

Kinetics and mechanism of *N*-chlorosaccharin oxidation of malic acid

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ABSTRACT: Kinetic study of *N*-chlorosaccharin (NCSA) oxidation of malic acid (MA) in aqueous acetic acid medium in presence of perchloric acid has been investigated. The reactions exhibit first-order dependency in oxidant and HClO_4 while order varies from one to zero in substrate. The reactions are acid catalyzed and retarded by the addition of saccharin, a byproduct of reaction. The rate of oxidation decreases with decrease in dielectric constant of the medium. The effect of temperature on the reaction has been investigated in the temperature range 313-333 K. The stoichiometric studies revealed 1:1 mole ratio. Various thermodynamic parameters have been computed and a possible operative mechanism is proposed.

Keywords: malic acid; mechanism; *N*-chlorosaccharin; bifunctional; hydroxy acid

Introduction

The prime aim of the authors is to probe the hitherto unreported results on the mechanistic routes of *N*-chlorosaccharin [1, 2] oxidation of malic acid. Recently reactions involving NCSA received limited attention. Although a variety of compounds like alcohol [3, 4], hydroxy acids [5, 6], acid [7], aldehyde [8], ketones [9, 10], benzaldehyde [11], amino acids [12, 13], keto acid [14] etc. has been oxidized employing this oxidant. Malic acid is an aliphatic hydroxy acid. It is a bi-functional compound with hydroxy and carboxyl function having active electron attracting species. Due to inductive effect of these groups, a negative center is created for the attack of HOCl and $\text{H}_2\text{O}^+\text{Cl}$, which is active species of NCSA. It has been found despite of great diversity in structure of

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hydroxy acids, the reactivity and rate are often markedly affected by changes in the carbon skeleton. Aliphatic hydroxy acids have been oxidized by a numerous oxidants namely Os (VII) [15], KMnO_4 [16], NBSA [17] etc. The peculiar properties of this oxidant are limited and therefore in view of widening the dimension of understanding, the present task has been probed kinetically. The investigation aimed to study the newer areas with broad vision by employing the hidden potentiality of NCSA as an oxidant and malic acid as the substrate.

Material and Methods

The sample of NCSA employed in this study was prepared in acetic acid (E. Merck). All other chemicals were of Analytical grade. The solutions used were standardized iodometrically. Demineralized distilled water was used for preparing the solution of hypo and others. Malic acid (E. Merck) was prepared in the requisite amount of acetic acid and water mixture. The kinetic measurements were initiated by mixing appropriate volumes of two solutions containing NCSA solution and the malic acid in aqueous acetic acid in presence of perchloric acid. The progress of the reaction was monitored by estimating unconsumed NCSA iodometrically. The stoichiometric results indicated consumption of mole ratio 1:1.



After complete oxidation of the system, the end product so obtained was detected by means of chromatography, and existing conventional methods [18, 19].

Results and Discussion

Oxidation kinetics has been carried out in binary solvent mixture of the acetic acid and water under the reaction condition $[\text{NCSA}] \ll [\text{Malic Acid}] [\text{H}^+]$.

Dependence of rate on oxidant

In a typical kinetic run, for the reaction ($[\text{NCSA}] = 2.5 \text{ mol dm}^{-3}$, $[\text{H}^+] = 0.05 \text{ moldm}^{-3}$ and $[\text{MA}] = 5.0 \times 10^2 \text{ moldm}^{-3}$), a plot of $\log(a-x)$ versus time (Fig. 1) gave a straight line, which indicates that reaction under the chosen condition follows pseudo first order kinetics. The order with respect to NCSA is unity (Table 1).

Effect of concentration of substrate

On varying malic acid concentration from 1.0 to 10.0 moldm^{-3} , there is an increase in rate of reaction. The plots of $\log k_1$ versus $\log [\text{MA}]$ (Fig. 2) gave straight line at lower concentration but bend at higher concentration, suggesting that order with respect to malic acid is fractional. A double reciprocal plot between k^{-1} versus $[\text{MA}]^{-1}$ (Fig. 3) has been found to be straight line with positive intercept at y-axis. That leads to follow

Michaelis-Menten kinetics indicating evidence for the intermediate complex formation between the species of oxidant and the substrate in a pre-equilibrium step. This kinetic evidence of complex formation between the substrate and the oxidant, further support the first order dependence.

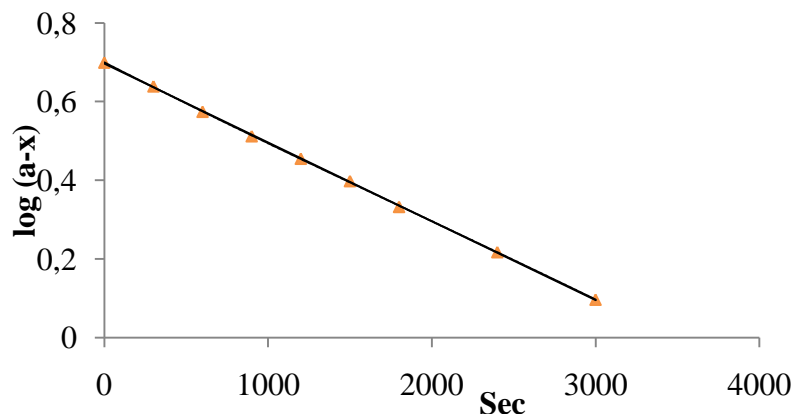


Figure 1. Plot of $\log(a-x)$ versus time.

Table 1. Effect of variation of [NCSA] on the rate constant k_1 $[MA] \times 10^2$, (mol dm^{-3}) = 5.0; $[H^+]$ (mol dm^{-3}) = 0.05; HOAc-H₂O, (%vol.) = 20; temperature (K) = 318.

$[NCSA] \times 10^3 (\text{mol dm}^{-3})$	$\leftarrow k_1 \times 10^4 (s^{-1}) \rightarrow$
1.0	4.671
2.0	4.669
2.5	4.683
4.0	4.682
5.0	4.662

Table 2. Dependence of rate on the variation of the concentration of malic acid. $[NCSA] \times 10^3$, (mol dm^{-3}) = 2.5; $[H^+]$ (mol dm^{-3}) = 0.05; HOAc-H₂O, (%vol.) = 20; temperature (K) = 318.

$[MA] \times 10^2 (\text{mol dm}^{-3})$	$\leftarrow k_1 \times 10^4 (s^{-1}) \rightarrow$
1.0	1.619
2.0	2.673
2.5	3.279
4.0	4.304
5.0	4.683
8.0	5.021
10.0	5.068

The effect of variation of hydrogen ion

On varying perchloric acid concentration from 0.1 to 0.5 mol dm^{-3} the negative catalyzed

kinetics was observed by the addition of HClO_4 and first-order was evaluated (Table 3). The plots of $1/k_1$ versus $\log [\text{H}^+]$ (Fig. 4) gave straight line with positive intercept, suggesting that acid plays a complex role in the reaction system. The retardation by $[\text{H}^+]$ may be mainly attributed to the conversion of the more reactive neutral species of malic acid to less reactive protonated form.

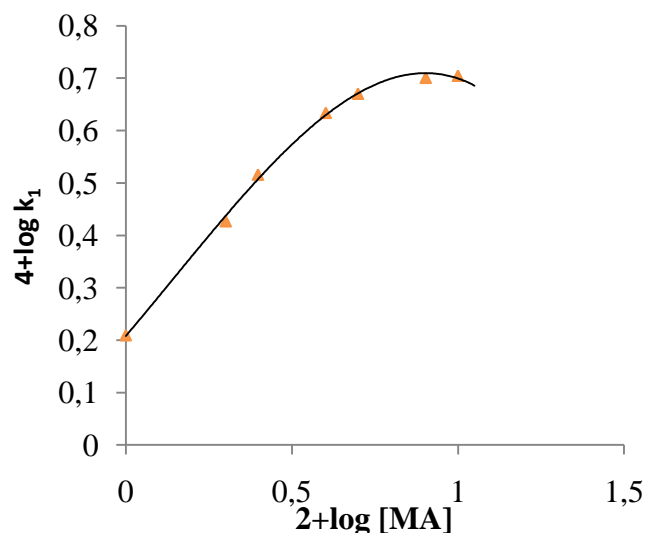


Figure 2. Plot of $\log k_1$ versus $\log [\text{MA}]$.

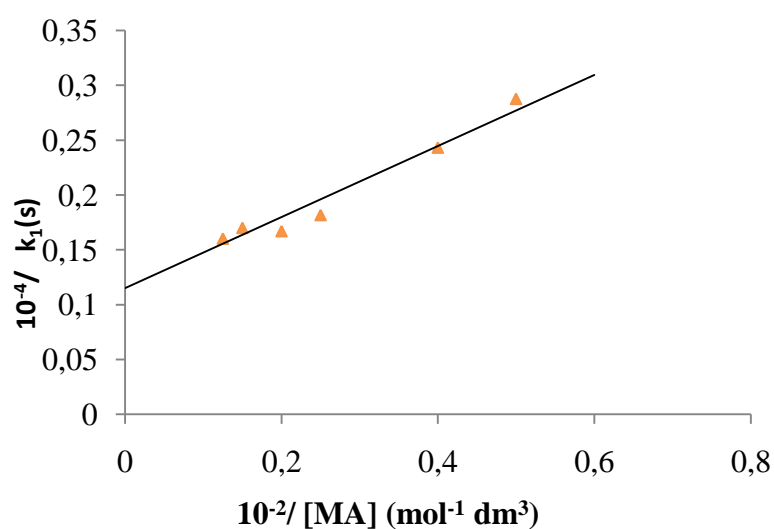


Figure 3. Plot of $1/k_1$ versus $1/[\text{MA}]$.

Table 3. Effect of change of concentration of H^+ . $[\text{NCSA}] \times 10^3$, (mol dm^{-3}) = 2; $[\text{MA}] \times 10^2$ (mol dm^{-3}) = 5.0; $\text{HOAc-H}_2\text{O}$, (% vol.) = 20; temperature (K) = 318.

$[\text{HClO}_4]$ (mol dm^{-3})	$k_1 \times 10^4$ (s^{-1})
0.10	1.619
0.20	2.673
0.25	3.279
0.40	4.304
0.50	4.683

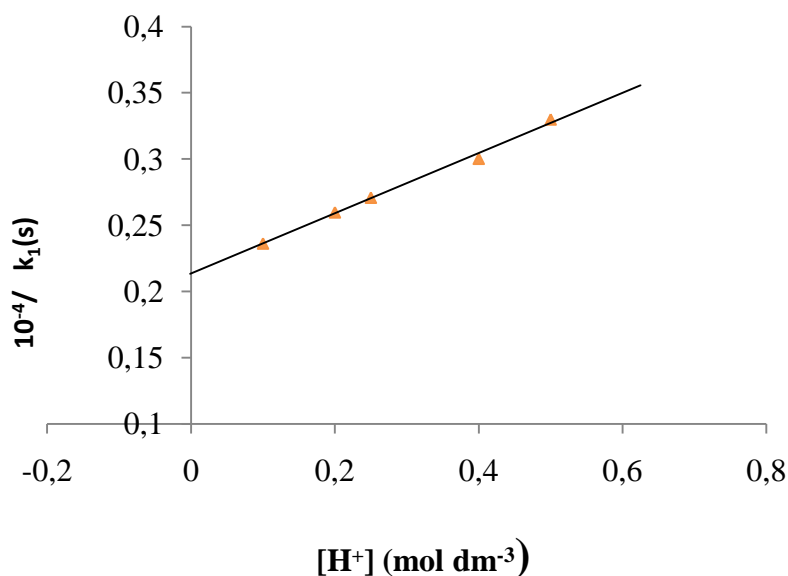


Figure 4. Plot of $1/k_1$ versus $[H^+]$.

Effect of variation of ionic strength, dielectric constant and saccharin

It was found that there is no substantial change in the reaction rate on varying the ionic strength from 1 to 10 mol dm⁻³ by the addition of neutral sodium perchlorate. The small salt effect suggests the participation of neutral species in rate determining step i.e., the substrate molecule and HOCl. This assumption further got support from effect of change in dielectric constant of the reaction medium. The effect of dielectric constant in reaction medium has been studied by adding acetic acid (10-60%) in the reaction medium at constant concentration of other reactants. The rate of reaction decreases by increasing the proportion of acetic acid in solvent medium; this supports the involvement of neutral species in the rate determining step. Addition of saccharin, one of the reaction products, from 0.0005 to 0.001 mol dm⁻³ at constant NCSA and malic acid concentration, decreases the rate of reaction. This supports that HOCl is the main oxidizing species. The oxidation of malic acid by NCSA failed to induce polymerization of acrylonitrile. Hence a free radical mechanism is ruled out.

Effect of temperature

By increasing temperature the rate of the reaction increases. The plot of $\log k$ versus $1/T$ (Fig. 5) is a straight line in the temperature range 313-333 K. This shows Arrhenius equation is valid for this reaction. From the linear Arrhenius plot activation parameters for overall reaction were evaluated (Table 4).

Reaction Mechanism

Before highlighting the mechanism of the oxidation reaction it is worthwhile at this

stage to have an idea regarding the reacting species of NCSA in aqueous acetic acid medium in the presence of perchloric acid. Thus the formation of different reactive oxidizing species may be assumed in the following manners:

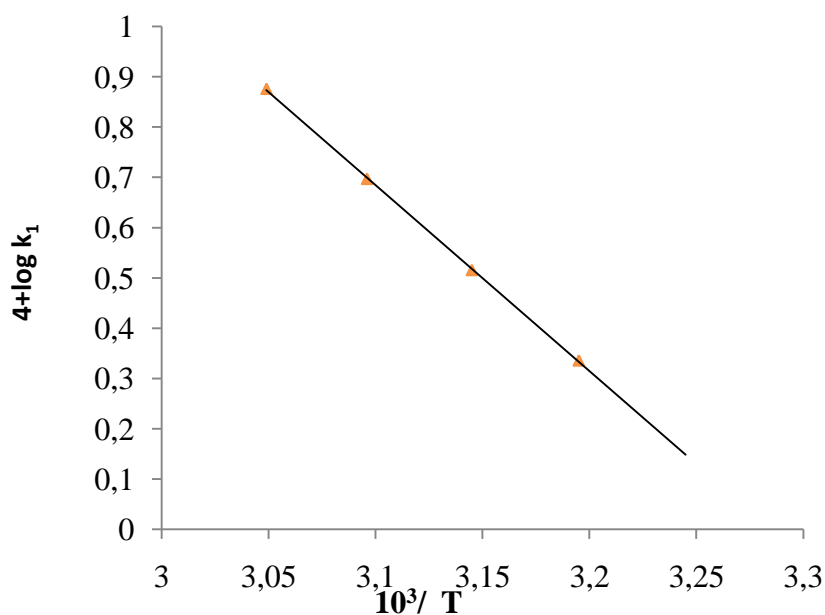
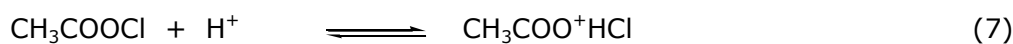
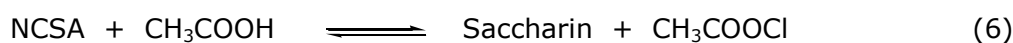
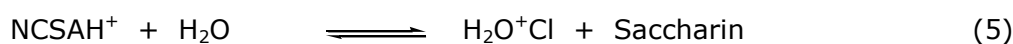
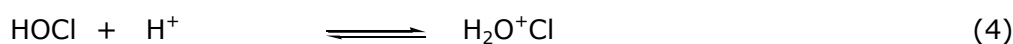


Figure 5. Arrhenius plot.

Table 4. Thermodynamic parameters of malic acid-NCSA system

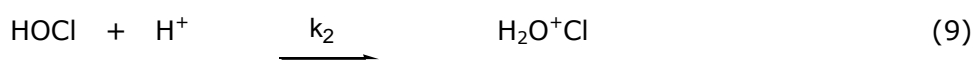
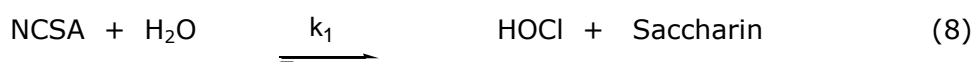
Hydroxy acid	E_a (kJ mol^{-1})	A (s^{-1})	ΔH^* (kJ mol^{-1})	ΔG^* (kJ mol^{-1})	$-\Delta S^*$ ($\text{JK}^{-1} \text{mol}^{-1}$)
Malic acid	68.359	6.745	64.060	89.668	0.813
	± 0.677	$\pm 0.671 \times 10^7$	± 0.599	± 0.433	± 0.006

The choice of species actively participated in initiation of the oxidation can be

explained on the basis of the following kinetic results as:

- (a) The retardation trend observed in reaction velocity, when the reduction product of oxidant, i.e. saccharin, is added. That is ruled out NCSA as an active oxidant species;
- (b) The large negative reaction constant suggest a high carbocationic reaction centre exist this eliminates the possibility of Cl^+ as a reactive species;
- (c) The possibility of CH_3COOCl and $\text{CH}_3\text{COO}^+\text{HCl}$, the acetate complex of NCSA (equations 6 and 7) may also be ruled out as inhibition in the rate of oxidation was observed with an increase in the percentage composition of CH_3COOH and H_2O . Kinetically it is not possible to, distinguish equation (1) and (4) from equation (5);
- (d) NCSA and HOCl undergo protonation in the presence of HClO_4 (equation 1, 4) which inhibit the rate of oxidation and therefore clearly ruling out that these cannot be assumed as the remote profile reacting species. The derecognition of activities is also due to the fact that H^+ does not involve in transformation of NCSA;
- (e) Thus the only choice and possibility is left that HOCl or $\text{H}_2\text{O}^+\text{Cl}$ [20] is a remote and prime active species.

Mechanistic paths involve the electrophillic attack of remote prime species of HOCl or $\text{H}_2\text{O}^+\text{Cl}$ on malic acid. On the basis of results the following oxidation kinetic mechanistic reaction scheme for malic acid-NCSA system is proposed.



On the basis of the aforementioned steps involved in the proposed mechanism and at steady state approximation condition, the final rate law is derived as:

$$k_{\text{obs}}^{-1} = \frac{1}{[\text{HA}]} \left[\frac{[\text{S}]}{k_1 K_1 K_3} + \frac{1}{k_1 K_3} + \frac{K_2 [\text{H}^+]}{k_1 K_3} \right] + \frac{1}{k_4} \quad (12)$$

According to the equation (12), a plot of k_{obs}^{-1} against $[HA]^{-1}$ (double reciprocal) should give a straight line with a positive intercept at y-axis. This supports the validity of the rate law (12) and hence confirms the proposed complex reaction mechanism.

Conclusion

The kinetic results and thermodynamic parameters support the C-C bond fission in the rate determining step. The flip of C-H bond is actually not involved in the rate determining step due to loss of translation and rotational freedom in the process. The mechanism involving C-C fission in the system is further supported by Bakore et al. [21].

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