 0.7	1.00 ± 0.06
2.0	2.0	1.6	13.3 ± 0.9	0.95 ± 0.07
2.0	1.5	0.5	5.26 ± 0.19	–
2.0	1.0	0.5	5.37 ± 0.23	–
2.0	0.5	0.5	5.38 ± 0.25	–

[a] General conditions : [$NaClO_4$] = 1.5 mol dm^{-3}, Solvent composition: 50% Acetic acid – 50% Water (v/v); [b] Estimated from pseudo–first order plots, the error quoted in k_1 values is the 95% confidential limit of 'Student t' test.[10]; [c] Individual k_2 values estimated as k_1/[KA] or k_1/[H$^+$].

The effect of temperature : The rate of reaction has been measured at different temperatures. The activation parameters for the oxidation of ketoacid by NCSA have been evaluated from the slope of the Arrhenius plots. The $\Delta H^{\#}$ and $\Delta S^{\#}$ values obtained were 22.1 kJ mol^{-1} and –202.1 J K^{-1} mol^{-1}, respectively.

Mechanism : It is clear from the literature[11] that the probable reactive species of NCSA in acid solution is H_2O^+Cl. The reaction is first order in [NCSA], [KA] and [H$^+$]. The reaction rate increases with increase in [H$^+$] at constant ionic strength, showing that the reaction proceeds completely through the acid–catalyzed pathway. The change in the polarity of the medium has a marked effect on the reaction rate. The trends observed may be due to more than one factor. It may be attributed to the lowering of dielectric constant of the medium, which favours reactions involving protonation. Further, the enolization of the ketoacid may be catalyzed by acetic acid and this may also contribute to rate enhancement. The plot of log k_1 *versus* 1/D is linear (r =

0.987) with positive slope, indicating an interaction between a positive ion and a dipole molecule. This supports the postulation of (H_2O^+Cl) as the reactive species.

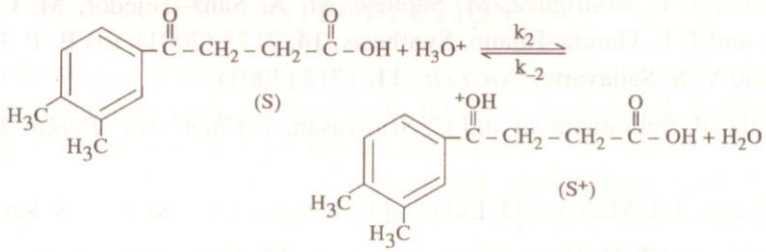
The retardation of reaction rate on the addition of saccharin suggests[12] a pre–equilibrium step involving a process in which saccharin is one of the products.

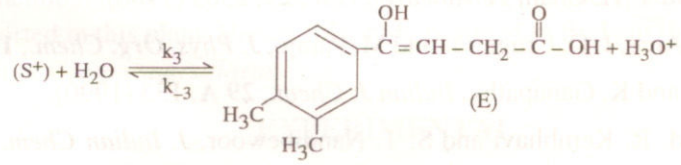
$$\text{NCSA} + H_3O^+ \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} H_2O^+Cl + \text{Saccharin} \qquad ...(2)$$

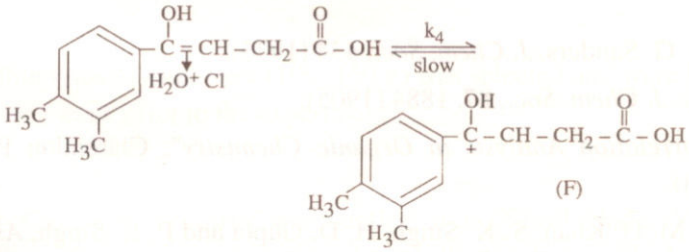
If this equilibrium is involved in the oxidation process, the retardation should be an inverse function of saccharin concentration, which is borne out by observation that the inverse of the rate constant gives a linear (r = 0.999) plot against [Saccharin].

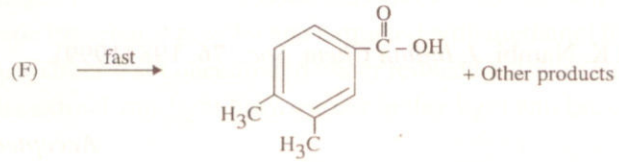
A mechanism has been proposed involving the attack of H_2O^+Cl on the enol form of the substrate (E) in the rate–determining step. It is known[11] that the enolization is proposed to be the necessary step prior to the oxidation of the substrate.

$$\text{NCSA} + H_3O^+ \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} H_2O^+ Cl + \text{Saccharin} \qquad ...(3)$$









Scheme–1

Scheme–1 leads to rate law (7)

$$\frac{-d[NCSA]}{dt} = \frac{k_2 k_3 k_4 [S] [H_3O^+] [H_2O^+Cl]}{k_{-2} k_{-3} K_a [Sac]} \quad ...(7)$$

Equation (7) clearly points out the observed results i.e. first order in [KA], [NCSA], $[H^+]$ and inverse order in [Saccharin].

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