Asian Journal of Chemistry Vol. 12, No. 4 (2000), 1113–1117

Kinetics of Oxidation of 3-Benzolypropionic Acid by N-Bromosuccinimide in Aqueous Acetic Acid Medium

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The kinetics of oxidation of 3-benzoylpropionic acid (KA) by N-bromosuccinimide (NBS) have been studied in 50% acetic acid-50% water (v/v) mixture. The reaction is first order each in [NBS] and [KA]. A small increase in rate is observed with increase in [H^+]. A decrease in the dielectric constant of the medium at constant concentration of other reactants was found to be negligible on the rate of reaction. Variation in ionic strength of the medium and the addition of the reaction products (succinimide) has no significant effect on the rates of reaction. From the kinetic data obtained, the activation parameters have been computed and a suitable mechanism has been proposed.

INTRODUCTION

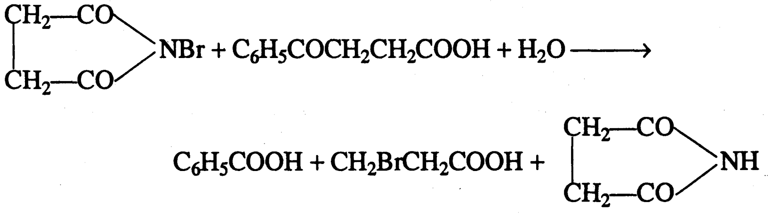
N-Bromosuccinimide is a source of positive halogen, and this reagent has been exploited as oxidant for a variety of substrates[1–3] in both acidic and alkaline medium. The nature of active oxidising species and mechanism depend on the nature of the halogen atom, and the groups attached to the nitrogen and the reaction conditions. In the recent studies[4] Hg(II) was introduced into the reaction mixture to trap the bromide ion catalysing the reaction and the reaction proceeded entirely through the Hg(II)-catalyzed pathway. We report herein the kinetics of oxidation of 3-benzoylpropionic acid (KA) by N-Bromosuccinimide (NBS) in 50% acetic acid-50% water (v/v) mixture in the presence of perchloric acid. The progress of the reaction was followed potentiometrically.

EXPERIMENTAL

All the chemicals used were of AR grade. 3-Benzolypropionic acid was prepared in the laboratory. Solutions of NBS were prepared afresh and standardised iodometrically. Acetic acid was purified by standard procedure[5]. Double distilled water was employed in all kinetic runs.

The kinetic studies were carried out under pseudo first order conditions ($[KA] \gg [NBS]$) in the presence of added mercury(II) acetate[6,7] (0.02 mol dm^{-3}) at the desired temperature maintained with an accuracy of ±0.1°C. The reaction was followed potentiometrically by setting up a cell made up of the reaction mixture into which the platinum electrode and 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 constant (k_1) in each kinetic run was evaluated from the slope of the linear plot of log ($E_t - E_\infty$) against time ($r = 0.993$). The second order rate constants (k_2) were obtained from $k_2 = k_1/[KA]$.

Different sets of reaction mixtures containing different quantities of NBS and KA at constant concentration of [H^+] and ionic strength were reacted for 24 h at 30°C and then analysed. The oxidation products were identified as succinimide and benzoic acid by their spot tests. The results are in good agreement with 1 : 1 stoichiometry. The overall stoichiometry of the oxidation reaction may be represented as:



$$(CH_2CO)_2NBr + C_6H_5COCH_2CH_2COOH + H_2O \longrightarrow C_6H_5COOH + CH_2BrCH_2COOH + (CH_2CO)_2NH$$

RESULTS AND DISCUSSION

The reaction is first-order in [NBS] as shown by the linearity of the plots of log ($E_t - E_\infty$) versus time ($r = 0.993$) and also by constant values of the pseudo first-order rate constant at different [NBS] at constant [KA] (Table-1). On varying [KA] at constant [NBS] the second order rate constants gave concordant values (Table-1). Further the logarithm of pseudo first-order rate constants showed a linear dependence on the log [KA] with a slope of 1.1 ($r = 0.997$). These results indicate that the order with respect of [KA] is also unity.

TABLE-1
DEPENDENCE OF RATE ON [NBS] AND [KA]

Solvent: 50%, AcOH–50%, H_2O (v/v) mixture, Temperature: 30°C

10^3 [NBS] (mol dm^{-3})	10^2 [KA] (mol dm^{-3})	10^4 k_1 (S^{-1})	10^3 k_2 (dm^{-3} mol^{-1} S^{-1})
2.00	3.00	1.12	3.73
2.00	4.00	1.67	4.10
2.00	5.00	2.04	4.08
2.00	6.00	2.65	4.41
2.00	7.00	3.05	4.35
3.00	3.00	1.22	4.06
4.00	3.00	1.18	3.93
5.00	3.00	1.23	4.10
6.00	3.00	1.22	4.06

The effect of $[H^+]$ was investigated in the range 0.01–0.025 mol dm^{-3} of $HClO_4$. The rate has a slight positive effect, indicating fractional order dependence on $[H^+]$. The effect of changing the dielectric constant in the reaction medium was studied by increasing the acetic acid concentration in the reaction medium at constant concentrations of other reactants. The effect was found to be negligible on the rate of reaction (Table-2). The effect of ionic strength was studied by varying the concentration of sodium perchlorate in the reaction medium. The rate of oxidation is unaffected by change in ionic strength (Table-3). This may presumably be due to the attack of an ion on a neutral molecule in the rate determining step[8].

TABLE-2
EFFECT OF VARYING SOLVENT COMPOSITION ON THE RATE OF OXIDATION

10^2 [KA] = 3.00 mol dm^{-3}, 10^3 [NBS] = 2.00 mol dm^{-3}, Temp = 30°C

D	$AcOH-H_2O$ (v/v%)	$10^4 k_1$ (S^{-1})
37.50	50–50	1.12
34.75	55–45	1.36
31.50	60–40	1.56
28.50	65–35	1.83
25.90	70–30	2.14

TABLE-3
EFFECT OF VARYING $[H^+]$ AND $[NaClO_4]$ ON THE RATE OF REACTION

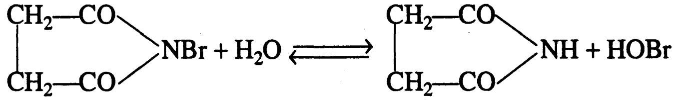
10^2 [KA] = 3.00 mol dm^{-3}, 10^3 [NBS] = 2.00 mol dm^{-3}, Temp = 30°C

$10^2 [H^+]$ (mol dm^{-3})	$[NaClO_4]$ (mol dm^{-3})	$10^4 k_1$ (S^{-1})
1.0	0.5	1.12
1.5	0.5	1.46
2.0	0.5	1.77
2.5	0.5	1.92
1.0	0.8	1.83
1.0	1.1	1.80
1.0	1.4	1.92
1.0	1.7	1.83

The reaction mixture was kept for 24 h with acrylonitrile in an inert atmosphere. Test for free radical was negative. This clearly establishes the absence of free radical formation during the NBS oxidation of KA. The rate of reaction was measured at different temperatures. The enthalpy and entropy of activation are 10 kcals deg^{-1} mol^{-1} and –74.49 cal deg^{-1} mol^{-1}. The value of entropy of activation is supportive of C—C bond cleavage in the substrate to the formation of benzoic acid.

The effect of mercuric(II) acetate[9] observed in the range 0.02–0.08 mol dm^{-3} was found to be negligible on the rates of reaction. The function of added mercuric(II) acetate is therefore only to fix up Br^- formed in the course of reaction as $HgBr_2$ or $HgBr_4^{2-}$.

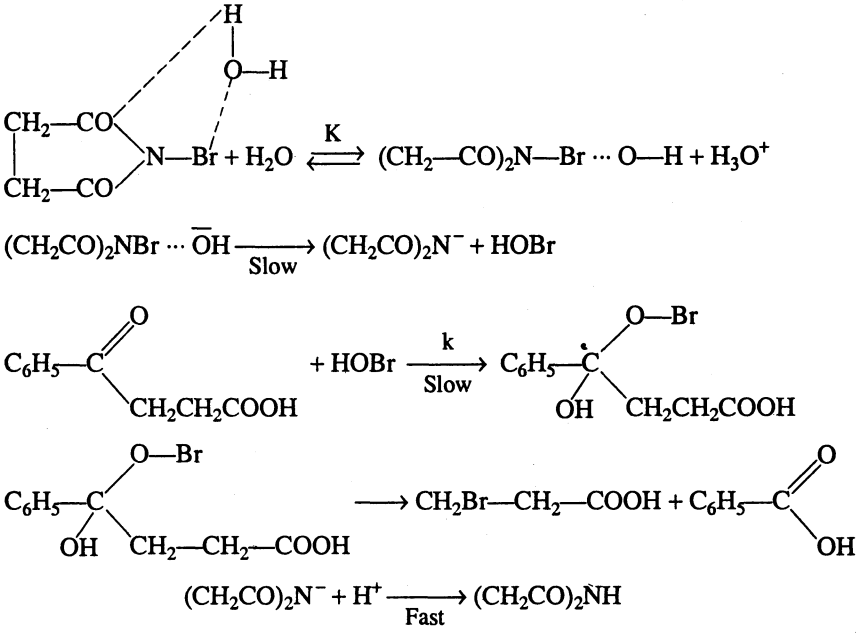
It is known[10] that the probable reactive species of NBS in acid solution are $>NBr$, HOBr, $>N^+HBr$, H_2OBr^-. The retardation of reaction on the addition of succinimide suggests a pre-equilibirum (see eqn.) in which succinimide is one of the products



In this oxidation process HOBr is the reactive oxidising species. In solutions containing acetic acid, one cannot exclude the possibility of (AcO—HBr) acting as a reactive oxidizing species. The observed negligible enhancement of the reaction rate with increase in amount of acetic acid content at constant [perchloric acid] might be due to involvement of neutral species in the reaction. If the reaction were to be catalyzed by acetate ion[11] there should not have been a large increase in rate with increase in acetic acid content of the medium. Hence catalysis by acetate ion is untenable.

To account for the unusual dependence of reaction rate on $[H^+]$, HOBr formed in a rate limiting hydrolysis of molecular NBS which in aqueous medium due to its positive bromine end is likely to associate with one water molecule, is proposed to react with the substrate in a fast step.

Based on the above discussion, the following mechanism is possible:



$$(CH_2CO)_2NBr \cdots \bar{O}H \xrightarrow[\text{Slow}]{} (CH_2CO)_2N^- + HOBr$$

$$(CH_2CO)_2N^- + H^+ \xrightarrow[\text{Fast}]{} (CH_2CO)_2NH$$

Based on the proposed mechanism, the rate law for the NBS oxidation of KA in protic solvent may be written as

$$\frac{-d[NBS]}{dt} = kK[KA][NBS][H^+]$$

The proposed mechanism and rate law are in conformity with the observed experimental features.

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(*Received:* 22 April 2000; *Accepted:* 26 June 2000) AJC-2062