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RESEARCH ARTICLE

Kinetics of Oxidation of 3-Benzoylpropionic Acid by *N*-Chloroacetamide in Aqueous Acetic Acid Medium

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Abstract: Kinetics of the oxidation of 3-benzoylpropionic acid (KA) by *N*-chloroacetamide (NCA) in aqueous acetic acid medium has been studied. The reaction followed potentiometrically at 298K. The effects of temperature, composition of solvent medium and concentration of added mineral acid on the rate of reaction were also studied. The reaction exhibits first order each [KA], [NCA] and hydrogen ions. Variation in ionic strength has no effect on the reaction rate, while the reaction rates are enhanced on lowering the dielectric constant of the reaction medium. There is no effect of added acetamide. Protonated NBB has been postulated as the reactive oxidizing species. The mechanism proposed involves the attack of the H_2O^+Cl on the enol form of the 4-oxo acid.

Keywords: Kinetics, Oxidation, *N*-Chloroacetamide, 4-Oxoacids, 3-Benzoylpropionic acid**.**

Introduction

Among the various organic compounds employed in oxidative studies, 4-oxo acids are attractive substrates in terms of their enolization. These compounds readily undergo oxidation with various oxidants, unlike their corresponding carboxylic acids, and various mechanisms have been proposed. Formation of a complex between the oxidant and the enolic form of the 4-oxo acid in the slow step followed by its decomposition into products in the fast step, has been proposed in the oxidation by acid permanganate[1], *N*-chlorosuccinimide[2], *N*-bromosuccinimide[3], *N*-chlorosaccharin[4] and pyridinium fluorochromate[5]. Formation of an intermediate ester between the protonated 4-oxo acid and MnO_{4-} in the equilibrium step followed by its breakdown to give products in the rate determining step has been proposed in the oxidation by permanganate in buffer media[6]. In the Os(VIII)-catalyzed oxidation by alkaline hexacyanoferrate(III) in sodium carbonate-bicarbonate buffer[7], the proposed mechanism involves complex formation between two similarly charged species, namely, the enolate anion of 4-oxo acid and $[OsO_4(OH)_2]^{2-}$ in the fast step, which decomposes into products in the slow step. In the alkaline hexacyanoferrate(III) oxidation of 4-oxo acids, a mesomeric radical-mediated mechanism, involving the formation of enolate anion from the oxo compound and subsequent rate-determining electron transfer by the oxidant has been proposed by Rangappa *et al*[8].

Although a lot of works have been reported on the oxidation of organic compounds by *N*-halo compounds[9-12] it is to be noted that no systematic kinetic investigation on the oxidation of 3-benzoylpropionic acid by *N*-chloroacetamide has yet been reported in the literature. Here we report the results of the kinetics of the oxidation of 3-benzoylpropionic acid (KA) with *N*-chloroacetamide (NCA) in aqueous acetic acid medium in the presence of perchloric acid.

Experimental

All the chemicals used were of p.a.grade. Their purity was checked by comparing their boiling or melting points with the literature values. Acetic acid was refluxed over chromic oxide for 6 h and then fractionated. Solutions of sodium perchlorate and perchloric acid were prepared in double-distilled water. Double-distilled water was employed in all kinetic runs.

The reaction was followed potentiometrically by setting up a cell containing the reaction mixture, into which a platinum electrode and a standard calomel electrode were dipped. The emf of the cell was measured periodically using a 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 ± 3%.

Results and Discussion

Reaction order

The reaction orders were determined from the slopes of log k_1 *versus* log (concentration) plots by varying the concentration of substrate (KA) and perchloric acid in turn while keeping others constant. The plot log k_1 against log [KA] is linear (r = 0.981) with a slope value of 0.985 and the plot log k_1 against log [H^+] is also linear (r = 0.992) with a unit slope. This is further supported by the fact that the plots of k_1 *versus* [KA] and k_1 *versus* [H^+] gives a straight line passing through the origin, the linearity of the plots of log [NCA] *versus* time indicates the order in [NCA] as unity, this is also confirmed by constant values of k_1 at varying [NCA] (Table 1). This indicates clearly that the reaction is first order with respect to [KA], [NCA] and [H^+].

Table 1. Rate constant for the oxidation of 3-benzoylpropionic acid by NCA in aqueous acetic acid medium at 30 ^{0}C^a

10^2 [KA] mol dim^{-3}	10^3 [NCA] mol dm^{-3}	[H^+]mol dm^{-3}	10^4 $k_1{}^b$,s^{-1}	10^3 $k_2{}^c$ dm^3 mol^{-1} s^{-1}
2.0	2.0	0.5	1.415	7.07
3.0	2.0	0.5	2.124	7.08
4.0	2.0	0.5	2.832	7.08
6.0	2.0	0.5	4.241	7.06
8.0	2.0	0.5	5.662	7.07
2.0	2.0	0.8	2.332	0.29
2.0	2.0	1.2	3.362	0.28
2.0	2.0	1.4	4.088	0.29
2.0	2.0	1.6	4.564	0.28
2.0	1.6	0.5	1.423	-
2.0	1.2	0.5	1.418	-
2.0	1.0	0.5	1.422	-
2.0	0.8	0.5	1.421	-

[a] *General conditions: [$NaClO_4$] = 0.5 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.*[13] [c] *Individual k_2 values estimated as k_1 / [KA] or k_1 / [H^+]*

Effect of products

The effect from adding acetamide was studied, which caused a decrease in the oxidation rate. Thus, retardation of the reaction rate upon addition of acetamide suggests that there is a pre-equilibrium step involving a process in which acetamide is a product.

$$\text{NCA} + H_3O^+ \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} H_2O^+Cl + \text{Acetamide} \qquad (1)$$

The effect of dielectric constant in the reaction medium was studied by adding acetic acid (40%-80%) in the reaction medium at constant concentrations of other reactants. The reaction rate increased remarkably with the increase in the proportion of acetic acid in the solvent medium. The effect of ionic strength was 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 reaction mixture was kept for 24 h with acrylonitrile in an inert atmosphere. Test for free radical was negative.

Effect of temperature

The rate of reaction was measured at different temperatures. The activation parameters for the oxidation of keto acid by NCA have been evaluated from the slope of the Arrhenius plots.

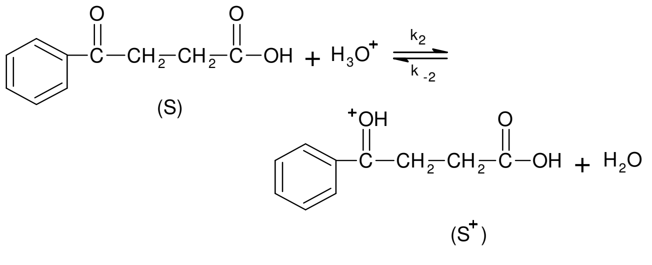
Mechanism

It is known that[14] the probable reactive species of NCA in acid solution is H_2O^+Cl. The reaction is first order in [NCA], [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 trend in the rate observed may be due to more than one factor. It may be attributed to the lowering of dielectric constant of the medium which favors reaction involving protonation. Further, the enolization of the keto acid 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 = 0.988) 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 acetamide suggests[15] a pre-equilibrium step involves a process in which acetamide is one of the products.

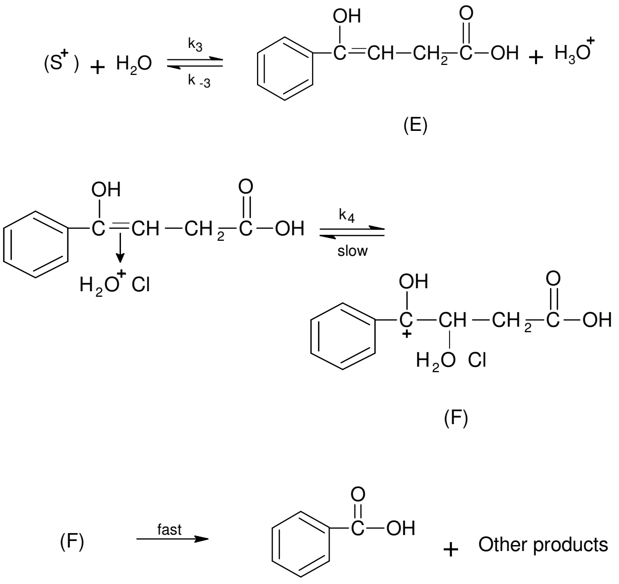
If this equilibrium is involved in the oxidation process, the retardation should be an inverse function of acetamide concentration, which is borne out by observation that the inverse of the rate constant gives a linear (r = 0.987) plot against [Acetamide].

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[14] that the enolization is proposed to be the necessary step prior to the oxidation of the substrate

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



(3)



(4)

(5)

(6)

Scheme 1

Scheme 1 leads to rate law (7)

$$\frac{-d[NCA]}{dt} = \frac{k_2 k_3 k_4 [S][H_3O^+][H_2O^+Cl]}{k_{-2} k_{-3} k_a [Acetamide]} \tag{7}$$

Equation (7) clearly points out the observed results *i.e.* first order in [KA], [NCA], [H$^+$] and inverse order in [Acetamide] on the rate of the oxidation.

Stoichiometry and reaction products

The stoichiometry of the reaction was determined by equilibrating reaction mixture of various [NCA] /[KA] ratios at 30^o C for 12 h, keeping all other reagents constant. Estimation of unconsumed NCA (iodometrically) revealed that one mole of 4-oxo acid consumed one mole of NCA (Eq. 1). The oxidation products were identified as benzoic acid and acetamide. It was confirmed by noting the mixed melting point, chemical methods and TLC techniques. The results are in good agreement with 1:1 stoichiometry.

$$C_6H_5COCH_2CH_2COOH + C_2H_4ClNO + 5\,H_2O \xrightarrow{H^+}$$

$$C_6H_5\,COOH + CH_3CONH_2 + 3CO_2 + 6H_2 + HCl \tag{8}$$

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