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Kinetics and Mechanism of Oxidation of 4-Oxoacids by N-Bromosuccinimide in Aqueous Acetic Acid Medium

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Kinetics and mechanism of oxidation of substituted and unsubstituted 4-oxoacids (**S**) by N-bromosuccinimide (NBS) in aqueous acetic acid medium have been studied potentiometrically. The reaction follows first-order kinetics, each in 4-oxoacids, NBS and H^+. The effect of changes in the electronic nature of the substrate reveals that there is a development of positive charge in the transition state. Based on the kinetic results and the product analysis, a suitable mechanism has been proposed for the reaction of NBS with 4-oxoacids.

Keywords: Kinetics, Oxidation, 4-Oxoacids, NBS

INTRODUCTION

In 4-oxoacids, two carbon atoms separate the carbonyl and the carboxyl groups and so they behave both as oxocompounds and as acids without the direct influence of the other group. Among the various organic compounds employed in these studies, 4-oxoacid is an attractive substrate in terms of its enolization. In the strong acid medium the substrate undergoes enolization. Enol as a reactive species of the substrate has been reported in the literature [1].

N-Bromosuccinimide is a source of positive halogen and this reagent has been exploited as oxidant for a variety of substrates in both acidic and alkaline medium [2]. The nature of active oxidizing species and the mechanism depends on the nature of the halogen atom, the groups attached to the nitrogen and the reaction condition. The species responsible for such oxidizing character may be different depending on the pH of the medium. The probable reactive species [3] of NBS in acid solution are >NX, HOX, $>N^+HX$, or H_2OX^+ and the reactive species in alkaline solutions are >NH, HOX, and OX^-.

In the recent years, studies of oxidation of various organic compounds by N-halo compounds in the presence of perchloric acid have attracted considerable attention [4]. A through literature survey reveals that only few works on the oxidation of 4-oxoacid have been reported so far [5,6]. Although the N-bromosuccinimide oxidation of a large variety of organic compounds has been studied, there seems to be no report on a systematic kinetic study of the oxidation of 4-oxoacids by N-bromosuccinimide.

We have carried out a systematic study on the reactions of 4-oxoacids (**S**) by N-bromosuccinimide (NBS). In this report we have examined the kinetic and mechanistic aspects of the oxidation of substituted and unsubstituted 4-oxoacids by N-bromosuccinimide in the presence of perchloric acid. The various unsubstituted and substituted 4-oxoacids (**S1**-**S7**) employed in the present study are listed below

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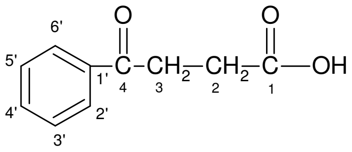


4-Oxoacid (**S1**)

S1: Unsubstituted, **S2:** 4'-Methoxy, **S3:** 4'-Methyl, **S4:** 4'-Phenyl, **S5:** 4'-Chloro, **S6:** 4'-Bromo, **S7:** 3'-Nitro.

EXPERIMENTAL SECTION

Materials

All the chemicals used were of AR 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 parent 4-oxoacid namely 4-oxo-4-phenylbutanoic acid (**S1**) and the phenyl substituted 4-oxoacids (**S2-S7**) were prepared by Friedel-Crafts acylation of the substituted benzene with succinic anhydride [7-11]. Nitration of oxoacids has been performed under mild conditions to prepare nitro compounds.

Procedure

The reaction was followed potentiometrically by setting up a cell made up of the reaction mixture into which a platinum electrode and a standard calomel electrode were dipped. The emf of the cell was measured periodically using an Equip-Tronics potentiometer, while the reaction mixture was continuously stirred. An electrically operated thermostat was used to maintain the desired temperature with an accuracy of ±0.1 °C. A double walled 100 ml beaker with inlet-outlet water circulation facility, specially designed for this experiment, was used as reaction vessel.

The emf values of the reaction mixture were determined at definite intervals of time. The pseudo-first order rate constants were computed from the plots of ln(E_t - E_∞) *vs.* time. The precision of rate constant values is given in terms of 95% confidence limit of the student's t test [12].

RESULTS AND DISCUSSION

Order of Reaction

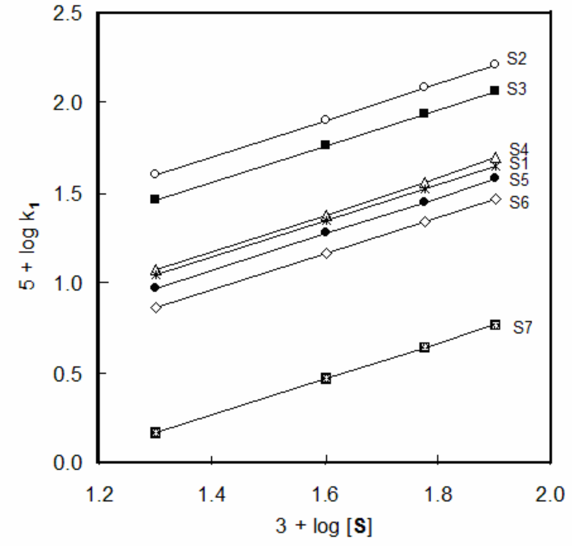


Fig. 1. Double logarithmic plots for the reaction between **S** and NBS.

The rate of oxidation is found to be first order each in [NBS] and [**S**]. Linear plot of logk_1 *vs.* log[**S**] with a slope of unity shows first order dependence of the rate on [**S**] (Fig. 1). The k_1 values at different [**S**] are given in Table 1. The k_1 values obtained at different initial concentrations of NBS reveal that the rates are almost independent of the initial concentration of NBS (Table 2). This ensures the order of the reaction with respect to NBS as one.

The dependence of the reaction rate on the hydrogen ion concentration has been investigated at different initial concentrations of perchloric acid, keeping the concentrations of the other reactants constant. The observed k_1 values are presented in the Table 3. It may be seen that the rate of the reaction increases linearly with increasing concentration of hydrogen ion. This establishes that the reaction is first order with respect to hydrogen ion concentration. A plot of k_1 *vs.* [H^+] is also linear passing through the origin (Fig. 2) showing that the reaction proceeds completely through an acid-catalyzed pathway [13].

It has been reported earlier in the case of N-halo oxidants that, in the absence of mineral acids, HOBr is the reactive oxidant species [14]. Bishnoi and Banerji have observed [15] in the oxidation of some α-hydroxy acids by NBS that linear increase in the oxidation rate with increasing [H^+] indicates the protonation of HOBr to give a cationic bromine species (see Eq.1), which is a

Table 1. Effect of Varying [**S**] on the Rate of Reaction[a]

[NBS] = 1.0 × 10^{-3} M, [H^+] = 0.5 M, Solvent: 50% Acetic Acid-50% Water (v/v), Temp. = 303 K

10^2 [**S**] (M)	10^4 k_1 (s^{-1}) [b]						
	S1	**S2**	**S3**	**S4**	**S5**	**S6**	**S7**
2.0	1.12 ± 0.10	4.01 ± 0.25	2.89 ± 0.09	1.21 ± 0.07	0.95 ± 0.06	0.74 ± 0.04	0.15 ± 0.02
4.0	2.25 ± 0.02	8.01 ± 0.52	5.83 ± 0.20	2.41 ± 0.11	1.85 ± 0.23	1.48 ± 0.10	0.30 ± 0.03
6.0	3.36 ± 0.01	12.1 ± 0.9	8.65 ± 0.49	3.64 ± 0.01	2.83 ± 0.20	2.22 ± 0.16	0.44 ± 0.03
8.0	4.50 ± 0.29	16.4 ± 1.3	11.5 ± 0.9	5.01 ± 0.16	3.82 ± 0.40	2.95 ± 0.26	0.59 ± 0.26

[a] As determined by potentiometric technique following the disappearance of oxidant, the error quoted in k values is the 95% confidence limit of 'Student t' test. [12]. [b] Estimated from pseudo-first order plots over 70% reaction.

Table 2. Effect of Varying [NBS] on the Rate of Reaction

[**S**] = 2.0 × 10^{-2} M, [H^+] = 0.5 M, Solvent: 50% Acetic Acid-50% Water (v/v), Temp. = 303 K

10^3 [NBS] (M)	10^4 k_1 (s^{-1})						
	S1	**S2**	**S3**	**S4**	**S5**	**S6**	**S7**
1.0	1.12 ± 0.10	4.01 ± 0.25	2.89 ± 0.09	1.21 ± 0.07	0.95 ± 0.06	0.74 ± 0.04	0.15 ± 0.02
0.8	1.14 ± 0.05	3.99 ± 0.08	2.90 ± 0.10	1.14 ± 0.05	0.96 ± 0.05	0.83 ± 0.03	0.15 ± 0.01
0.4	1.14 ± 0.03	3.90 ± 0.07	2.89 ± 0.11	1.14 ± 0.03	0.96 ± 0.04	0.82 ± 0.04	0.14 ± 0.01
0.2	1.12 ± 0.03	3.89 ± 0.18	2.84 ± 0.10	1.12 ± 0.03	0.95 ± 0.04	0.82 ± 0.03	0.15 ± 0.02

Table 3. Effect of Varying [H^+] on the Rate of Reaction

[NBS] = 1.0 × 10^{-3} M, [**S**] = 2.0 ×10^{-2} M, Solvent: 50% Acetic Acid-50% Water (v/v), Temp. = 303 K

[H^+] (M)	10^4 k_1 (s^{-1})[b]						
	S1	**S2**	**S3**	**S4**	**S5**	**S6**	**S7**
0.5	1.12 ± 0.10	4.01 ± 0.25	2.89 ± 0.09	1.21 ± 0.07	0.95 ± 0.06	0.74 ± 0.04	0.15 ± 0.02
0.8	1.80 ± 0.14	6.41 ± 0.19	4.61 ± 0.25	1.93 ± 0.11	1.52 ± 0.07	1.32 ± 0.07	0.23 ± 0.04
1.2	2.65 ± 0.12	9.62 ± 0.45	6.92 ± 0.26	2.89 ± 0.02	2.26 ± 0.15	1.98 ± 0.11	0.35 ± 0.03
1.4	3.16 ± 0.17	11.3 ± 0.9	8.10 ± 0.66	3.35 ± 0.19	2.63 ± 0.17	2.27 ± 0.13	0.41 ± 0.01

stronger electrophile and oxidant.

$$HOBr + H_3O^+ \rightleftharpoons H_2O^+Br + H_2O \qquad (1)$$

Thus, the most probable oxidizing species is hypobromous acidium ion, (H_2O^+Br). The participation of hypohalous acidium ions in many electrophilic substitution and oxidation reactions is well documented [16].

Effect of Ionic Strength

The ionic strength of the reaction medium was changed by

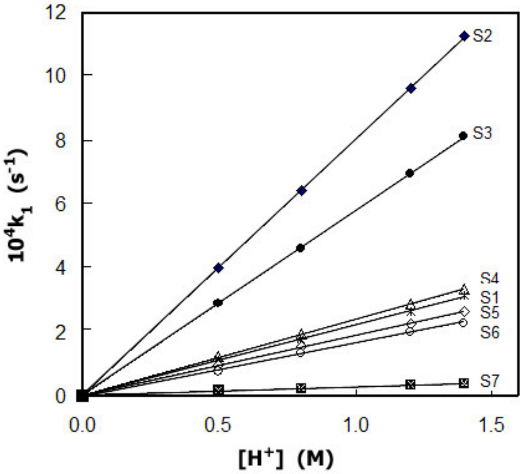


Fig. 2. Plots of k_1 *vs.* [H^+] for the reaction between S and NBS.

the addition of anhydrous sodium perchlorate and the influence of ionic strength on the reaction rate was studied. It was found that the ionic strength of the reaction medium has no significant effect on the reaction rate.

Effect of Products

The effect of added succinimide was studied by the addition of succinimide, which found to decrease the rate of oxidation reaction. Thus, the retardation of reaction rate on the addition of succinimide suggests a pre-equilibrium step involving a process in which succinimide is one of the products.

$$\text{NBS} + H_3O^+ \rightleftharpoons H_2O^+Br + \text{Succinimide} \qquad (2)$$

If this equilibrium is involved in the oxidation process, the rate should be an inverse function of succinimide concentration, which is borne out by the observation that the inverse of the rate constant gives a linear plot (r = 0.999) against [succnimide]. Similar conclusions have been arrived at in the N-chloronicotinamide [17] oxidation of amino acids, and N-bromoacetamide oxidation of some α-hydroxy acids.

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 $HgBr_2$ or $HgBr_4^{2-}$.

Effect of Free Radical Inhibitor

The oxidation reactions of **S1** with NBS catalyzed by perchloric acid at different initial concentrations of acrylonitrile have been investigated [13,18]. The reaction neither induces polymerization nor retards the reaction. Under the experimental conditions, there is no reaction between NBS and acrylonitrile. Consequently, it may be inferred that free radicals are not involved in the rate controlling step of the present reaction.

Effect of Solvent Composition

The effect of changing solvent composition on the reaction rate was studied by varying the concentration of acetic acid from 50-80%. The pseudo first-order rate constants for the oxidation reactions of all oxoacids, **S1-S7,** with NBS were estimated in the presence of perchloric acid at constant ionic strength. The rate constants listed in Table 4 suggest that the rate of the reaction increases with increasing acetic acid content of the solvent mixture. A plot of $\log k_1$ *vs.* 1/D is linear with positive slope. The observed effect is similar to those reported in the oxidation of other organic compounds by NBS [19]. In the solution containing acetic acid one can not exclude the possibility of (AcO^+HBr) acting as a reactive oxidizing species.

The enhancement of the reaction rate with an increase in the amount of acetic acid may generally be attributed to two factors, *viz* (i) increase in acidity at constant [perchloric acid] and (ii) decrease in dielectric constant with increase in HOAc content. The plots of $\log k_1$ against the inverse of dielectric constant are linear with positive slopes, indicating an interaction between a positive ion and a dipole molecule [19]. This supports the postulation of H_2O^+Br as the reactive species.

Rate of Enolization by Bromination Method

It has been reported earlier that, in the case of oxidation of keto compounds, the oxidation proceeds *via* enolization of the keto compounds [20]. The rate of

Table 4. Effect of Solvent Polarity on the Rate of Reaction
[S] = 2.0 × 10^{-2} M, [NBS] = 1.0 × 10^{-3} M, [H^+] = 0.5 M, Temp. = 303 K

	10^4 k_1 (s^{-1})^a					
S	CH_3COOH-H_2O (v/v)%					
	50-50	60-40	70-30	80-20	Slope^b	r^b
S1	1.12 ± 0.10	1.64 ± 0.12	2.38 ± 0.13	3.42 ± 0.12	21.6	0.987
S2	4.01 ± 0.25	4.86 ± 0.13	5.37 ± 0.21	6.13 ± 0.15	7.8	0.984
S3	2.89 ± 0.09	3.80 ± 0.06	4.68 ± 0.22	5.08 ± 0.29	13.6	0.978
S4	1.21 ± 0.07	1.64 ± 0.07	2.38 ± 0.12	3.02 ± 0.12	20.4	0.996
S5	0.95 ± 0.06	1.23 ± 0.06	1.60 ± 0.14	1.98 ± 0.17	14.3	0.982
S6	0.74 ± 0.04	1.14 ± 0.05	1.52 ± 0.16	1.97 ± 0.17	18.5	0.988
S7	0.15 ± 0.02	0.36 ± 0.03	0.70 ± 0.07	1.08 ± 0.19	44.3	0.997

^{a}Estimated from pseudo first-order plots. ^{b}The values calculated from the plots drawn between logk_1 and 1/D.

enolization of keto compound is found to be faster than the rate of oxidation. The reactive species of the substrate may be determined by enolization, which is an acid catalyzed or a base catalyzed reaction and proceeds by a concerted or push-pull mechanism. The rate of enolization was determined by bromination method [21] for the system under investigation.

Effect of Substituents

The oxidation of 4-oxo-4-phenylbuanoic acid (**S1**) and substituted 4-oxoacids (**S2-S7**) were carried out in the temperature range of 303 K-323 K. The observed rate constants found to increase with temperature for all the compounds. The activation parameters for the oxidation of 4-oxoacid by NBS have been evaluated from the slope values of the Arrhenius plots (Fig. 3). The logk_2 value is obtained by dividing the K_{obs} value by 4-oxoacids concentration.

A close look at the activation parameters presented in Table 5 shows that the activation energies for the oxoacids with electron-releasing substituents are relatively lower than that with electron-withdrawing substituents. The entropy of activation is negative for all the 4-oxoacids ranging from -64.9 to -226.3 J K^{-1} mol^{-1}. The large negative entropy of activation in conjunction with other experimental data supports the mechanism outlined in the scheme 1.

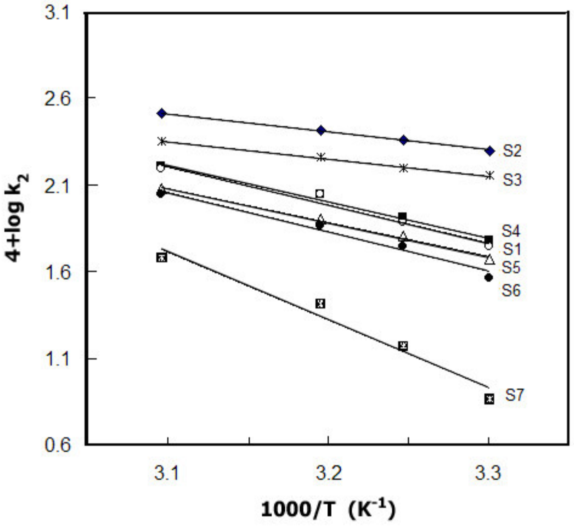


Fig. 3. Arrhenius plots for the oxidation of S by NBS.

It is interesting to note that the reactivity decreases for substituents in the order 4-Methoxy > 4-Methyl > 4-Phenyl > 4- H > 4-Cl > 4-Br > 3-NO_2.

The Hammett's plot for the oxidation of **S** by NBS at various temperatures was found to be linear. The Hammett's plot is shown in Fig. 4. The values of reaction constants (ρ) are shown in Table 6.

he ρ value indicates the sensitivity of a reaction to the effects of electronic perturbation. It also provides information

Table 5. Activation Parameters and Rate Constants for the Oxidation of **S1-S7** by NBS in Aqueous Acetic Acid Medium. [**S**] = 2.0×10^{-2} M, [NBS] = 1.0×10^{-3} M, [H^+] = 0.5 M, Solvent Composition: 50% Acetic Acid-50% Water (v/v)

S	10^4 k_1 (sec^{-1})^b				E_a	$\Delta H^\#$	$\Delta S^\#$	$\Delta G^\#$
	303 K	308 K	313 K	323 K	(kJ mol^{-1})	(kJ mol^{-1})	(kJ mol^{-1})	(J K^{-1} mol^{-1})
S1	1.121±0.10	1.554±0.13	2.238±0.00	3.139±0.13	42.0	39.5	-154.4	86.2
S2	4.006±0.25	4.624±0.09	5.256±0.00	6.552±0.26	19.9	17.3	-220.4	84.1
S3	2.885±0.09	3.186±0.06	3.716±0.00	4.548±0.21	18.9	16.4	-226.3	84.9
S4	1.207±0.07	1.646±0.10	2.237±0.00	3.244±0.12	40.1	37.6	-163.5	87.1
S5	0.947±0.06	1.290±0.00	1.622±0.00	2.434±0.00	37.9	35.3	-173.0	87.8
S6	0.739±0.04	1.122±0.00	1.465±0.00	2.232±0.00	43.7	41.2	-155.7	88.4
S7	0.147±0.02	0.298±0.00	0.524±0.00	0.966±0.00	75.3	72.8	-64.9	92.4

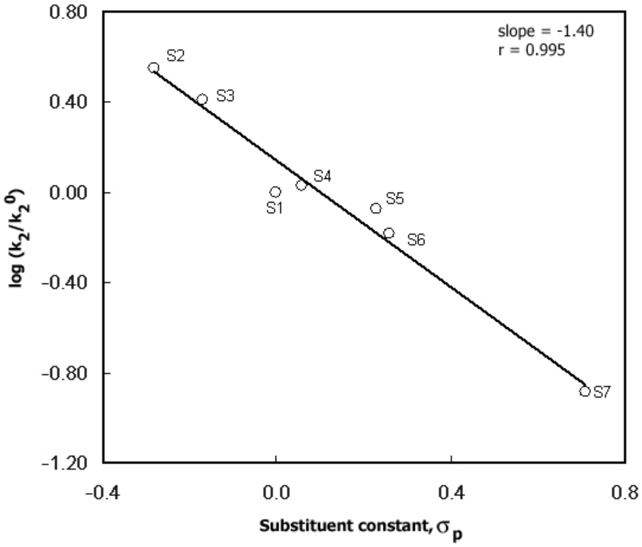


Fig. 4. Hammett plot (at 303 k) for the oxidation of **S** by NBS.

Table 6. Reaction Constant Values at Different Temperatures^a

Temperature (K)	Reaction constant (ρ)^b	Correlation coefficient	SD
303	-1.40 ± 0.20	0.995	0.056
308	-1.17 ± 0.15	0.995	0.042
313	-0.99 ± 0.06	0.998	0.017
323	-0.81 ± 0.09	0.997	0.026

^{a}σ values were taken from reported works [22]. ^{b}The values were obtained by correlating $\log(k_2/k_2^0)$ with σ_p for the reactions of oxidations **S1-S7** with NBS.

about the nature of the transition state involved during the reaction. A reaction involving a development of positive charge in the transition state is aided by electron-releasing substituents and the ρ value is negative [23].

In the present investigation, the acceleration of reaction rate with the electron-releasing substituents and the negative value of the reaction constant, ρ indicate explicitly that the mechanism of oxidation involves the development of positive charge in the transition state.

It is generally recognized that oxidations lead to electron deficient species which are radical cations, radicals or carbocations. These reactions normally have a negative ρ value and the magnitude of ρ value depends on the extent of electron deficiency. Oxidation reactions involving free radical formation in the rate controlling step usually have a small negative ρ value and the oxidations involving the formation of carbocation have a large negative ρ values. Based on these arguments we expect a large ρ value but the measured ρ value is in the range -1.40 to -0.81. The low ρ value may be attributed to the nature of observed rate constant. The observed rate constant is composite of several terms and is shown in Eq. (12).

The terms shown in Eq. (12) deserve comment. The rate constant k_3 depends on the concentration of the protonated substrate (S^+) and the electron donating substituents tend to delocalize the positive charge on S^+ and hence favors the formation of this positive species. In the rate limiting step (Eq. 6) of the Scheme 1, the formation of the carbocation is facilitated by electron releasing substituents.

Thus we get a slightly low negative ρ value of -1.40 (at 303 K) because k_{obs} is composite of the enolization as well as the oxidation of the 4-oxoacids. Hence in the present investigation the measured ρ value and other findings fit in with the formulation of mechanism outlined in the Scheme 1.

The dependence of reaction rate on the structure of the reacting molecule is related to activation parameters. The decisive term concerning the dependence on the structure is neither free energy nor enthalpy but potential energy which is experimentally not accessible. Many authors support the opinion that the activation energy at a certain temperature is a better approximation towards the unknown potential energy [26].

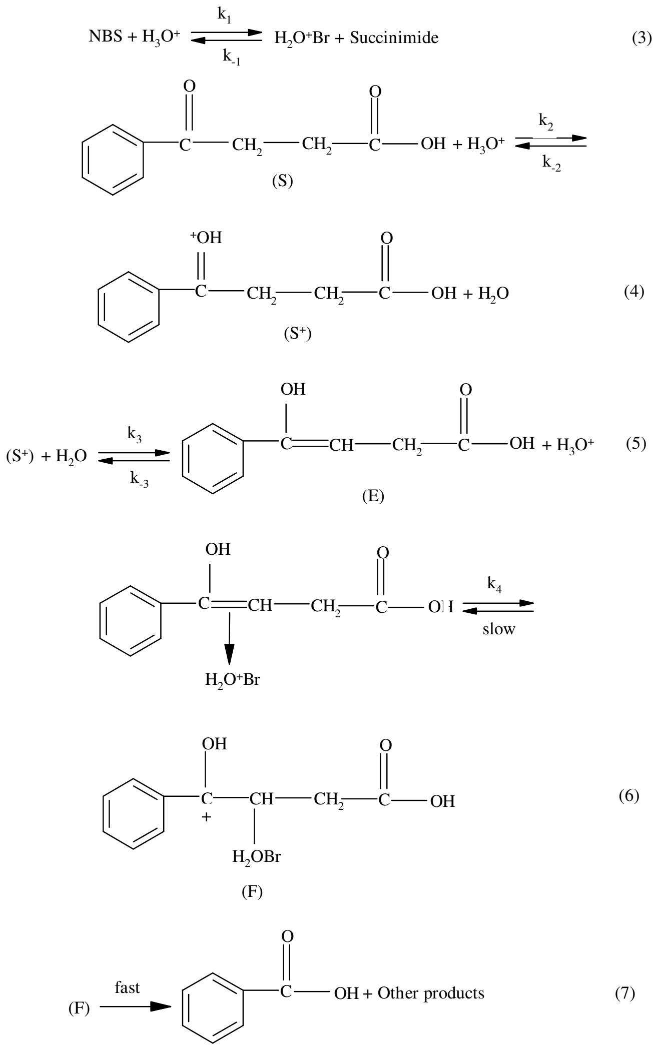
The validity of the isokinetic relation can be tested graphically by plotting by Exner plots. The isokinetic temperature evaluated from the Exner plots was found to be 353 K. As the experiment has been carried out at a temperature far away from the isokinetic temperature the application of Hammett equation to the observed kinetic data is valid. The validity of isokinetic relationship in the present study implies that all the 4-oxoacids undergo oxidation by the same mechanism [27].

Mechanism

A probable mechanism for the oxidation of 4-oxoacids by NBS has been proposed based on the experimental results and in analogy with the oxidation of oxo compounds with other oxidants.

DERIVATION OF RATE LAW

Based on kinetic observations and the mechanism proposed, the following rate expression can be derived applying steady-state approximation,



Scheme 1

The rate of the reaction is given by

$$\frac{-d[NBS]}{dt} = k_4\,[E][H_2O^+Br] \tag{8}$$

Applying steady state approximation for [E]

$$\frac{-d[NBS]}{dt} = \frac{k_2k_3k_4\,[H_3O^+][\mathbf{S}][H_2O^+Br]}{k_{-2}k_{-3}\,[H_3O^+] + k_4\,(k_{-2} + k_3)[H_2O^+Br]} \tag{9}$$

At high concentration of $[H_3O^+] = 0.5$ M

$$k_{-2}\,k_{-3}\,[H_3O^+] \;>>\; k_4\,(k_{-2} + k_3)\,[H_2\overset{+}{O}Br]$$

So the Eq. (9) simplifies to the form

$$\frac{-d[NBS]}{dt} = \frac{k_2k_3k_4\,[H_3O^+][\mathbf{S}][H_2O^+Br]}{k_{-2}k_{-3}\,[H_3O^+]} = \frac{k_2k_3k_4\,[\mathbf{S}][H_2O^+Br]}{k_{-2}k_{-3}} \tag{10}$$

The value of $[H_2\overset{+}{O}Br]$ can be obtained from Eq. (3) given in the Scheme 1.

$$k_a = \frac{k_1}{k_{-1}} = \frac{[H_2O^+Br][Succinimide]}{[NBS][H_3O^+]}$$

Therefore, $[H_2\overset{+}{O}Br] = K_a\,[NBS]\,[H_3O^+]/[Succinimide]$
Using the value of $[H_2O^+Br]$ in Eq. (10)

$$\frac{-d[NBS]}{dt} = \frac{k_2k_3k_4\,[\mathbf{S}]k_a[H_3O^+][NBS]}{k_{-2}k_{-3}\,[Succinimide]} \tag{11}$$

Hence, at higher concentration of mineral acid, the reaction is first order each with respect to the oxoacid (**S**), [NBS] and $[H_3O^+]$.

The observed rate constant at high $[H_3O^+]$ is

$$k_{obs} = \frac{k_2k_3k_4k_a}{k_{-2}k_{-3}} \tag{12}$$

Stoichiometry and Product Analysis

The identification of the product namely, benzoic acid was made by comparing the R_f values of the authentic samples. The stoichiometric results obtained that one mole of the oxoacid required one mole of NBS for oxidation.

$$C_6H_5COCH_2CH_2COOH + (CH_2CO)_2NBr + 5H_2O \xrightarrow{H^+} CH_5COOH + (CH_2CO)_2NH + 3CO_2 + 6H_2 + HBr \tag{13}$$

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