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Kinetic Study of Oxidation of 5-Halogeno-4-Oxopentanoic Acids by N-Bromosachharin using Potentiometric Method

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ABSTRACT: Kinetic and mechanistic studies of oxidation of various 5-substituted and unsubstituted 4-oxopentanoic acids (4-OPA) by N-bromosaccharin (NBSa) in acidic medium have been performed potentiometrically. The reaction has been found to follow first-order kinetics, each in [4-OPA], [NBSa] and [H^+]. The changes in the electronic nature of the substrate show that the reaction proceeds through the positively charged transition state. A most plausible mechanistic scheme has been proposed for the oxidation of 4-oxopentanoic acids at par with kinetic results and product analysis.

Keywords: 5-halogeno-4-oxopentanoic acid, N-Bromosachharin, Potentiometric, kinetics, oxidation.

Introduction

Elucidation of oxidation kinetics of substituted 4–oxo acids by different oxidizing agents is of great importance[1] due to their property of enolization. These acids readily undergo enolization in acidic medium which leads to the oxidative cleavage in the presence of strong oxidizing agents. There have been several studies concerning kinetics and mechanisms of oxidation of various 4–oxo acids, however, these are largely centered around aryl substituted 4–oxo acids[2-8]. Being a source of bromonium ions, Br^+ in both acidic as well as alkaline medium, NBSa is an effective oxidizing agent. However, few studies have been carried out on NBSa as oxidizing agent[9].

The present study concerns the effect of substituted groups on oxidation of different 4-oxoacids by NBSa in acidic medium.

Experimental

Reagents and Apparatus

Double distilled deionized water was used to prepare all the solutions. All analytical reagent grade chemicals, N-bromosachharin (Merck, India) and perchloric acid (Merck, India) were used throughout the study. The substrates, 5-Chloro-4-oxopentanoic acid (S1), 5-Bromo-4-oxopentanoic acid (S2) and 5-Iodo-4-oxopentanoic acid (S3) were prepared according to the method described in literature[10].

Systronics Digital potentiometer was used to measure the change in potential during the reaction. Toshniwal digital pH meter was used for the measurement of pH. The pH meter was standardized by use of BDH buffers of pH 4 and 7.

Kinetics Measurements

The reaction was started by mixing the appropriate amounts of each reactant in an Erlenmeyer flask in the sequence buffer, NBSA, and substrate. The reaction mixture was shaken thoroughly and potential of the reaction mixture was observed using Systronics digital potentiometer. The potential was recorded as a function of time under various conditions. The initial rate was computed from the slope of graph between change in potential (dE) and time (dt).

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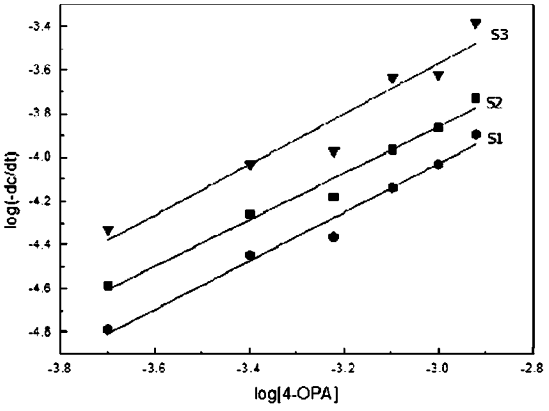
Result and Discussion

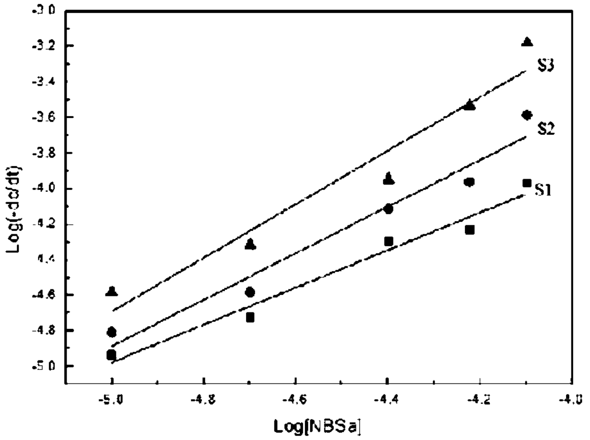
Effect of [S]

The rate of reaction was observed for the different concentration of substrates ranging from 2×10^{-4}M to 1.2×10^{-3}M. A graph plotted between log[S] and log(–dc/dt) was found to be linear suggesting first order dependence in [S] (Fig.1).



Effect of [NBSa]

The rate of reaction was studied as the function of [NBSa] ranging from 1.0×10^{-5}M to 8.0×10^{-5}M keeping other variables fixed at optimum values. The linearity of graph plotted between log[NBSa] vs. log(-dc/dt) shows first order dependence in [NBSa] (Fig. 2).



Effect of [H⁺]

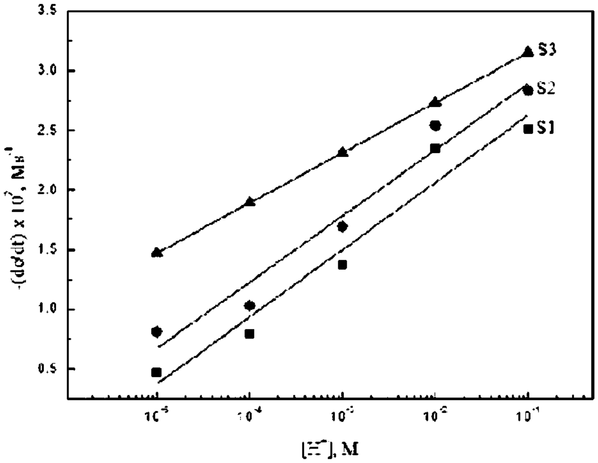
The effect of $[H^+]$ on the rate of reaction was observed by varying the $[H^+]$ from 10^{-5}M to 10^{-1}M in order to obtain an optimum value of pH for the reaction. The rate of the reaction was found to increase linearly with increasing concentration of hydrogen ion. A plot of –(dc/dt) vs. $[H^+]$ is linear passing through the origin (Fig. 3) showing that the reaction proceeds completely through an acid-catalyzed pathway. The observed dependence on $[H^+]$ suggests the participation of enol form as well as hypobromous acidium ion.

Effect of Ionic Strength

The ionic strength of the medium was varied from .01M to 0.5M using $NaClO_4$. A plot of Bronsted – Bjerum equation suggested no significant effect of ionic strength on the reaction.

Effect of Acrylonitrile

The rate of reaction was studied at different concentrations of acrylonitrile for the detection of any free radical species, if formed during the reaction. No alteration in the rate of reaction was observed and also no polymerization occurred at any time during the course of reaction. These observations completely ruled out the formation of free radical.



Kinetics of Reaction

The rate of reaction can be given by eq. 1

$$-\frac{dc}{dt} = k_3[C][H_2O^+Br] \qquad (1)$$

Applying steady state approximation for [C]

$$-\frac{dc}{dt} = \frac{k_1k_2k_3[A][H_2O^+Br][H_3O^+]}{k_{-1}k_{-2}[H_3O^+] + k_3(k_{-1} + k_2)[H_2O^+Br]} \qquad (2)$$

At high $[H_3O^+]$

$$k_{-1}k_{-2}[H_3O^+] >> k_3(k_{-1}+k_2)[H_2O^+Br]$$

Eq. (2) can be written as

$$-\frac{dc}{dt}=\frac{k_1k_2k_3[A][H_2O^+Br]}{k_{-1}k_{-2}} \quad (3)$$

$[H_2O^+Br]$ can be calculated as follows

$$K_a=\frac{[NBSa][H_3O^+]}{[H_2O^+Br][Sa]}$$

Therefore,

$$[H_2O^+Br]=\frac{[NBSa][H_3O^+]}{K_a[Sa]} \quad (4)$$

Replacing the value of $[H_2O^+Br]$ in eq. (3)

$$-\frac{dc}{dt}=\frac{k_1k_2k_3[A][H_2O^+Br][NBSa][H_3O^+]}{k_{-1}k_{-2}K_a[Sa]} \quad (5)$$

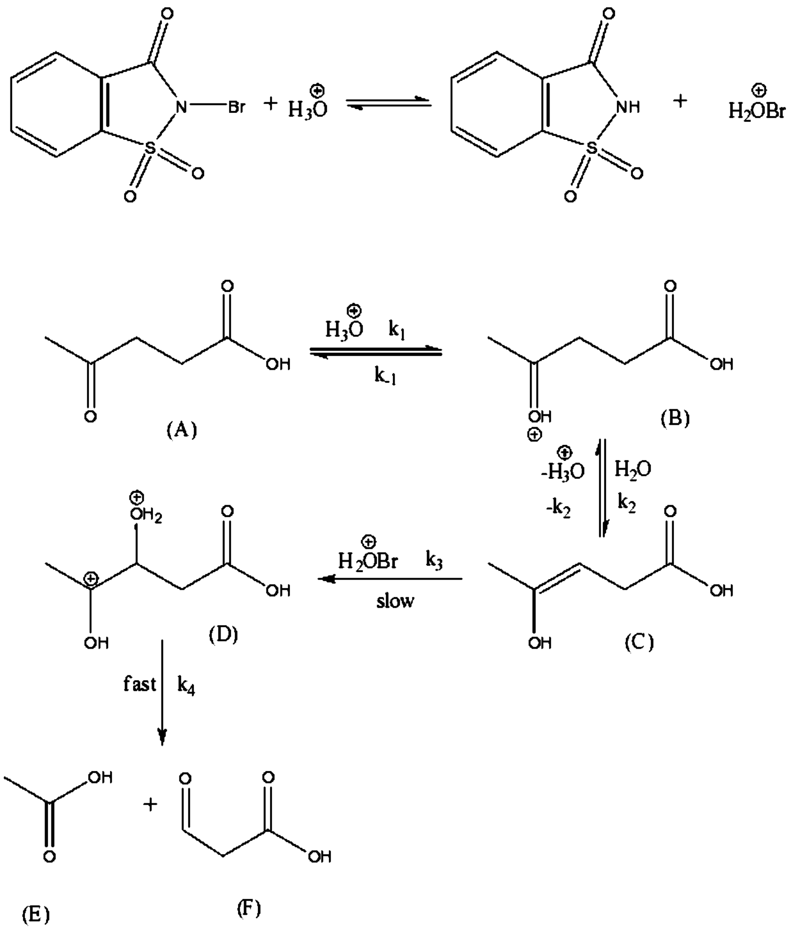
The observed rate constant for the reaction can be given by eq. (6)

$$k_{obs}=\frac{k_1k_2k_3}{k_{-1}k_{-2}K_a} \quad (6)$$

Compound	$k \times 10^3$, $molL^{-1}$	Activation Parameters		
		$\Delta H^{\neq}$ ($kJ\ mol^{-1}$)	E_a ($kJ\ mol^{-1}$)	$\Delta S^{\neq}$ ($JK^{-1}mol^{-1}$)
S1	2.02	23.92	21.97	–134.78
S2	4.16	18.95	15.30	-139.13
S3	7.92	12.56	09.68	-149.66

Reaction Conditions: $[NBSa] = 6 \times 10^{-5}$ M, $[4\text{–}OPA] = 8 \times 10^{-4}$ M, $[H^+] = 10^{-2}$ M

Mechanistic Scheme



Conclusion

This work sheds light on the Hg(II)-catalyzed oxidation of substituted oxo acids by NBSa. A most probable mechanistic scheme has been proposed to incorporate all the experimental observations. Under these experimental conditions, the effective and predominant oxidizing species is H_2O^+Br.

REFERENCES

[1] Reddy, C.S., Manjari, P.S.: Kinetics and mechanism of acid bromate oxidation of substituted 4-oxo-acids. Indian J. Chem. 49A, 418–424 (2010)

[2] Mohamed Farook, N.A.: Kinetics of oxidation of 4-oxo acids by N-bromosuccinimide in aqueous acetic acid medium. J. Iranian Chem. Soc. 3, 378–386 (2006)

[3] Mohamed Farook, N.-A.: Kinetics of oxidation of 4-oxo acids by N-chlorosaccharin in aqueous acetic acid. J. Solution Chem. 36, 345–356 (2007)

[4] Mohamed Farook, N.-A., Seyed Dameem, G.-A.: Kinetics of oxidation of 3-benzoylpropionic acid by N-chlorobenzamide in aqueous acetic acid medium. J. Chem. 8, 561–564 (2011)

[5] Freeda Gnana Rani, D., Maria Pushparaj, F.-J., Alphones, I., Rangappa, K.-S.: Kinetics and mechanism of oxidation of 4-oxoacids by hexacyanoferrate(III) catalysed by Os(VIII). Indian J. Chem. 41B, 2153–2159 (2002)

[6] Mohamed Farook, N.-A., Dameem, S.: Kinetics of oxidation of 3-benzoylpropionic acid by N-bromoacetamide in aqueous acetic acid medium. J. Chem. 8, 479–482 (2011)

[7] Mohamed Farook, N.-A., Prabhkaran, R., Rahini, S., Senthil Kumar, R., Raja Mahendran, G., Gopala Krishnan, G.: Kinetics of oxidation of some amino acids by N-chlorosaccharin in aqueous acetic acid medium. J. Chem. 2, 127–131 (2004)

[8] Mohamed Farook, N.-A., Alhaji, N.-M.-I.: Kinetics of oxidation of substituted c-ketoacid by N-chlorosaccharin in aqueous acetic acid medium. Int. J. Chem. Sci. 2, 76–80 (2004)

[9] Gupta, M.-K., Rekha, L., Sharma, P.-K., Sharma, K., Sharma, V.-K.: Oxidation of glycolic acid by N-bromosaccharin–A kinetic and mechanistic study in presence and absence of cationic surfactant. Asian J. Chem. 18, 1340–1346 (2006)

[10] Aldenkortt: Method for obtaining 5-Halogenolaevulinic acid alkyl ester. US Patent 7,339,073 B2, March 2008.