

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

N. A. MOHAMED FAROOK* and A. AFROOS BANU

P. G & Research Department of Chemistry
Khadir Mohideen College, Adirampattinam - 614 701, India
nafarook@hotmail.com

Received 10 January 2015/ Accepted 15 February 2015

Abstract: The kinetics of the oxidation of 3-benzoylpropionic acid (KA) by *N*-bromobenzamide (NBB) to yield the corresponding carboxylic acid were studied potentiometrically in 50:50 (v/v) aqueous acetic acid medium at 298 K. The effects of temperature, composition of solvent medium and concentration of added mineral acid on the rate of reaction were also studied. The reaction was first order with respect to the [KA], [NBB] and hydrogen ions. There is no effect of added benzamide. Protonated NBB has been postulated as the reactive oxidizing species.

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

Introduction

The chemistry of reactions of *N*-halo compounds forms a separate branch, which is of great synthetic importance¹⁻⁴. *N*-halo compounds have been extensively employed as oxidizing agents for organic substrates^{5,6}. *N*-Halo compounds are the source of positive halogen and have been exploited as oxidant for a variety of substrates in both acidic and alkaline media. The species responsible for such oxidizing character may be different depending on the pH of the medium^{7,8}. Although a lot of works have been reported on the oxidation of organic compounds by *N*-halo compounds⁹⁻¹² it is to be noted that no systematic kinetic investigation on the oxidation of 3-benzoylpropionic acid by *N*-bromobenzamide 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*-bromobenzamide (NBB) 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 $\log (E_t - E_\infty)$ 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 $\log [NBB]$ versus time indicates the order in $[NBB]$ as unity, this is also confirmed by constant values of k_1 at varying $[NBB]$ (Table 1). This indicates clearly that the reaction is first order with respect to $[KA]$, $[NBB]$ and $[H^+]$.

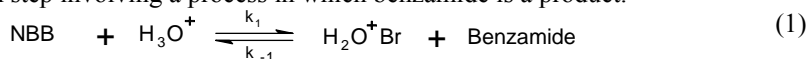
Table 1. Rate constant for the oxidation of 3-benzoylpropionic acid by NBB in aqueous acetic acid medium at 30 °C^a

$10^2 [KA]$ mol dm ⁻³	$10^3 [NBB]$ 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	1.615	8.08
3.0	2.0	0.5	2.422	8.07
4.0	2.0	0.5	3.224	8.06
6.0	2.0	0.5	4.854	8.09
8.0	2.0	0.5	6.441	8.05
2.0	2.0	0.8	2.562	0.32
2.0	2.0	1.2	3.839	0.32
2.0	2.0	1.4	4.482	0.32
2.0	2.0	1.6	5.121	0.32
2.0	1.6	0.5	1.621	-
2.0	1.2	0.5	1.624	-
2.0	1.0	0.5	1.618	-
2.0	0.8	0.5	1.621	-

^aGeneral conditions: $[NaClO_4] = 0.5$ mol dm⁻³, Solvent composition: 50% Acetic acid - 50% Water (v/v). ^bEstimated from pseudo-first order plots, the error quoted in k_1 values is the 95% confidential limit of 'Student t' test.¹³ ^cIndividual k_2 values estimated as $k_1 / [KA]$ or $k_1 / [H^+]$

Effect of products

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

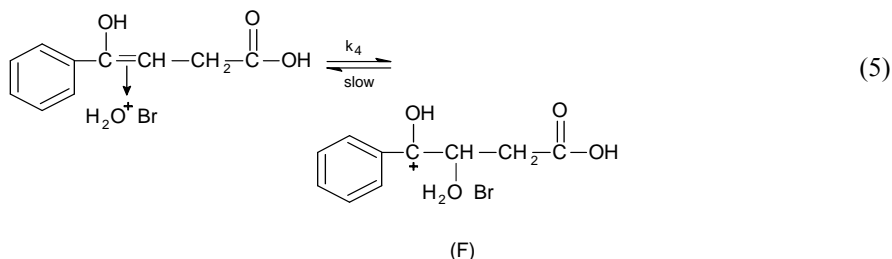
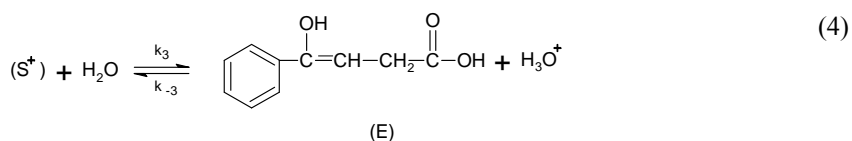
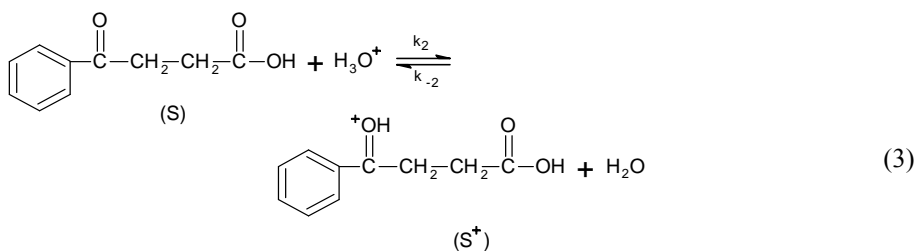
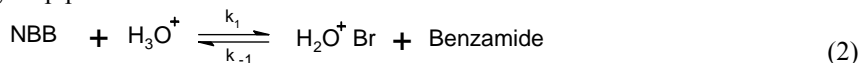
The rate of reaction was measured at different temperatures. The activation parameters for the oxidation of keto acid by NBB have been evaluated from the slope of the Arrhenius plots.

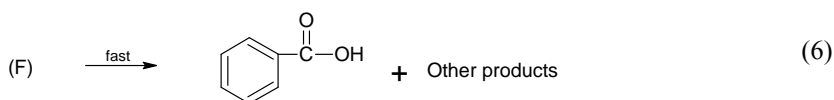
Mechanism

It is known that¹⁴ the probable reactive species of NCA in acid solution, H_2O^+Br . The reaction is first order in [NBB], [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^+Br) as the reactive species. The retardation of reaction rate on the addition of saccharin suggests¹⁵ a pre-equilibrium step involves a process in which benzamide is one of the products.

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

A mechanism has been proposed involving the attack of H_2O^+Br on the enol form of the substrate (E) in the rate determining step. It is known¹⁴ that the enolization is proposed to be the necessary step prior to the oxidation of the substrate





Scheme 1

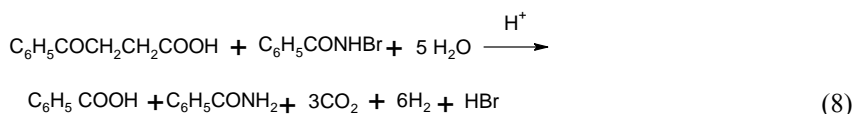
Scheme 1 leads to rate law (7)

$$\frac{-d[\text{NBB}]}{dt} = \frac{k_2 k_3 k_4 [\text{S}][\text{H}_3\text{O}^+][\text{H}_2\text{O}^+\text{Br}]}{k_{-2} k_{-3} k_a [\text{Benzamide}]} \quad (7)$$

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

Stoichiometry and reaction products

Different sets of reaction mixtures containing different quantities of NBB and KA at constant [H⁺] and ionic strength were reacted for 24 h at 30 °C and then analyzed. The remaining NBB was estimated. The oxidation products were identified as benzoic acid and benzamide. It was confirmed by noting the mixed melting point, chemical methods and TLC techniques. The results are in good agreement with 1:1 stoichiometry.



Reference

1. Amauri F Patrocino and Paulo J S Moran., *Organomet Chem.*, 2000, 603, 220-224.
2. Sameer P Dhuru, Nikhil U Mohe and Manikrao M Salunkhe, *Synth Commun.*, 2001, 31(23), 3653-3657.
3. Canibano V, Rodriguez J F, Santose M, Sanz-Tejedor M A, Carreno M C, Gonzalez G and Garcia-Ruano J L, *Synthesis*, 2001, 14, 2175-2179.
4. Bandgar B P, Uppalla L S and Sadavarte V S, *Syn Lett.*, 2001, 11, 1715-1718.
5. Duraisamy Thenraja, Perumal Subramaniam and Chockalingam Srinivasan, *J Chem Soc Perkin Trans 2*, 2002, 2125-2129.
6. Teruaki Mukaiyama, Jun-ichi Matsuo, Daisuke Lida and Hideo Kitagawa, *Chem Lett.*, 2001, 8 846-847.
7. Thenraja D, Subramaniam P and Srinivasan C, *J Chem Soc Perkin Trans 2*, 2002, 2125.
8. Mukaiyama T, Matsuo J I, Lida D and Kitagawa H, *Chem Lett.*, 2001, 8, 846.
9. Hambly G F and Chan T H, *Tetrahedron Lett.*, 1986, 27, 2563.
10. Antelo J M, Arce F, Crueiras J O and Parajo M, *J Phys Org Chem.*, 1997, 10, 631-636.
11. Karunakaran C and K Ganapathy K, *Indian J Chem.*, 1990, 29A, 133.
12. Harihar A L, Kembhavi M R and Nandibewoor S T, *J Indian Chem Soc.*, 1999, 76, 128-130.
13. Shorter J, *Correlation Analysis in Organic Chemistry*, Clarendon Press, Oxford, Chapter 2, 1973.
14. Shahnaz Khan, Khan M U, Singh S K, Gupta H D and Singh P K, *Asian J Chem.*, 2003, 15, 595.
15. Vivekanandan K and Nambi K, *J Indian Chem Soc.*, 1999, 76, 198-201.