"Mechanism of α-Crotonic Acid towards N-Chlorosaccharin Oxidation"

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Abstract: ***The oxidative study of α-crotonic acid in aqueous acetic acid by N-chlorosaccharin resulted in the formation of hydroxy aldehyde. The mechanism involving α-C-H fission from substrate to oxidant via an intermediate complex in rate determining step is discussed. The effect of dielectric constant of the medium indicates the rection to be of ion-dipole type. The reaction is first-order in [NCSA] and fractional-order to [H$^+$]. Various kinetic and thermodynamic parameters were determined.***

Key words: Crotonic acid, N-chlorosaccharin, rate constant, oxidation, kinetics.

1. INTRODUCTION

A variety of halo-oxidant [1-7] have proved to be useful reagents capable of oxidizing almost every oxidisable function group. NCSA has been developed to improve the selectivity of organic compounds and as a positive source of halogen for last few decades N-chlorosaccharin has been reported as a new, mild eco-friendly halo-oxidant. This is more efficient for quantitative oxidation aspects of several organic substrates such as alcohol,[8] aldehydes, [9] hydroxy acids, [10] ketones, [11] paracetamol[12] etc. The kinetics and mechanism of oxidation of unsaturated acids by several oxidants[13-15] have been earlier reported. It has certain advantages over analogous oxidants in terms of the quantity of oxidant, and solvent required, short reaction times and high yields available in the literature. There seems to be no reports on the oxidation of crotonic acid aspects of NCSA are available or documented.
The main aims of the present investigation are to determine kinetic parameters, deduce rate law, and to postulate the suitable mechanism for the oxidation process.

2. EXPERIMENTAL

Materials : N-chlorosaccharin (Across) commercial sample's was purified and its appropriate amount is dissolved in acetic acid (E. Merck) fractionally distilled (118^{0}C) and standardized [16] by an iodometric determinations. The solution of crotonic acid A.G. grade (Across) was prepared by a suggested method.[17] All solutions of reagents were prepared in twice distilled water and were standardized by their usual methods.[18]

Kinetic measurements

The pseudo first-order conditions were attained by maintaining an excess (×10 or more) of [crotonic acid] over [NCSA]. The solvent was CH_3COOH unless mentioned otherwise. The reaction was carried out in blackened flasks from the outside to save any photochemical reactions. The reaction was carried out in a water-bath (± 0.1 K) at pre-set conditions and was followed upto 80% to 85% of the extent of reaction, by monitoring the decrease in [NCSA]. The rate constant (k_{obs}) was computed from the integration method by slopes of plots of log [NCSA] versus time. Duplicate runs showed that k_{obs} were reproducible ± 3%.

Stoichiometry and product analysis

The stoichiometry study for the oxidation of α-crotonic acid by NCSA was carried out with oxidant in excess. The concentration of unreacted NCSA was determined. The reaction exhibited a 1:1 mole ratio. The stoichiometric analysis showed that the overall rection.

The oxidation product led to the formation of hydroxy aldehyde characterized by spot test and qualitative and quantitative analysis[13] (Loc. cit.) (2:4 DNP derivatives).

A one - electron oxidation giving rise to free radicals is unlikely because acrylonitrile and butylated hydroxy toluene (B.H.T.) failed to produce any effect on rate of oxidation .

4. Results and Discussion

The mechanism, rate laws and other observed kinetic parameters were determined for the NCSA- α-crotonic acid probe. The results are interpreted here. The kinetics oxidation of α-crotonic acid by NCSA was studied at 313 K in aqueous acetic acid medium. The reaction was of first-order with respect to [NCSA]. Further more, the values of k_{obs} were independent of the initial [NCSA].
The existence of complex was established in the study of effect of α-crotonic acid by NCSA. The -dc/dt of α-crotonic acid initially linearly increases but slightly deviates and takes the shape of curvature plot of k vs. [crotonic acid] (Fig.1) at its higher concentrations under experimental conditions (Table 1). The Michaelis-Menten type of kinetics plot $1/k_{obs}$ vs. 1/[α-crotonic acid] yields non-zero intercept on ordinate axis is also supporting evidence for formation of complex.

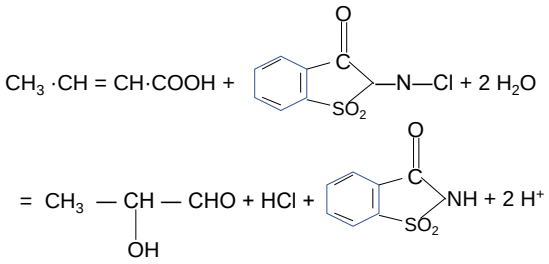


Table 1: Dependence rate on α-crotonic acid at 313 K

10^3 [NCSA] = 3.33 ×10^{-3} (mol dm^{-3}); Ac-H_2O = 40 %, (v/v)

10^2× [α-crotonic] (mol dm^{-3})	← 10^4 k (s^{-1}) →
0.80	1.73
1.25	2.65
2.00	3.80
2.50	4.40
3.33	4.93
4.00	5.26
5.00	5.62

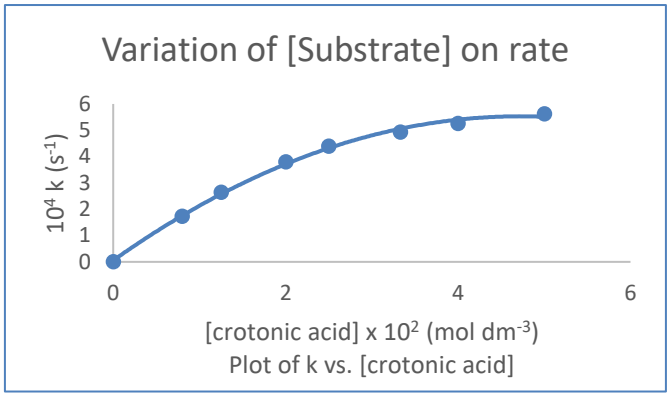


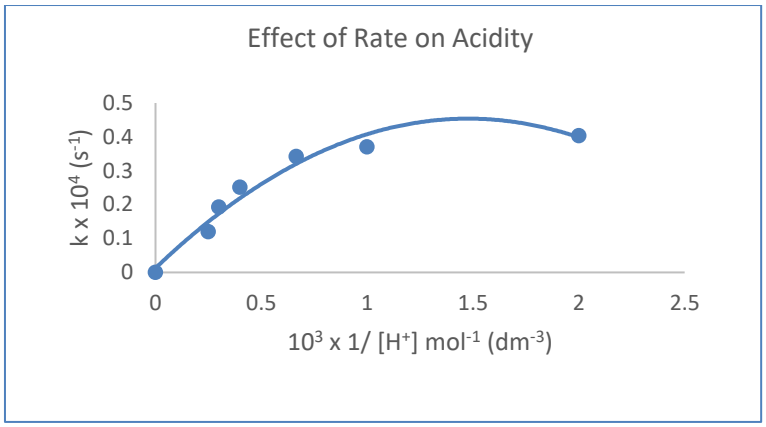
Fig. 1 [NCSA] = 3.33 ×10^{-3} (mol dm^{-3}) ;
Ac-OH-H_2O = 40 % (v/v) ; Temp. = 313 K

The reaction is not sensitized by varying concentration (5X or greater) of mineral acid (Table 2). The non-linear plots of k vs. 1/ [H^+] results a curvature type (Fig. 2). The rate of reaction retards by raising the concentration of [H^+] indicating fraction-order kinetics with respect to [H^+].

Table 2: Dependence of rate on Acidity at 313 K

[α-crotonic acid] = 1.25 ×10^{-2} (mol dm^{-3}); [NCSA] = 3.33 ×10^{-3} (mol dm^{-3});
Ac-H_2O = 40 %, (v/v)

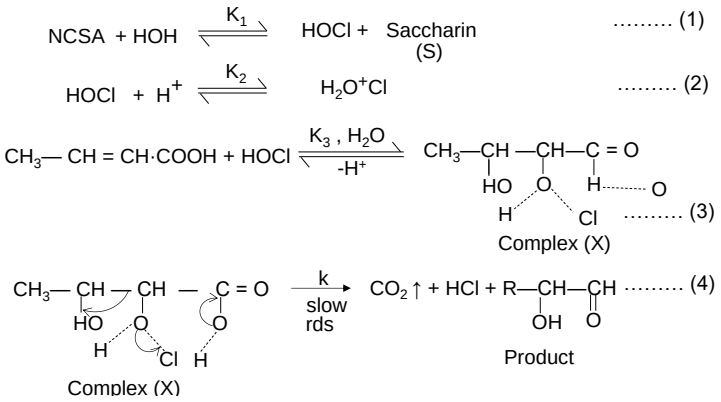
[H^+]× 10^{-2} (mol dm^{-3})	← 10^4 k (s^{-1}) →
0.50	2.54
1.00	2.35
1.50	2.20
2.50	1.79
3.33	1.56
4.00	1.32



Plot of k vs. 1 / [H^+]
Fig. 2 [α-crotonic acid] = 1.25×10^{-2} (mol dm^{-3}) ;
[NCSA] = 3.33×10^{-3} (mol dm^{-3}) ;
Ac-OH-H_2O = 40% (v/v) ; Temp. = 313 K

The effect from solvent composition of the reaction rate was estimated. The rate of oxidation increases markedly with the rise in the proportion of acetic acid in the medium at pre-set conditions. The solvent effect supports Amis plot and decrease in dielectric constant of the medium i.e. an increase in the acetic acid content. This indicates that the reaction involves a cation dipole type interaction in the rate determining step.
The ionic strength of the medium (μ), primary salt effect, and saccharin, a reductant product of oxidant (NCSA) did not bring out any appropriate change in reaction rate.
The most reactive species of N-chlorosaccharin (oxidant) was assigned HOCl in light of observation of several kinetic results.

Mechanism
Under the employed experimental conditions in the present study, and considering various kinetic parameters taken in account, the mechanism may be postulated as :



Since, $[Complex\ (X)] = \frac{K_1 K_3 [Substrate][NCSA]}{[SAc.]}$ …….(6)
Applying steady-state approximation, the rate expression can be obtained as :

$$k_{obs} = \frac{k\ K_1 K_3\ [Substrate]}{[Sac.] + K_1 + K_1 K_2 [H^+] + K_1 K_3\ [Substrate]} \quad \ldots.(7)$$

Transforming equation (7) as to equation (8), we get

$$k_{obs}^{-1} = \frac{1}{k_1 K_3 [Substrate]} \left\{ \frac{[Sac.]}{K_1} + 1 + K_2 [H^+] + \frac{1}{K_1} \right\} \quad \ldots.(8)$$

The Equation (8) discounts the possibility of one-electron oxidation. The observed solvent effect supports a transition state which is more polar than the reactant state. The study reveals that Michaelis-Menten type kinetics is existed in the system.
The thermodynamic parameters such as Ea, $\Delta H^{\#}$, $\Delta G^{\#}$ and entropy of activation ($\Delta S^{\#}$) were measured.

Conclusion

The results of solvent effects show that the lowering of dielectric constant of the medium accelerates the reaction rate significantly. The reaction does not induce polymerization rules out the presence of free radical intermediate in the oxidation of stoichiometrically 1:1 mole ratio. The cleavage of α-C-H bond occurs in laid down mechanism. The rection was found first-order with respect to oxidant [NCSA] and fractional-order each in [α-crotonic acid] and [H^+].

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Conflict of Interest
The authors declare conflict of no interest whatsoever.

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