Study on Oxidative Degradation of Unsaturated Acids by N-chloroisonicotinamide

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Abstract

The corresponding aldehydes products were obtained when N-chloroisonicotinamide is reduced by unsaturated acids (α-crotonic acid and cinnamic acid) stoichiometrically (1:2) under nitrogen atmosphere. The reaction is believed to be initiated by formation of complex at transition state. The rate of reaction exhibits fractional-order kinetics with respect to acid. The involvement of a non-free radical process is believed to be indicated by the formation of polymer during the oxidation of unsaturated acids. The proposed mechanism was supported by derived rate law and activation parameters.

Keywords: α-crotonic Acid, Cinnamic Acid, N-chloroisonicotinamide, Oxidative Degradation

1. Introduction

The unsaturated acids (aliphatic and aromatic) contain carboxylic functional group with double bond play an important role in several bio-chemical processes[1] occurring particularly in cellular respiration cell has received considerable attention and of academic importance. A very few reports on oxidations of unsaturated carboxylic acids[2-6] are available in literature before four to five decades. More recently however, it has become common to carryout catalysed and uncatalyzed methyltributylammonium permanganate oxidation[7] and other halo-oxidants such as chloramine-T[8] and NBIN[9] with the aid of phase transfer agents in aqueous and non-aqueous solvents.[10] Despite this useful procedure, practically no mechanistic information available with respect to the oxidation of α-crotonic acid and cinnamic acid with N-chloroisonicotinamide. Although in a closely related reaction, the oxidation of few compounds has been made.[11-13]

2. Experimental

The oxidizing agent, N-chloroisonicotinamide (NCIN) was synthesized[11] (Loc. cit.) and solution was prepared by dissolving its requisite quantity in 100% glacial acetic acid (B.D.H.). because of its instability, its standardized solution was stored in the dark at low temperature. The reducing agents were obtained commercially and purified by either fractional distillation or crystallization. The solutions of cinnamic acid and crotonic acid both transform were prepared according to the procedure as laid down in literature.[14] All others required solutions of related chemicals were made in double distilled water.

Procedure

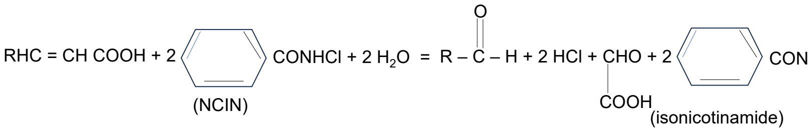
The kinetic experiments were all carried out in under pseudo first-order condition [substrate] >> [oxidant]. In a typical experiment, a 50 ml volumetric flask containing a solution of substrate in aqueous acetic acid was held for about 30 minutes in a thermostated bath at 40° C while in another flask, the oxidant solution of appropriate amount was kept.

The NCIN was then added and solution vigorously stirred until homogeneous. About 2 ml of the aliquot was immediately transferred to a titrating flask and kinetic results were periodically recorded until the reaction was complete.

The reaction rates were followed by measuring the concentration of NCIN left after regular intervals of time by means of a iodometric technique in a thermostated bath (± 0.1 K). The pseudo first-order rate constants were obtained from the slopes of log (a-x) vs. time plots.

Stoichiometry

Several determinations of the stoichiometry of the reactions iodometrically conform in equation (1), could therefore account for the observed mechanism :



..... (1)

Where, R = CH_3– and C_6H_5– for α-crotonic acid and cinnamic acid respectively.

The final products obtained from the reduction of NCIN by unsaturated acids in reaction solution are aldehydes (CH_3CHO and C_6H_5CHO) which were analyzed by spectroscopic, chemical, and chromatographic methods and also by forming their 2:4-DNP derivatives.

4. Results and Discussion

Plots of ln (a-x) vs. time are linear thus indicating of the reaction rates are first-order with respect to oxidizing reagent. This was confirmed by measuring the initial rates of oxidation of α-crotonic acid and cinnamic acid at several NCIN concentrations (Table 1). The initial rates are proportional to the initial [NCIN] (Figure 1).

Table 1: Dependence of the Initial Rate for the N-chloroisonicotinamide Concentration

10^3 × [NCIN] mol dm^{-3} = 2.00 (1, 2); 10^2 × [substrate] mol dm^{-3} = 3.33 (1, 2);
CH_3COOH-H_2O %, (v/v) = 40 (1), 50 (2); Temperature = 40° C (1, 2)

Time (sec.)	α-crotonic Acid (a-x)	Cinnamic Acid (a-x)
0	4.00	4.00
600	3.10	-
900	-	3.30
1200	2.40	-
1800	1.90	2.65
2400	1.40	-
2700	-	2.15

Time (sec.)	α-crotonic Acid (a-x)	Cinnamic Acid (a-x)
3000	1.15	-
3600	0.90	1.80
4200	0.70	-
4500	-	1.40
5400	-	1.15
6300	-	0.95

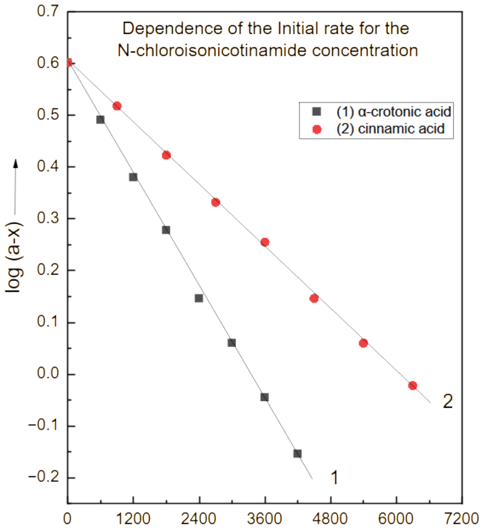


Fig. 1

Plot of log (a-x) vs. time

10^3 x [NCIN] (mol dm^{-3}) = 3.33 (1, 2) ;
10^2 x [substrate] (mol dm^{-3}) = 2.00 (1, 2) ;
CH_3COOH-H_2O = 40 (1), 50 (2) ;
Temperature ^{0}C = 40 (1, 2)

The dependence of reaction rate on reductant's concentration showed fractional-order kinetics. The values of k_{obs} and k_2 were evaluated (Table 2) from the double reciprocal graphics ($\frac{1}{k_{obs}}$ vs. $\frac{1}{[S]}$ (Figure 2) also established the complexity, nature of the reductants at electron-rich transition state.

Table 2: Dependence of Rate Constants for the Concentration of Unsaturated Acids

10^3 × [NCIN] mol dm^{-3} = 3.33 (1, 2), 4.0 (2); CH_3COOH-H_2O %, (v/v) = 40 (1), 50 (2);
Temperature = 40° C (1, 2)

10^2 × [Substrate] mol dm^{-3} Variant	⟵ k ×10^4 (s^{-1}) ⟶	
	α-crotonic Acid (1)	Cinnamic Acid (2)
1.00	2.52	1.35
1.66	-	1.98
2.00	4.20	2.26
3.33	5.37	3.46

$10^2 \times$ [Substrate] mol dm^{-3} Variant	⟵ $k \times 10^4$ (s^{-1}) ⟶	
	α-crotonic Acid (1)	Cinnamic Acid (2)
4.00	5.74	3.65
5.00	5.80	4.16
6.66	6.06	4.37

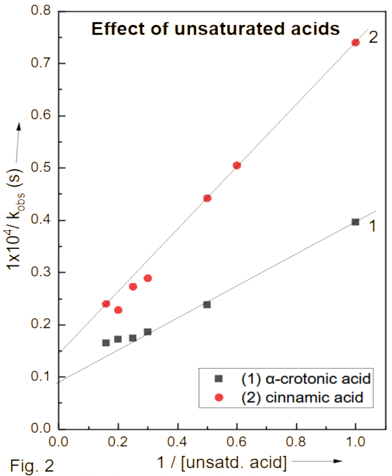


Fig. 2 Reciprocal plot of $1/k_{obs}$ vs. 1 / [S]

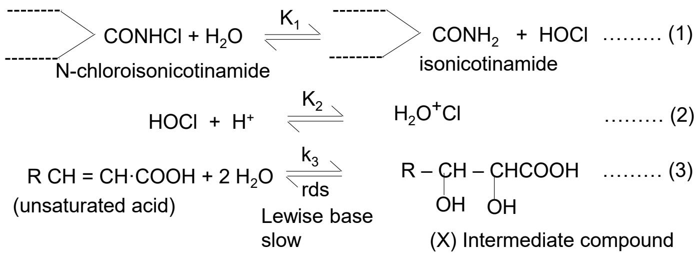
$10^3 \times$[NCIN] mol dm^{-3} = 3.33 (1,2) ;
CH_3COOH-H_2O %, (v/v) = 40 (1), 50 (2) ;
Temperature = 40^0C (1,2)

The results indicate that the reaction is subject to acid catalysis primarily at low [H^+] and order falls 1 to 0 order at its higher concentration. It is instructive to consider possible points in the reaction sequence where acid catalysis could logically occur. The rates of oxidation of both unsaturated acid are accelerated by the increase in percentage composition of acetic acid.[15] The unsaturated acid does not polymerized during the course of these reaction indicates the absence of free radicals. It should be noted that addition of neutral salt such as sodium chloride, does not affect the, rate thus eliminating the possibility of ascribing the suppression in rate caused by NaCl to a salt effect. The inhibition trend in rate was observed by addition of isonicotinamide, a reductant product of oxidant rules out completely being a part of reacting species in the present reaction.

Mechanism

The mechanism for the related reactions are initiated by the formation of a complex in which the double bond is attacked by reacting protonated species H_2O^+Cl.

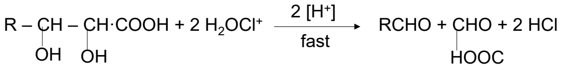
Equation (3) is known to be an important intermediate in these reaction.



$$\text{CONHCl} + H_2O \overset{K_1}{\rightleftharpoons} \text{CONH}_2 + \text{HOCl} \quad \text{.........} (1)$$

$$\text{HOCl} + H^+ \overset{K_2}{\rightleftharpoons} H_2O^+Cl \quad \text{.........} (2)$$

$$\text{R CH = CH·COOH} + 2\,H_2O \underset{\text{rds}}{\overset{k_3}{\rightleftharpoons}} \text{R} - \underset{\text{OH}}{\text{CH}} - \underset{\text{OH}}{\text{CH}}\text{COOH} \quad \text{.........} (3)$$



$$R-\underset{OH}{CH}-\underset{OH}{CH}\cdot COOH + 2\,H_2OCl^+ \xrightarrow[\text{fast}]{2\,[H^+]} RCHO + \underset{HOOC}{CHO} + 2\,HCl \qquad \text{......... (4)}$$

The rate law was derived for slow process as:

$$k_{obs} = K_1 K_2 k_3 [NCIN][S]$$

Transforming equation (5) as

$$[NCIN] \times \frac{1}{k_{obs}} = \frac{1}{K_2 k_3 [S]}$$

Equation (6) apparently accounts for the Michaelis-Menten type kinetic facts.
The order of reactivity was observed as:

α-crotonic acid > cinnamic acid
($CH_3CH=CH\cdot COOH$) ($C_6H_5CH=CH\cdot COOH$)

α-crotonic acid contain CH_3 group with single, double bond shows positive inductive (+I) effect on the other hand cinnamic acid has bulky C_6H_5– group with double bond withdraws the electron, and retards the rate.

The attack of electrophile H_2O^+Cl at C=C in the last step requires cleavage of this bond, consequently, it seems reasonable to consider this last step to be rate-limiting to give aldehydes as the main products. Plots of log k vs. $\frac{1}{T}$ were linear in all cases, and the activation parameters for the oxidation of two typical unsaturated acids are summarized in Table 3.

A highly structured transition state is also consistent with the large negative entropies of activation ($\Delta S^\#$). Activation energy (Ea) is lowest for fastest reaction. The almost close values of ($\Delta G^\#$) points the prevalence of identical mechanism found in them. The reactions are assessed by enthalpy controlled.

Table 3: Activation Parameters for the Oxidation of Unsaturated Acids by NCIN in Aqueous Acetic Acid Medium

Substrate	Ea kJ mol^{-1}	$\Delta H^\#$ kJ mol^{-1}	$\Delta G^\#$ kJ mol^{-1}	$-\Delta S^\#$ JK^{-1} mol^{-1}
α-crotonic Acid	60.48	58.73	87.10	89.92
Cinnamic Acid	64.38	61.45	88.91	85.93

Conclusion

The proposed reaction is proceeded via cleavage of C=C in rate-determining step to yield aldehydes as the main products. The stoichiometry revealed 1:2 mole ratio. The protonated form of NCIN species participate in the reaction. The reaction is first-order in [NCIN] and fractional-order each in [unsaturated acid] and [H^+]. The negative values of entropy of activation provided support for the formation of rigid activated complex.

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Conflict of Interest

The authors declare no conflict of interest whatsoever.

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