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Kinetics of Oxidation of 4-Oxoacids by N-Chlorosaccharin in Aqueous Acetic Acid Medium

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Kinetics of oxidation of substituted and unsubstituted 4-oxoacids (S) by N-chlorosaccharin (NCSA) in aqueous acetic acid medium have been studied. The reaction follows first-order kinetics, each in 4-oxoacids, NCSA 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. On the basis of the kinetic results and product analysis, a suitable mechanism has been proposed for the reaction of NCSA with 4-oxoacids.

Key Words: Kinetics, Oxidation, N-chlorosaccharin, 4-Oxoacids.

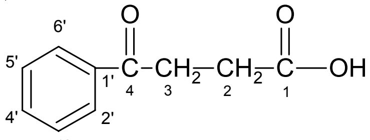
INTRODUCTION

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-Chlorosaccharin (NCSA) is a source of positive halogen and this reagent has been exploited as an oxidant for a variety of substrates in both acidic and alkaline medium[2]. The nature of active oxidizing species and mechanism depends on the nature of 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 NCSA in acid solution are >NX, HOX, $>N^+HX$ or H_2OX^+ and the reaction 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-chlorosaccharin oxidations of a large variety of organic compounds have been studied, there seems to be no report on a systematic kinetic study of the oxidation of 4-oxoacids by N-chlorosaccharin.

A systematic study on the reactions of 4-oxoacids (S) by N-chlorosaccharin (NCSA) has been carried out in present work. In this report, the kinetic and mechanistic aspects of the oxidation of substituted and unsubstituted 4-oxoacids by N-chlorosaccharin in the presence of perchloric acid have been examined. The various unsubstituted and substituted 4-oxoacids (**S1-S7**) employed in the present study are listed below



4-Oxoacid (**S1**)

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

EXPERIMENTAL

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.

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 ± 0.1ºC. 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 $(E_t - E_\infty)$ *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: The rate of oxidation is found to be first order each in [NCSA] and [S]. Linear plots of log k_1 *vs.* log [S] with unit slope (**S1:** slope = 1.01 ± 0.03, r = 0.999; **S2:** slope = 0.998 ± 0.01, r = 0.999; **S3:**

slope = 1.02 ± 0.01, r = 0.989; **S4:** slope = 1.04 ± 0.03, r = 0.997; **S5:** slope = 0.999 ± 0.04, r = 0.989; **S6:** slope = 1.03 ± 0.03, r = 0.999; **S7:** slope = 1.01 ± 0.02, r = 0.997) shows first order dependence of the rate on [**S**]. The k_1 values at different [**S**] are given in Table-1. The k_1 values obtained at different initial concentrations of NCSA reveal that the rates are almost independent of initial concentration of NCSA (Table-1.). This ensures the order of the reaction with respect to NCSA is one.

The dependence of the reaction rate on the H^+ 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-1. It may be seen that the rate of the reaction increases linearly with increase in concentration of H^+. This establishes that the reaction is first order with respect to H^+ concentration. A plot of k_1 *vs.* $[H^+]$ is also linear passing through the origin (Fig. 1) showing that the reaction proceeds completely through the acid-catalyzed pathway[13].

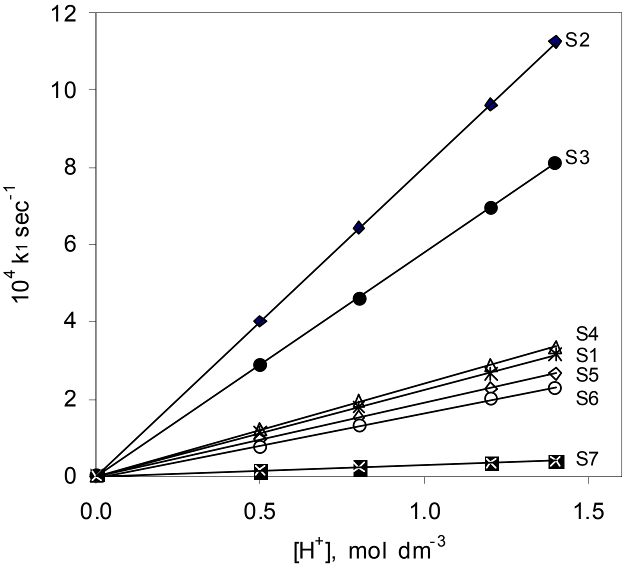


Fig. 1. Plots of k_1 *vs.* $[H^+]$ for the reaction between S and NCSA

It has been reported earlier in the case of N-halo oxidants that in the absence of mineral acids, HOCl is the reactive oxidant species[14]. Bishnoi and Banerji have observed[15] in the oxidation of some α-hydroxy acids by NCSA that linear increase in the oxidation rate with an increase in $[H^+]$ indicates the protonation of HOCl to give a cationic chlorine species (eqn. 1), which is a stronger electrophile and oxidant.

$$HOCl + H_3O^+ \rightleftharpoons H_2O^+Cl + H_2O \qquad (1)$$

TABLE-1

EFFECT OF VARYING [S] [NCSA] AND [H$^+$] ON THE RATE OF REACTION[a]
SOLVENT: 50 % ACETIC ACID-50 % WATER (v/v), TEMP = 303 K

10^2[S] mol dm^{-3}	10^3 [NCSA] mol dm^{-3}	[H$^+$] mol dm^{-3}	10^4 k_1[b] s^{-1}						
			S1	**S2**	**S3**	**S4**	**S5**	**S6**	**S7**
2.0	1.0	0.5	1.72 ± 0.10	5.84 ± 0.60	4.14 ± 0.58	1.84 ± 0.11	1.07 ± 0.17	0.99 ± 0.10	0.26 ± 0.03
4.0	1.0	0.5	3.30 ± 0.17	11.6 ± 0.70	8.27 ± 0.86	3.66 ± 0.13	2.24 ± 0.20	1.96 ± 0.10	0.53 ± 0.06
6.0	1.0	0.5	4.47 ± 0.02	17.0 ± 1.20	12.3 ± 0.90	5.42 ± 0.18	3.15 ± 0.17	2.94 ± 0.12	0.79 ± 0.06
8.0	1.0	0.5	7.33 ± 0.25	22.9 ± 2.20	16.5 ± 0.20	7.42 ± 0.43	4.35 ± 0.22	3.88 ± 0.23	1.06 ± 0.09
2.0	0.8	0.5	1.73 ± 0.05	5.60 ± 0.08	4.18 ± 0.10	1.88 ± 0.05	1.15 ± 0.07	0.92 ± 0.11	0.27 ± 0.02
2.0	0.4	0.5	1.75 ± 0.03	5.66 ± 0.07	4.17 ± 0.11	1.85 ± 0.03	1.11 ± 0.13	0.95 ± 0.10	0.27 ± 0.01
2.0	0.2	0.5	1.74 ± 0.03	5.84 ± 0.18	4.14 ± 0.10	1.84 ± 0.08	1.10 ± 0.04	0.97 ± 0.03	0.27 ± 0.02
2.0	1.0	1.0	3.34 ± 0.14	11.8 ± 0.50	8.24 ± 0.25	3.54 ± 0.26	2.11 ± 0.07	1.98± 0.07	0.48 ± 0.04
2.0	1.0	1.2	4.41 ± 0.18	14.2 ± 0.60	9.94 ± 0.26	4.54 ± 0.22	2.51 ± 0.15	2.37 ± 0.11	0.64 ± 0.03
2.0	1.0	1.4	5.46 ± 0.29	6.1 ± 0.10	11.8 ± 0.60	5.35 ± 0.19	2.94 ± 0.17	2.75 ± 0.13	0.81 ± 0.01

[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

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

Effect of varying ionic strength: The ionic strength of the reaction medium was changed by the addition of anhydrous sodium perchlorate and the influence of ionic strength on the reaction rate was studied. It is found that the ionic strength of the reaction medium has no significant effect on the reaction rate.

Effect of products: The effect of added saccharin was studied by the addition of saccharin decreases the rate of oxidation reaction. Thus the retardation of reaction rate on the addition of saccharin suggests a pre-equilibrium step involving a process in which saccharin is one of the products.

$$\text{NCSA} + H_3O^+ \rightleftharpoons H_2O^+Cl + \text{Saccharin} \quad (2)$$

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

Effect of free radical inhibitor: The oxidation reactions of **S1** with NCSA 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 NCSA 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 NCSA were estimated in the presence of perchloric acid at constant ionic strength. The rate of the reaction increases remarkably with increase in the proportion of acetic acid in the medium (Table-2). When acetic acid content increases in the medium, the acidity of the medium is increased while the dielectric constant of the medium is decreased. These two effects cause the rate of the oxidation to increase remarkably. The observed effect is similar to those reported in the oxidation of other organic compounds by NCSA[19a-c]. When acetic acid content of the medium is increased from 50-80 %, the pH of the medium changes leading to the increase in [H^+] and hence catalysis by acetate ion is untenable.

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 acetic acid 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^+Cl as the reactive species.

Rate of enolization by bromination method: It has been reported earlier in the case of oxidation of keto compounds that the oxidation proceeds *via* enolization of the keto compounds[20]. The rate of 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 as well as 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.

TABLE-2

EFFECT OF SOLVENT POLARITY ON THE RATE OF REACTION

$[S] = 2.0 \times 10^{-2}$ mol dm^{-3}, $[NCSA] = 1.0 \times 10^{-3}$ mol dm^{-3}, $[H^+] = 0.5$ mol dm^{-3}, Temp : 303 K

S	$10^4 k_1{}^a$, s^{-1}					
	$CH_3COOH–H_2O$ (v/v) %					
	50-50	60-40	70-30	80-20	Slope[b]	r[b]
S1	1.72 ± 0.10	2.54 ± 0.24	3.35 ± 0.14	5.83 ± 0.29	23.8	0.998
S2	5.84 ± 0.60	7.23 ± 0.36	8.31 ± 0.48	9.96 ± 0.60	10.1	0.983
S3	4.14 ± 0.58	5.30 ± 0.25	6.73 ± 0.54	7.94 ± 0.54	12.7	0.985
S4	1.84 ± 0.11	2.36 ± 0.07	3.30 ± 0.14	4.55 ± 0.18	17.6	0.998
S5	1.07 ± 0.17	1.47 ± 0.06	2.20 ± 0.11	3.44 ± 0.01	19.0	0.998
S6	0.99 ± 0.04	1.19 ± 0.05	1.85 ± 0.15	2.87 ± 0.15	14.7	0.994
S7	0.26 ± 0.03	0.52 ± 0.03	0.86 ± 0.07	1.26 ± 0.08	37.9	0.998

[a] Estimated from pseudo first-order plots.

[b] The values calculated from the plots drawn between log k_1 and 1/D.

Effect of Substituents: The oxidation of 4-oxo-4-phenyl butanoic acid (**S1**) and substituted 4-oxoacids (**S2-S7**) are carried out in the temperature range of 303-323 K. The observed rate constants increase with temperature for all the compounds. The activation parameters for the oxidation of 4-oxoacid by NCSA have been evaluated from the slope values of the Arrhenius plots.

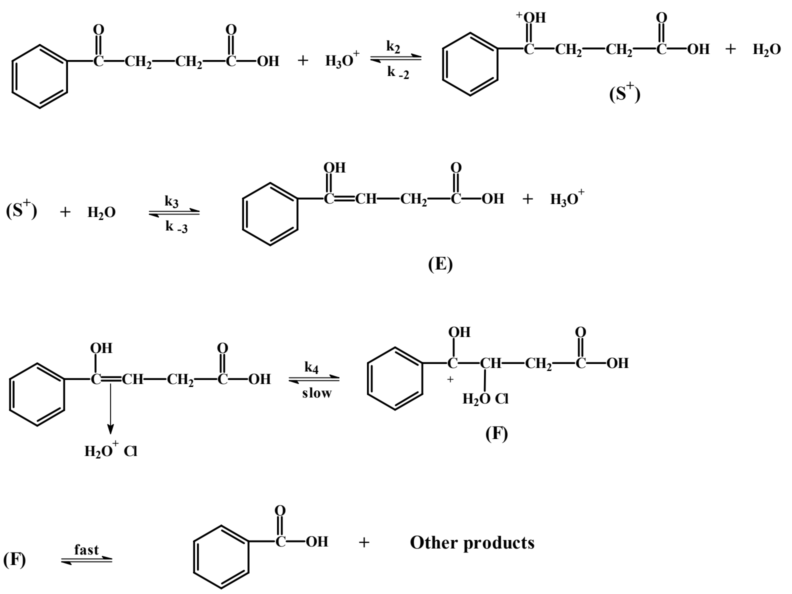
A close look at activation parameters presented in Table-3 shows that the activation energies for the oxoacids with electron-releasing substituents are relatively lower than that with electron-withdrawing substituents.

TABLE-3
ACTIVATION PARAMETERS AND RATE CONSTANTS FOR THE OXIDATION OF **S1-S7** BY NCSA IN AQUEOUS ACETIC ACID MEDIUM
[**S**] = 2.0 × 10^{-2} mol dm^{-3}, [NCSA] = 1.0 × 10^{-3} mol dm^{-3}, [H^+] = 0.5 mol dm^{-3},
Solvent composition : 50% Acetic acid-50% Water (v/v)

S	10^4 k_1^b, s^{-1}				E_a kJ mol^{-1}	$\Delta H^\#$ kJ mol^{-1}	$\Delta S^\#$ J K^{-1} mol^{-1}	$\Delta G^\#$ kJ mol^{-1}
	303 K	308 K	313 K	323 K				
S1	1.72±0.10	2.14±0.17	2.84±0.28	4.00±0.64	34.4	31.9	-179.4	86.2
S2	5.84±0.60	6.36±0.60	7.84±0.82	8.55±0.58	15.8	13.3	-230.8	83.2
S3	4.14±0.58	4.72±0.30	5.28±0.40	6.20±0.68	16.3	13.8	-231.9	84.0
S4	1.84±0.11	2.54±0.10	3.24±0.02	4.58±0.16	35.9	33.4	-173.7	86.0
S5	1.07±0.17	1.35±0.14	1.66±0.08	2.36±0.26	32.0	29.5	-191.5	87.5
S6	0.99±0.04	1.12±0.01	1.47±0.01	2.23±0.01	34.2	31.7	-184.7	87.7
S7	0.26±0.03	0.41±0.01	0.61±0.01	1.04±0.01	55.4	52.9	-125.6	91.0

The entropy of activation is negative for all the 4-oxoacids ranging from -125.6 to -231.9 J K^{-1} mol^{-1}. The large negative entropy of activation in conjunction with other experimental data supports the mechanism outlined in the **Scheme-I**.

$$\text{NCSA} + H_3O^+ \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} H_2O^+Cl + \text{Saccharin} \qquad (3)$$



Scheme-I

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 NCSA at various temperatures is found to be linear. The Hammett's plot is shown in Fig. 2. The values of reaction constants (ρ) are shown in Table-4.

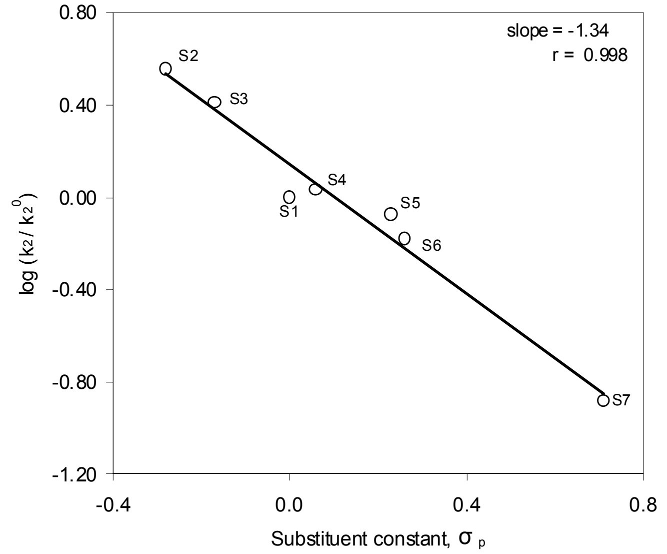


Fig. 2. Hammett plot (at 303K) for the oxidation of S by NCSA

TABLE-4
REACTION CONSTANT VALUES AT DIFFERENT TEMPERATURES[a]

Temperature (K)	Reaction constant[b] (ρ)	Correlation coefficient	Standard deviation
303	-1.34 ± 0.09	0.998	0.027
308	-1.23 ± 0.17	0.998	0.050
313	-1.11 ± 0.20	0.998	0.057
323	-0.93 ± 0.19	0.998	0.056

[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 NCSA.

The ρ value indicates the sensitivity of a reaction to the effects of electronic perturbation. It also provides information 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[21-25].

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. On the basis of these arguments, a large ρ value is expected but the measured ρ value is in the range -1.34 to -0.93. 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 eqn. 12.

The terms shown in eqn. 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 favours the formation of this positive species. In the rate limiting step eqn. 6 of the **Scheme-I**, the formation of the carbocation is facilitated by electron releasing substituents.

Thus, a slightly low negative ρ value of -1.34 (at 303 K) is obtained 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-I**.

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 Exnler plots. The isokinetic temperature evaluated from the Exnler plots is found to be 378 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].

Derivation of rate law

Based on kinetic observations and the mechanism proposed, the rate expression can be derived applying steady-state approximation, The rate of the reaction is given by

$$\frac{-\,d[\text{NCSA}]}{dt} = k_4[\text{E}]\,[\text{H}_2\text{O}^+\text{Cl}] \tag{8}$$

Applying steady state approximation for [E]

$$\frac{-\,d[\text{NCSA}]}{dt} = \frac{k_2k_3k_4[\text{H}_3\text{O}^+]\,[\text{S}]\,[\text{H}_2\text{O}^+\text{Cl}]}{k_{-2}k_{-3}[\text{H}_3\text{O}^+] + k_4(k_{-2}+k_3)\,[\text{H}_2\text{O}^+\text{Cl}]} \tag{9}$$

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

$K_{-2}\ k_{-3}\ [H_3O^+] >> k_4\ (k_{-2} + k_3)\ [H_2O^+Cl]$

So the eqn. 9 simplifies to the form

$$\frac{-\,d[\text{NCSA}]}{dt} = \frac{k_2k_3k_4[\text{H}_3\text{O}^+]\,[\text{S}]\,[\text{H}_2\text{O}^+\text{Cl}]}{k_{-2}k_{-3}[\text{H}_3\text{O}^+]}$$

$$= \frac{k_2k_3k_4\,[\text{S}]\,[\text{H}_2\text{O}^+\text{Cl}]}{k_{-2}k_{-3}} \tag{10}$$

The value of $[H_2O^+Cl]$ can be obtained from equation 3 given in the **Scheme-I**.

$$K_a = \frac{k_{-1}}{k_1} = \frac{[\text{NCSA}]\,[\text{H}_3\text{O}^+]}{[\text{H}_2\text{O}^+\text{Cl}]\,[\text{Saccharin}]}$$

Therefore, $[H_2O^+Cl] = \dfrac{[\text{NCSA}]\,[\text{H}_3\text{O}^+]}{K_a\,[\text{Saccharin}]}$

Using the value of $[H_2O^+Cl]$ in eqn. 10

$$\frac{-\,d[\text{NCSA}]}{dt} = \frac{k_2k_3k_4[\text{S}]\,[\text{H}_3\text{O}^+]\,[\text{H}_2\text{O}^+\text{Cl}]}{k_{-2}k_{-3}K_a\,[\text{Saccharin}]} \tag{11}$$

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

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

$$k_{obs} = \frac{k_2k_3k_4}{k_{-2}k_{-3}k_a} \tag{12}$$

Product analysis and stoichiometry: In a typical experiment, 4-oxo acid (0.1M), perchloric acid (0.5) and NCSA (0.5) were mixed in acetic acid-water (1:1 v/v) mixture in a closed vessel with an outlet and allowed to react. The ensuing gas was identified as carbon dioxide. After 24 h, the solution was extracted with ether. The ether extract was dried over anhydrous sodium sulphate and the solvent evaporated. The colourless and solid obtained was identified as benzoic acid by noting the mixed melting point, chemical method and TLC techniques.

Different sets of reaction mixture containing different quantities of NCSA and oxo acid at constant concentration of perchloric acid and sodium perchlorate were allowed to react for 24 h at 30ºC and then analysed. The remainig NCSA was assayed iodometrically and the results are in good agreement with 1:1 stoichiometry and that may be represented

$$C_6H_5COCH_2CH_2COOH + C_6H_4SO_2CONCl + 5H_2O \xrightarrow{H^+} C_6H_5COOH + C_6H_4SO_2CONH + 3CO_2 + 6H_2 + HCl \quad (13)$$

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