

Oxidation of Some Unsaturated Acids Using N-Chlorosaccharin in Aqueous Acetic Acid Medium - A Kinetic Approach

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Abstract: The oxidation of acrylic acid and cinnamic acid by N-chlorosaccharin (NCSA) in aqueous acetic acid medium under first-order kinetic conditions to the halo-oxidant was discussed. The oxidation was monitored by titrimetric estimation of the unreacted oxidant at regular intervals in the temperature range 308-328 K. The unsaturated acids reaction with NCSA in 1:1 mole ratio yielding the products of oxidation as hydroxy aldehydes. However, Michaelis-Menten type kinetics were observed with respect to substrates. The thermodynamic activation parameters and rate law have been interpreted as the molecular dynamics and reaction mechanism suggested for the oxidation process. Based on kinetic parameters the sequence of rates of unsaturated acids have been explained.

Key words: N-chlorosaccharin, acrylic acid, cinnamic acid, oxidation, kinetics.

1. INTRODUCTION

The quantitative transformation of unsaturated acids to the corresponding aldehydes/ ketones has been kinetically exhaustively reported earlier in literature^[1-3] by different oxidants (CAT, NBIN, and MTBPA). The unsaturated acids are very useful in polymer industry, bio-technology and in synthesis of organometallic compounds. N-chlorosaccharin has long been known,^[4] and subsequently several papers have appeared on the oxidation of hydroxy acids,^[5,6] aldehydes,^[7] ketones,^[8] alcohol,^[9] paracetamol and phenolic compounds.^[10] Nevertheless, a systematic kinetics study of the oxidation of unsaturated compounds by NCSA has not been made so far and work appears to be incomplete in many respects.

Herein, we report the kinetic and thermodynamic aspects of oxidation of industrially important acids such as acrylic acid and cinnamic acid by halo-oxidant (N-chlorosaccharin) in aqueous acetic acid medium. The sequence of oxidation rates has been interpreted in term of steric, structural characteristics of the unsaturated acids.

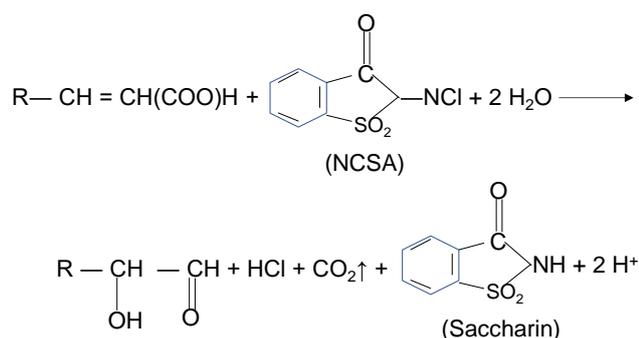
2. EXPERIMENTAL

Materials : The unsaturated acids were of A.G. grade (Across), obtained and distilled before use. NCSA (Across) commercial sample (weighed) was used directly by preparing its solution in 80% in acetic acid (E. Merck). The concentration of its solution was determined analytically.^[11] All other chemicals and reagents used were of A.R. analytical grade.

The oxidation of unsaturated acids was investigated under first-order [oxidant] \ll [acid]. The solutions of acid and oxidant in required amount were allowed to equilibrate in a earlier adjusted thermostat with an accuracy ± 10.1 K. After the temperature equilibrium was attained, both the solutions were mixed to start the reaction. Aliquots of the reaction mixture were withdrawn at regular time intervals and the unreacted oxidant (NCSA) was estimate iodometrically. The reaction velocity (k_{obs}) were evaluated from the linear plots of log [unreacted, NCSA] versus time.

Stoichiometry

The stoichiometry of the reactions were determined by taking a known excess of [NCSA] over [unsaturated acids]. The stoichiometry observed were identical and it could be represented as :



where, R = -H and -C₆H₅ for acrylic acid and cinnamic acid respectively.

The oxidation products were corresponding hydroxy aldehydes,^[12] identified by their characteristics spot test^[13] and transforming into 2,4-DNP derivatives.^[14]

The oxidation of unsaturated acids by NCSA, in a stream of nitrogen, completely failed to induce polymerization of acrylonitrile / BHT (butylated hydroxy toluene), which was recorded unchanged almost quantitatively.

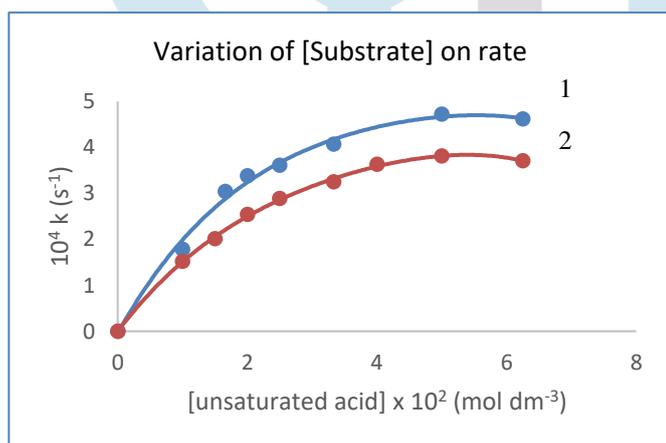
4. Results and Discussion

The rate laws and other experimental data were determined for all the unsaturated acids investigated, The results are reported here. **NCSA (N-chlorosaccharin) dependence** : The oxidations of the unsaturated acids were performed under pseudo first-order concentrations with [substrates] have been 5X higher than that of [NCSA]. Analysis of the data shows the order with respect to [NCSA] oxidant is unity. Plots of log [NCSA] versus time were linear even upto 80% conversion of [NCSA]. The order with respect to unsaturated acids was less than one (Table 1). The plots of k_{obs} versus [UA] a downward curvature, showing existence of a complex (Fig. 1). This is further confirmed by Michaelis-Menten type kinetics and becomes the base for postulation of mechanism and rate law.

Table 1: Dependence of rate on oxidation of unsaturated acids by NCSA

$10^3 \times [\text{NCSA}] \text{ (mol dm}^{-3}\text{)} = 3.33 \text{ (1, 2)}$; $\text{CH}_3\text{COOH-H}_2\text{O} \%$, (v/v) = 25 (1), 40 (2) ; Temperature K = 313 (1), 318 (2)

[Substrate] × 10 ³ (mol dm ⁻³)	← 10 ⁴ k (s ⁻¹) →	
	Acrylic acid (1)	Cinnamic acid (2)
1.00	1.78	1.52
1.50	-	2.01
1.66	3.04	-
2.00	3.38	2.54
2.50	3.61	2.89
3.33	4.07	3.25
4.00	-	3.63
5.00	4.72	3.81
6.25	4.62	3.71



$[\text{NCSA}] \times 10^3 \text{ (mol dm}^{-3}\text{)} = 3.33 \text{ (1, 2)}$;
 $\text{CH}_3\text{COOH-H}_2\text{O} \%$ (v/v) = 25(1), 40 (2) ;
 Temperature K = 313 (1), 318 (2)

Hydrogen-ion Dependence : The H^+ ion concentration was varied with H_2SO_4 at constant ionic strength adjusted to KCl. The rate decreases with increasing $[H^+]$ (Table 2). The plots of k vs. $[H^+]^{-1}$ were linear with varying intercepts and slopes (Fig.2) for different ranges of substrates. This shows that the order is less than 1 for $[H^+]$.

Table 2: Dependence of k_{obs} on $[H^+]$

$10^3 \times [NCSA]$ (mol dm^{-3}) = 3.33(1,2); $10^2 \times [\text{unsaturated acid}]$ (mol dm^{-3}) = 1.66(1), 2.0 (2) ;
 $CH_3COOH-H_2O$ %, (v/v) = 25 (1), 40 (2) ; Temperature K = 313 (1), 318 (2)

$[H^+] \times 10^{-3}$ (mol dm^{-3})	$10^4 k_{obs.} (s^{-1})$	
	Acrylic acid (1)	Cinnamic acid (2)
0.50	2.92	-
1.00	-	2.10
1.50	-	1.95
1.66	2.65	-
2.00	2.60	2.71
2.50	2.54	1.53
3.33	-	1.24
4.00	-	0.92
5.00	1.70	0.51

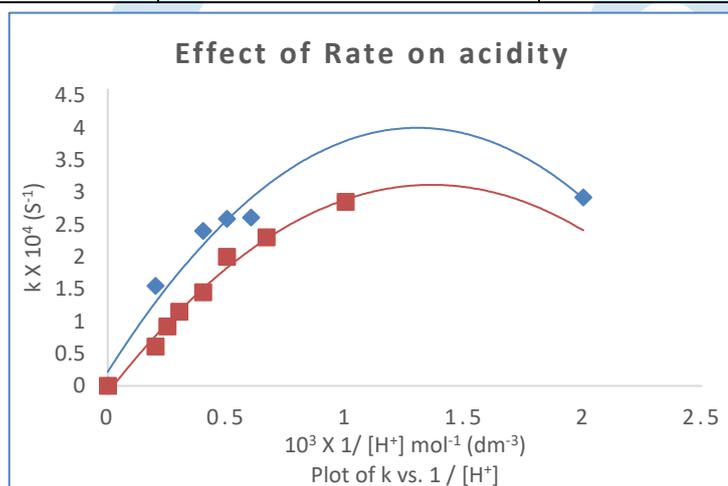


Fig. 2 $10^3 \times [NCSA]$ (mol dm^{-3}) = 3.33 (1,2);
 $10^2 \times [\text{unsaturated acid}]$ (mol dm^{-3}) = 1.66(1), 2.0 (2) ;
 $CH_3COOH-H_2O$ %, (v/v) = 25 (1), 40 (2) ;
 Temperature K = 313 (1), 318 (2)

There was no reaction with the chosen solvents. The kinetics were similar in the solvent taken for investigation. The k_{obs} was noticed to increase within 10% to 50% (v/v) range of acetic acid at earlier set condition. The Amis plots (log k vs. $1/D$) found linear with positive slopes shows polar transition states are involved in the system. The rate of oxidation was not influenced by primary salt and no more changes were noticed by successive addition of saccharin to NCSA-unsaturated acid system.

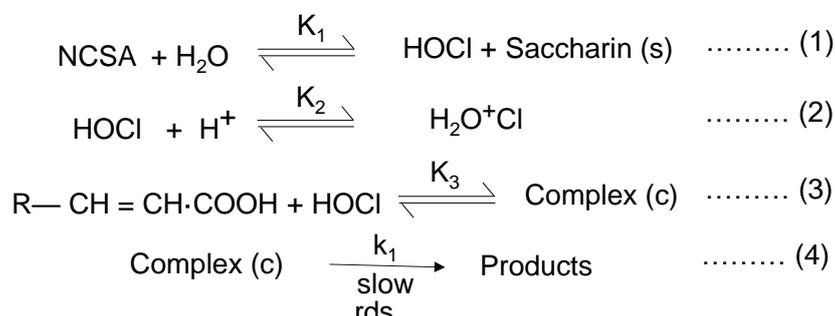
The most useful responsible profile of reacting species of oxidant (NCSA), was HOCl judged based on kinetic observation.

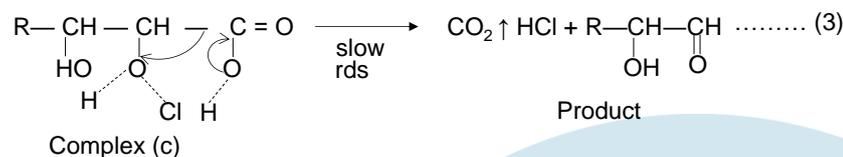
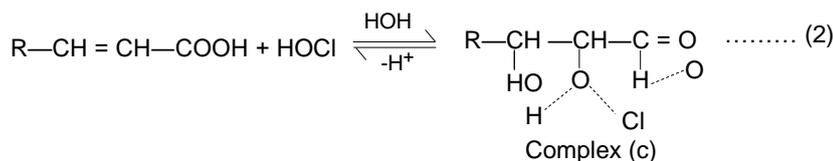
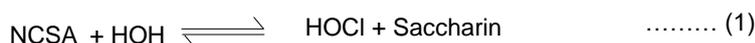
Mechanism

The mechanism based on postulated HOCl reacting species is realistic in accounting for many of the observed kinetic data may be proposed as :

Rate law

The rate expression can be deduced as :





$$\text{Rate} = k_1[\text{Complex } (C_1)] \quad \dots (5)$$

$$\therefore [\text{Complex } (c)] = K_1 K_3 \frac{[\text{Substrate}][\text{NCSA}]}{[\text{Saccharin}]} \quad \dots (6)$$

At steady-state condition, the final rate law observes as :

$$k_{obs} = \frac{k_1 K_1 K_3 [\text{Substrate}]}{[\text{Sacc}] + K_1 + K_1 K_2 [\text{H}^+] + K_1 K_3 [\text{Substrate}]} \quad \dots (7)$$

writing equation (7) in inverse form as equation (8)

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

Equation (8) explains complex features of the reaction.

The comparative account of the reactions follow the sequence

Acrylic acid > Cinnamic acid

The rate suggesting that transition state must be electron deficient. The bulky design -C₆H₅ (phenyl) group showing inductive effect. The activation energy (E_a) is lowest for fastest reaction rate and vice-versa (Table 3). The entropy of activation (-ΔS[#]) is negative for all the substrates leads polar nature of the transition state to the immobilization of solvent molecules around the charged ends which causes loss of (ΔS[#]) i.e. reduces transition and rotational degree of freedom of the complex. Due to strain the cinnamic acid with bulky design of molecule will experience high ground state energy and observed decrease in ΔH[#] [15] from acrylic acid to cinnamic indicate that transition state has the same (ΔH[#]) for the unsaturated acids studied. The bulky group creates hindrance in the reaction, consequently, ΔS[#] value increases for cinnamic acid. The close values of ΔG[#] for acrylic acid and cinnamic acid suggests that an identical mechanism is prevailing in them. Assessing all the above cited points, it was found that reactions are enthalpy (ΔH[#]) controlled.

Table 3. Thermodynamic parameters for the oxidation of unsaturated acids by N-chlorosaccharins

Substrate	E _a kJ/mol ⁻¹	ΔH [#] kJ mol ⁻¹	ΔG [#] kJ mol ⁻¹	-ΔS [#] JK ⁻¹ mol ⁻¹
Acrylic acid (HCH=CH·COOH)	60.56	57.00	87.46	96.57
Cinnamic acid (C ₆ H ₅ CH=CH·OOH)	63.89	61.29	89.85	89.17

Conclusion

The reactions exhibited Michaelis-Menten type kinetics with polar nature of transition state. The reactions are first-order to oxidant and fractional-order kinetics each with [H⁺] and substrates only. HOCl species of NCSA is proposed to the reacting species with stoichiometric mole ratio 1:1. An α-C-H bond fission is caused in the rate determining step. The decomposition of complex produced hydroxy aldehydes as oxidation products.

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Conflict of Interest

The authors declare conflict of no interest whatsoever.

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