

# Phosphotungstic Acid Catalysed Oxidation of Propionaldehyde by N-Chlorosaccharin in Aqueous Acetic Acid Medium Using Spectrophotometer

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## Abstract

Using a spectrophotometer, the kinetics of oxidation of propionaldehyde by N-chlorosaccharin (NCSA) in aqueous acetic acid medium in the presence of phosphotungstic acid were examined. In [NCSA], [PTA], and fractional order to [Et.CHO], the measured rate of oxidation is first order. Acetic acid is the major byproduct of oxidation. The influence of ionic strength on reaction rate is negligible. The effect of increasing the medium's dielectric constant on the rate suggests that the reaction is dipole-dipole. The reactive oxidising species has been proposed to be protonated hypochlorous acid. The mechanism's reaction constants have been calculated. The activation parameters are calculated in terms of the mechanism's slow step. Key words: Propionaldehyde, N-chlorosaccharin, ionic strength, Hypochlorous acid, phosphotungstic acid.

## INTRODUCTION

Despite being more electrophilic than the structurally equivalent N-haloimides,<sup>[1]</sup> N-halosaccharins have received little attention in the literature. Unlike N-iodo<sup>[1,2]</sup> and N-fluorosaccharin<sup>[3]</sup>, N-chloro- and N-bromosaccharin are typically described as analytical<sup>[4,5]</sup> and/or oxidising reagents. These compounds are weak oxidants of aldehydes,<sup>[6,7]</sup> alcohols,<sup>[8,9]</sup> glycols,<sup>[9]</sup> amino-<sup>[10]</sup> and  $\alpha$ -hydroxyacids,<sup>[9]</sup> and other aromatic compounds, and their usage as a halogenating reagent for aromatic compounds<sup>[11,12]</sup> and allylic,<sup>[13]</sup> benzylic,<sup>[13,14]</sup> and  $\alpha$ -carbonylic<sup>[14,15]</sup> positions is highly beneficial. The typical<sup>[16-18]</sup> process for preparing N-chloro- and N-bromosaccharin is the reaction of the sodium salt of saccharin with the halogen, with a few exceptions. However, handling and manipulating hazardous and corrosive halogens on a multigram scale is difficult.

Using a spectrophotometer, we present the oxidation kinetics of Propionaldehyde with N-chlorosaccharin in aqueous acetic acid medium in the presence of phosphotungstic acid as catalyst and alkaline  $\text{KMnO}_4$  as co-oxidant. In recent decades, N-chlorosaccharin, the chloride of orthosulphobenzoic acid, has been used as a potent oxidant for the oxidation of different functional groups. For the first time, the kinetics and mechanistic pathways of phosphotungstic acid catalyzed

Propionaldehyde oxidation by N-chlorosaccharin (NCSA) in aqueous acetic acid medium were investigated in this work.

## **EXPERIMENTAL**

The oxidation of certain aliphatic aldehyde viz. Propionaldehyde by N-chlorosaccharin in the presence of phosphotungstic acid in an aqueous acetic acid solution was investigated kinetically. The optical density was read using a (Elico-CI-157) colorimeter with a uniform transmission scale. Water bath system equipped with relay, heater, and stirrer and regulated by a column thermo regulator was used having accuracy  $\pm 0.01^\circ\text{C}$ . Citizen electronic balance, CX 220 was used for weighing purposes. The least count of balance is 0.0001 mg. All reagents were either of AnalaR or guaranteed reagent grade and used as supplied. Further details regarding their preparations etc. are mentioned in the respective chapters. Doubly distilled water, second distillation being from alkaline potassium permanganate solution in all glass assembly, was employed in all the preparations and kinetic studies.

## **KINETIC MEASUREMENT**

Solutions of the substrate and NCSA of appropriate concentration were prepared in aqueous acetic acid and thermostated for 2 hrs. Un-reacted NCSA was estimated calorimetrically using alkaline  $\text{KMnO}_4$  as co-oxidant. The rate constant of a particular reaction can be determined by measuring Optical density at specific time intervals.

The initial concentrations of the oxidant, substrates, and catalyst used for experimental study were as follows:

Before starting kinetic runs, the reactants were thermostat to attain equilibrium. Required amount of  $\text{HClO}_4$  solution with a micro-pipette was added to a solution of substrate slowly with cooling. NCSA solution was added with proper shaking, with catalyst solution and the absorbance of reaction mixture was measured at different time intervals at 530 nm using aqueous-alkaline potassium permanganate ( $\text{KMnO}_4$ ;  $0.000001 \text{ mol.dm}^{-3}$ ) was as a co-oxidant. The reaction was followed beyond 80% completion. The rate constants ( $k_{\text{obs}}$ ) were determined from the slopes of linear plots of  $\log(\text{O.D.})$  against time (t). Similar procedure was adopted for all remaining substrates.

The kinetic reactions were allowed for more than 70-80% completion of reaction and first order kinetics was observed. The optical density (D) will be substituted for the concentration changes required the rate law. The optical density (D) of a single chemical species in solution related to its concentration by the Beer-Lambert law to measure first order rate law by equation -

$$k = \frac{2.303}{t} \log \frac{D_0}{(D_0 - D_t)}$$

Where,  $D_0$  is the optical density at zero time and,  $D_t$  at is the optical density at time 't'. The rate constants,  $k_{obs}$  were reproducible within  $\pm 5\%$ .

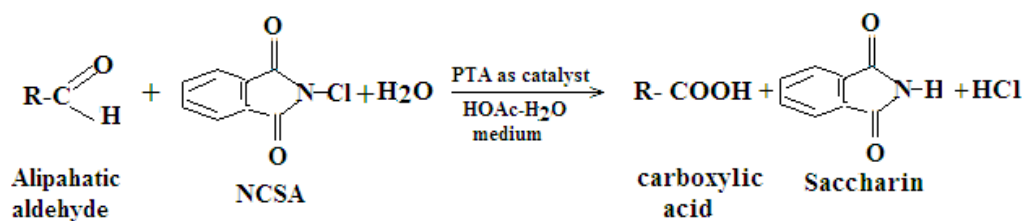
### STOICHIOMETRY AND PRODUCT ANALYSIS

In order to find out the total amount of oxidant consumed by oxidation one mole of substrate, various sets of reaction mixture were taken in which concentration of oxidant was large excess than that of substrate. The entire conical flasks containing the reaction mixture were allowed to stand for several 72Hrs. at room temperature. The NCSA un-reacted in each reaction mixture is, then estimated separately, periodically by titrating against left a definite volume of the reaction mixture iodometrically<sup>19</sup>. Thus, the amount of NCSA used up to oxidize a definite quantity of each substrate is completely amount

calculated. The results are recorded in Table:

[Et.CHO]X10 <sup>3</sup> (mol.dm. <sup>-3</sup> )	Initial [NCSA]X10 <sup>2</sup> (mol.dm. <sup>-3</sup> )	Final [NCSA]X10 <sup>3</sup> (mol.dm. <sup>-3</sup> )	Consumed [NCSA]X10 <sup>3</sup> (mol.dm. <sup>-3</sup> )	Mole ratio $\frac{[NCSA]_{consumed}}{[Et. CHO]}$	From these
1.25	1.25	11.30	1.20	0.96	
2.00	2.00	17.85	2.15	1.07	

stoichiometric data, it is found that for complete oxidation of one mole of substrate one mole of NCSA is required. The stoichiometric equations empirically can be therefore, represented as:



Where, R is standing for CH<sub>3</sub>-CH<sub>2</sub>-, In case of Propionaldehyde,

The end-product of oxidation reaction was identified as propionic acid of PTA catalyzed oxidation reaction Propionaldehyde with NCSA confirmed by analyzing IR spectroscopic spectra as: sp<sup>3</sup> C-H bend (alkane) --- 1480~1430 and 1395~1340 cm<sup>-1</sup>; medium to weak; sharp. sp<sup>3</sup> C-H stretch (alkane) --- 2990~2850 cm<sup>-1</sup>; medium to strong; sharp. C=O stretch (carboxylic acid) --- 1725~1700 (saturated) and 1715~1680 cm<sup>-1</sup> (conjugated); strong; sharp. C-O stretch (carboxylic acid) --- 1300~1000 cm<sup>-1</sup>; strong; sharp. O-H stretch (carboxylic acid) --- 3200~2500 cm<sup>-1</sup>; medium to

weak; broad. These data of IR spectra confirmed the presence of acetic acid as an end -product of PTA catalyzed oxidation reaction Propionaldehyde with NCSA.

## RESULTS AND DISCUSSION

**Effect of oxidant:** The linear plots of  $\log(a-x)$  vs. Time, suggested that the first-order rate dependency with respect to oxidant. The value of first-order rate constant evaluated from the plot is excellently in good agreement with those calculated from first-order rate equation, (Fig.1).

**Effect of substrate:** The reaction rate increased with increase in Et.CHO] Plot of  $k_1$  versus [Et.CHO] initially linear passing through origin at low concentrations but at higher concentrations of substrate it bent to x-axis tends 1 to 0 orders. This confirmed the existence of equilibrium between Propionaldehyde and oxidant (NCSA) and appeared before the slow step (Fig.2, Table: 1).

**Effect of phosphotungstic acid:** The plots of  $k_1$  vs. [PTA] are linear, intercepted at origin (Fig.3), suggesting that the reactions are fully catalyzed by the concentration of PTA.

**Effect of  $HClO_4$ :** it is observed that the reactions are slightly catalyzed (almost negligible) by the concentration of perchloric acid in the presence of phosphotungstic acid.

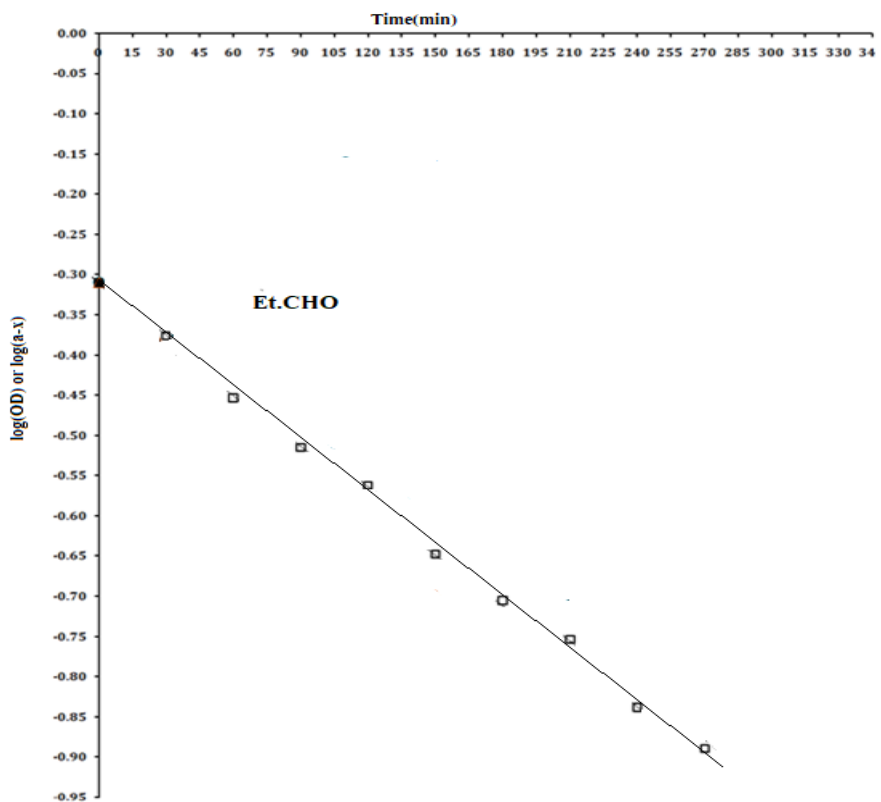
**Effect of solvent composition:** The effect of solvent composition on the reaction rate was studied by varying in concentration of acetic acid from 20-60 %. The rate constants suggest that the rate of reaction slightly (say almost negligible) increases with increasing acetic acid content of the solvent mixture.

**Effect of concentrations of saccharin:** Variation in the added concentrations of saccharin, one of the products of oxidation, had retarded effect on the rate of reaction.

The oxidation reactions of Propionaldehyde with NCSA catalyzed by PTA at different initial concentrations of acrylonitrile have been investigated. The reaction neither induces polymerization nor retards the reaction rate, which may be attributed to the inertness shown by free radicals.

**Reactive Species:** Kinetic data / findings suggested that hydrated form of Propionaldehyde postulated as reacting species of substrate. NCSA like other similar N-halo imides may exist in various forms in acid medium viz. free NCSA, protonated NCSA,  $Cl^+$ , HOCl,  $H_2O^+Cl$ . If  $H_2O^+Cl$  are the reactive oxidizing species, then the rate of reaction should be an inverse function of saccharin (sac) which is observed in the present study. Also the possibility of chlorinating action of chloride is ruled out. The rate constants suggest that the rate of reaction increases with increasing acetic acid content of the solvent mixture. This observation coupled with slight enhancement in the reaction rate with ionic strength of the medium also supports the participation of one ionic species in the rate determining step. Therefore  $H_2O^+Cl$  are the probable oxidizing species under the present experimental condition. The proton released during the reaction by PTA alter sufficient reaction rate but are responsible for

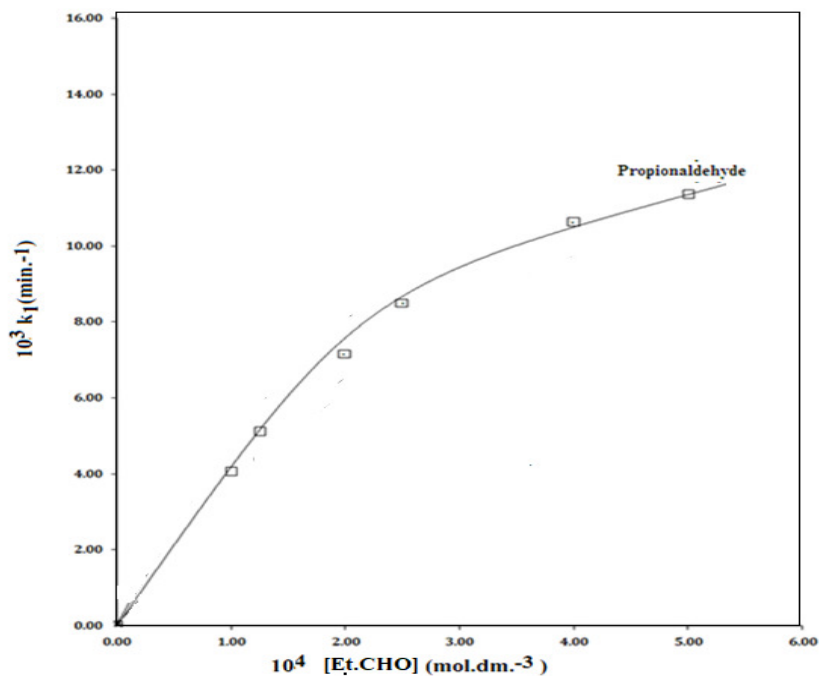
protonation of HOCl, Protonated  $H_2O^+Cl$ . are involved in reaction mechanism which may be attributed to the slightly positive effect of variation of mineral acid on the reaction rate<sup>13</sup>.



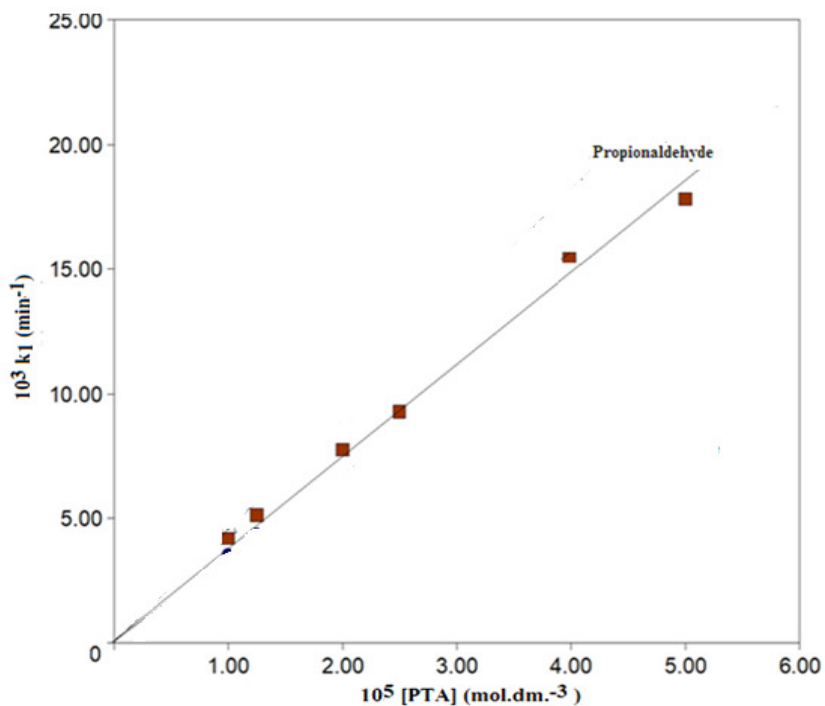
**Fig. 1: Rate dependence on initial concentrations of oxidant (NCSA);**

**Plot had been drowning at experimental conditions are:**

$[NCSA]=0.000025(\text{mol.dm}^{-3})$ ,  $[Et.CHO] = 0.000125 (\text{mol.dm}^{-3})$ ,  $[PTA] =0.0000125(\text{mol.dm}^{-3})$ ,  
 $HOAc-H_2O= 30 \%(v/v)$ , Temp. 308K



**Fig.2: plot drawn at experimental condition as:**  
 [NCSA]=0.000025(mol.dm.<sup>-3</sup>),  
 [PTA]=0.0000125(mol.dm.<sup>-3</sup>), HOAc-H<sub>2</sub>O= 30 % ( v/v), Temp. 308K.



**Fig.3: plot drawn at experimental condition as:**  
 [NCSA]=0.000025(mol.dm.<sup>-3</sup>), [Et.CHO] = 0.000125 (mol.dm.<sup>-3</sup>).

[HOAc-H<sub>2</sub>O= 30 % (v/v), Temp. 308K

**Table: 1**

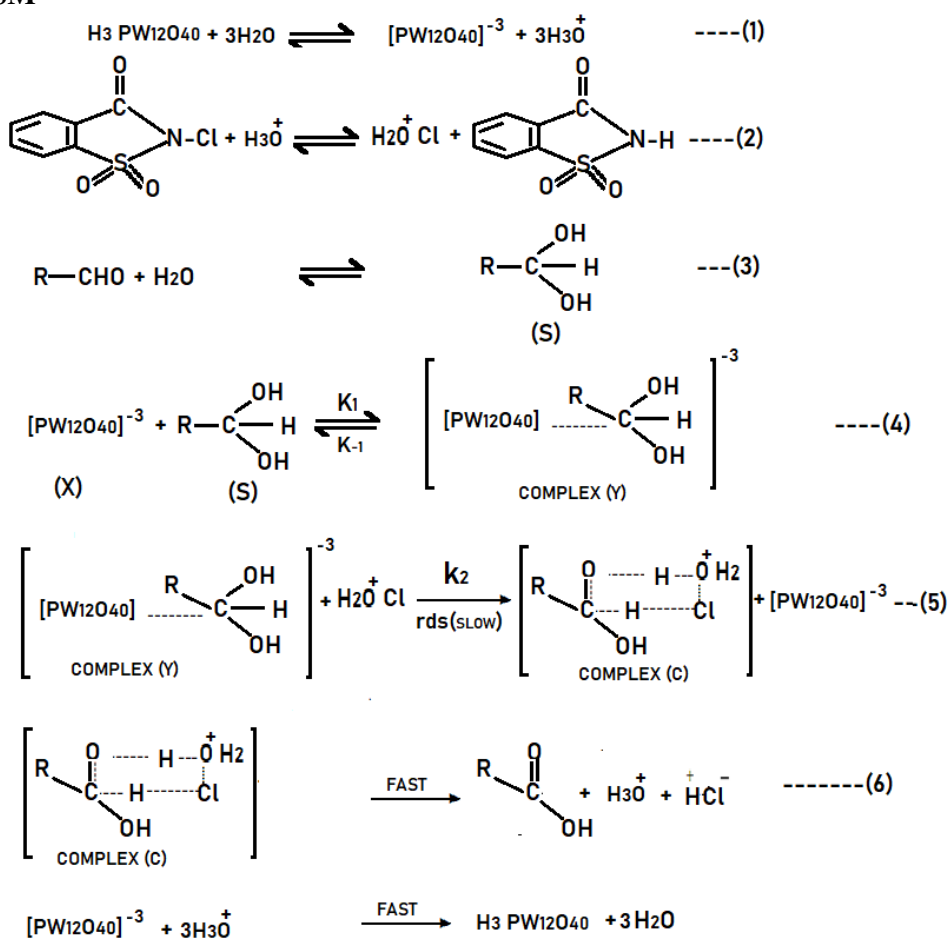
**Rate of oxidation reaction dependency on the varying in the concentrations of Propionaldehyde**

NCSA]=0.000025(mol.dm.<sup>-3</sup>),

[PTA]= 0.0000125 (mol.dm.<sup>-3</sup>), HOAc-H<sub>2</sub>O= 30 % (v/v), Temp. 308K.

[Et.CHO] (mol.dm. <sup>-3</sup> )	$10^3 k_1 (\text{min}^{-1})$
0.000100	4.26
0.000125	5.11
0.000200	6.56
0.000250	6.92
0.000400	8.10
0.000500	8.36

**MECHANISM**



Where R is standing for CH<sub>3</sub>CH<sub>2</sub>- (Et )

**RATE LAW:**

The reaction rate in term of consumption of concentration of reaction during species H<sub>2</sub>O<sup>+</sup>Cl of oxidant (NCSA) may be expressed as:

$$-\frac{d}{dt} [H_2O^+Cl] = k_2[Y] \text{ --- (7)}$$

Applying steady state treatment to the concentration of [Y], we can determine the concentration of [Y] as;

$$\frac{d[Y]}{dt} = K_1[X][S] - K_{-1}[Y] - k_2[Y] = 0 \text{ --- (8)}$$

Or,

$$[Y] = K_{-1} + k_2 = K_1[X][S] \text{ --- (9)}$$

Or,

$$[Y] = \frac{K_1[X][S]}{K_{-1} + k_2} \text{ --- (10)}$$

On substituting the value of [Y] in equation (7) we get-

$$-\frac{d}{dt} [H_2O^+Cl] = \frac{k_2 K_1[X][S]}{(K_{-1} + k_2)} \text{ --- (11)}$$

$$[X]_T = [X] \left( 1 + \frac{K_1[S]}{(K_{-1} + k_2)} \right) \text{ --- (12)}$$

$$[X]_T = \frac{[X] + K_1[X][S]}{(K_{-1} + k_2)} \text{ --- (13)}$$

$$[X] = \frac{[X]_T + (K_{-1} + k_2)}{(K_{-1} + k_2) + K_1[S]} \text{ --- (14)}$$

On comparing equation (11) and (14) we get as:

$$-\frac{d}{dt} [H_2O^+Cl] = \frac{k_2 K_1 [X]_T [S] \{K_{-1} + k_2\}}{\{K_{-1} + k_2\} (K_{-1} + k_2) + K_1 [S]} \text{ --- (14)}$$

$$-\frac{d}{dt} [H_2O^+Cl] = \frac{k_2 K_1 [X]_T [S]}{(K_{-1} + k_2) + K_1 [S]} \text{ --- (15)}$$

On assuming  $k_2 \gg K_{-1} + K_1[S]$

The neglecting the second term in the equation (14) we get-

$$-\frac{d}{dt} [H_2O^+Cl] = k_2 [X]_T [S] \text{ --- (16)}$$

$$k_{obs.} = k_2 [X]_T [S] \text{ --- (17)}$$

Above rate equation (17) explain all the facts of chemical kinetics observed experimentally.

## CONCLUSIONS

The complexing capability of catalyst PTA was explained. The complex nature of Propionaldehyde was discussed. The stoichiometric ratio of substrate to oxidant (1:1) was observed in the reaction kinetics. Oxidation product as acetic acid was isolated. Arrhenius plot has been discussed. In addition to order thermodynamic parameters have been evaluated, which supported our proposed mechanism and rate law.

Study is probably the most useful in the field of pharmaceuticals' for industrial application because of aliphatic aldehydes and aliphatic carboxylic acids are widely used as a fixative in the perfume industry and intermediates in pharmaceuticals (including antihistamines), agrochemicals and other organic compounds.



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