



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

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Abstract: The kinetics of oxidation of 3-benzoylpropionic acid (KA) with *N*-bromoacetamide (NBA) have been studied potentiometrically in 50:50 (v/v) aqueous acetic acid medium at 298 K. The reaction was first order each with respect to [KA], [NBA] and [H⁺]. The main product of the oxidation is the corresponding carboxylic acid. The rate decreases with the addition of acetamide, 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. A mechanism consistent with observed results has been proposed and the related rate law was deduced.

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

Introduction

The generation and reactivity of *N*-halo compounds and their importance in biological systems have been reviewed¹. The aqueous solution of halogen has a strong oxidizing character. The species responsible for such oxidizing character may be different depending on the pH of the medium²⁻³. Although a lot of works have been reported on the oxidation of organic compounds by *N*-halo compounds⁴⁻⁷ it is to be noted that no systematic kinetic investigation on the oxidation of 3-benzoylpropionic acid by *N*-bromoacetamide 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*-bromoacetamide (NBA) in aqueous acetic acid medium in the presence of perchloric acid.

Experimental

All the chemicals used were of p.a. grade. Acetic acid (BDH) was first refluxed over chromic acid for 6 h and then distilled. Solutions of sodium perchlorate, perchloric acid and mercuric acetate 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 $\log (E_t - E_\infty)$ against time were reproducible within $\pm 3\%$.

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 ($r = 0.989$) with a slope value of 0.988 and the plot $\log k_1$ against $\log [H^+]$ is also linear ($r = 0.996$) 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 $\log [NBA]$ versus time indicates the order in $[NBA]$ as unity, this is also confirmed by constant values of k_1 at varying $[NBA]$ (Table 1). This indicates clearly that the reaction is first order with respect to $[KA]$, $[NBA]$ and $[H^+]$.

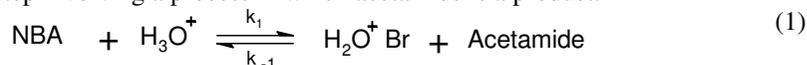
Table 1. Rate constant for the oxidation of 3-benzoylpropionic acid by NBA in aqueous acetic acid medium at 30 °C^a

$10^2 [KA]$ mol dm ⁻³	$10^3 [NBA]$ mol dm ⁻³	$[H^+]$ mol dm ⁻³	$10^4 k_1$ s ⁻¹	$10^3 k_2$ dm ³ mol ⁻¹ s ⁻¹
2.0	2.0	0.5	1.312	6.55
3.0	2.0	0.5	1.905	6.35
4.0	2.0	0.5	2.568	6.42
6.0	2.0	0.5	3.906	6.51
8.0	2.0	0.5	5.184	6.48
2.0	2.0	0.7	1.891	0.27
2.0	2.0	1.0	2.261	0.26
2.0	2.0	1.2	3.243	0.27
2.0	2.0	1.6	4.481	0.28
2.0	1.6	0.5	1.333	-
2.0	1.0	0.5	1.294	-
2.0	0.8	0.5	1.302	-
2.0	0.4	0.5	1.311	-

^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. ^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.



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 mercury(II) acetate

The effect of concentration of mercury(II) acetate observed in the range 0.002-0.02 M was found to be negligible on the rates of reaction. The function of added mercuric acetate is therefore only to fix up Br⁻ formed in the course of reaction as HgBr₂ or HgBr₄²⁻

Effect of temperature

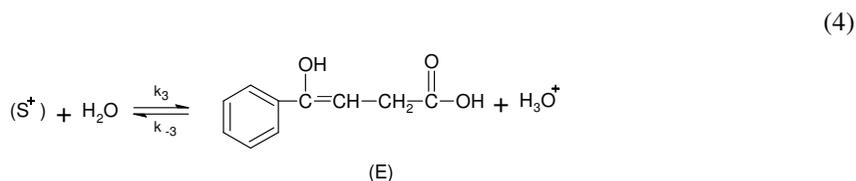
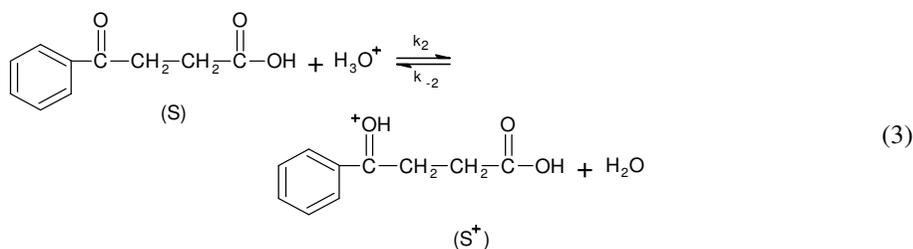
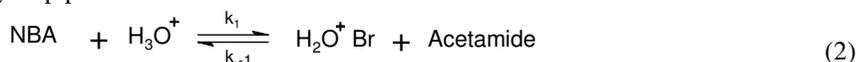
The rate of reaction was measured at different temperatures. The activation parameters for the oxidation of keto acid by NBA have been evaluated from the slope of the Arrhenius plots.

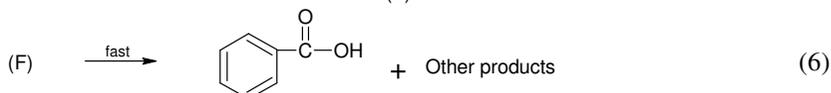
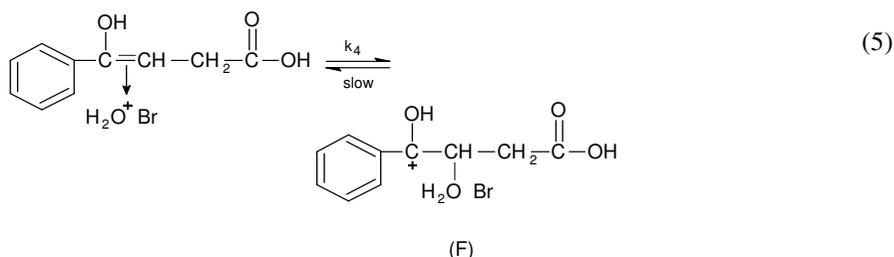
Mechanism

It is known that⁹ the probable reactive species of NBA in acid solution, H₂O⁺Br. The reaction is first order in [NBA], [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 k₁ versus 1/D is linear (r = 0.986) with positive slope, indicating an interaction between a positive ion and a dipole molecule. This supports the postulation of (H₂O⁺Br) as the reactive species. The retardation of reaction rate on the addition of saccharin suggests¹⁰ 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 saccharin concentration, which is borne out by observation that the inverse of the rate constant gives a linear (r = 0.989) plot against [acetamide].

A mechanism has been proposed involving the attack of H₂O⁺Br on the enol form of the substrate (E) in the rate determining step. It is known⁹ that the enolization is proposed to be the necessary step prior to the oxidation of the substrate



**Scheme 1**

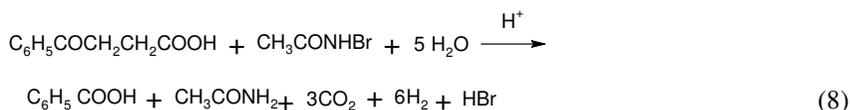
Scheme 1 leads to rate law (7)

$$\frac{-d[NBA]}{dt} = \frac{k_2 k_3 k_4 [S][H_3O^+][H_2O^+ Br]}{k_{-2} k_{-3} k_a [Acet]} \quad (7)$$

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

Stoichiometry and reaction products

Different sets of reaction mixtures containing different quantities of NBA and KA at constant [H⁺] and ionic strength were reacted for 24 h at 30 °C and then analyzed. The remaining NBA was estimated. 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.



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