



# Kinetic and Mechanistic study of oxidation of Benzyl alcohol by N-Chlorosuccinimide

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## Abstract

The Kinetics of oxidation of Benzyl alcohol by N-Chlorosuccinimide (NCS) has been studied in presence of Sulphuric acid in aqueous acetic acid medium leads to the formation of benzaldehyde. The reaction is first order with respect to Benzyl alcohol, NCS and fractional order with to acid. The activation parameters for the decomposition of complex have been determined. The effect of solvent composition indicates that the reaction rate increases with an increase in polarity of the medium. A suitable mechanism has been proposed.

**Key words:** Benzyl alcohol, N-Chlorosuccinimide, oxidation, thermodynamic parameters.

## Introduction

Selective oxidation of alcohols to their corresponding aldehydes and ketones is an important transformation in organic chemistry which has received the most attention over years, especially in the search of versatile and selective reagent for this purpose. Kinetics of oxidation of organic substrates with variety of oxidizing agents such as Cerium (IV), KBrO<sub>3</sub>, Potassium Permanganate [1-4] etc. we have reported earlier. In recent years, significant improvement were achieved by the use of new oxidizing agents such as Quinolinium fluorochromate (QFC) [5-7] Pyridinium Fluorochromate (PFC) [8-10], Pyridinium Chlorochromate [11], 2,2-Bipyridinium Chlorochromate (BPCC) [12,13], Isoquinolium bromochromate [14]. For the study of kinetics and mechanism of oxidation of various organic compounds, we have synthesized new oxidising reagent N-Chlorosuccinimide (NCS) which is mild, efficient, selective, and stable oxidizing reagent. Literature survey reveals that there no report is available on kinetics and mechanism of oxidation of Benzyl alcohol by NCS; hence we have considered it to study the kinetics and mechanism of oxidation of Benzyl alcohol by NCS.

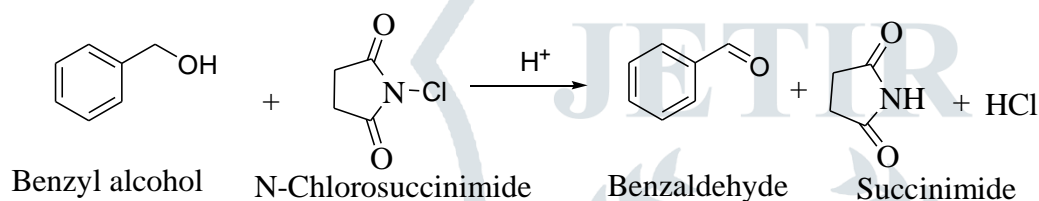
## Experimental

All the chemicals and reagents were of analytical grade. All the solutions used in the study were prepared by using distilled acetic acid [15] and doubly distilled water. N-Chlorosuccinimide was prepared by using suitable method.

The N-Chlorosuccinimide was stored in polyethylene bottle for long period of time. NCS was soluble in water, DMF, acetonitrile, acetone and DCM and was sparingly soluble in benzene, chloroform and hexane.

## Determination of Stoichiometry and Product Analysis

The Stoichiometry of the reaction was determined by carrying out several sets of experiment with varying amount of (NCS) largely in excess over Benzyl alcohol in acetic acid by using 0.1N  $\text{H}_2\text{SO}_4$ . The remaining (NCS) was then analyzed spectrophotometrically. The result indicated that 1 mole of alcohols react with 1 mole (NCS).



The product analysis was carried out under kinetic conditions. In a typical experiment, Benzyl alcohol (0.05 mol) and NCS (0.01) were made up to 50 ml in 20% acetic acid and kept in dark for about 24 hours to ensure the completion of the reaction. The solution was then treated with an excess (200 ml) of a saturated solution of 2, 4-dinitrophenylhydrazine in 2 mol  $\text{dm}^{-3}$  HCl and kept overnight in a refrigerator. The precipitated 2, 4-dinitrophenylhydrazone (DNP) was filtered off, dried, weighed, recrystallized from ethanol and weighed again. The yield of DNP before and after recrystallization was 2.0 g (90%) and 1.7 g (75%) respectively. The DNP was found identical with the DNP of benzaldehyde by melting point. The products were also characterized by TLC, IR spectra [16].

## Kinetic Measurements

The reactions were followed under pseudo-first-order conditions by keeping large excess ( $\times 10$  or greater) of the Benzyl alcohols over NCS. The temperature was kept constant to  $\pm 0.1$  K. The solvent was acetic acid. The reactions were followed by monitoring the decrease in the concentration of NCS spectrophotometrically at 345 nm for 80% completion of the reaction. The pseudo-first-order rate constants  $k'$  were evaluated from the linear ( $r^2 = 0.995$ ) plots of  $\log [\text{NCS}]$  against time. Duplicate kinetic runs showed that the rate constants were reproducible to within  $\pm 3\%$ .

## Result and Discussion

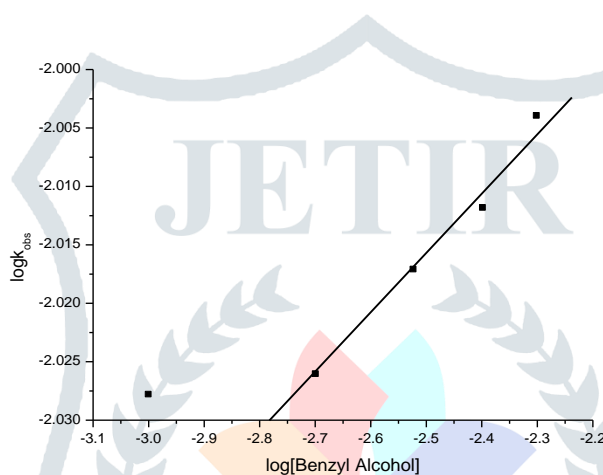
### Effect of variation of concentration Benzyl alcohol

The oxidation of Benzyl alcohol with NCS in 20% of acetic acid in presence of sulphuric acid yields benzaldehyde. By keeping constant  $[\text{NCS}]$  and  $[\text{H}_2\text{SO}_4]$ , the increase in  $[\text{Benzyl alcohol}]$  increases the rate of reaction. The plot of  $\log$  of  $k_{\text{obs}}$  versus  $\log [\text{Benzyl alcohol}]$  for different initial concentration of

Benzyl alcohol is linear with unit slope demonstrates the first order dependence of rate on Benzyl alcohol. (Table-1)

**Table No. 1: Effect of variation of concentration of Benzyl alcohol**

[Benzyl alcohol]	$k_{obs}$
0.001	0.00937962
0.002	0.009417665
0.003	0.009613653
0.004	0.009731168
0.005	0.009909311



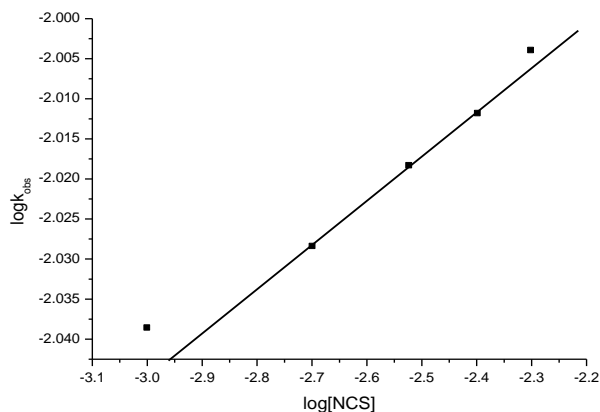
**Figure-1:- Oxidation of Benzyl alcohol by NCS: A Typical Kinetic Run**

#### Effect of variation of concentration of NCS

At constant [Benzyl alcohol] and  $[H_2SO_4]$ , the increase in [NCS] increases the rate of reaction. The plot of  $\log k_{obs}$  versus  $\log [NCS]$  for different initial concentration of NCS is linear with unit slope present the first-order dependence of rate on NCS [18]. (Table-2)

**Table No.2 : Effect of variation of concentration of N-Chlorosuccinimide**

[NCS]	$k_{obs}$
0.001	0.00914962
0.002	0.00936665
0.003	0.00958653
0.004	0.00973118
0.005	0.00990911



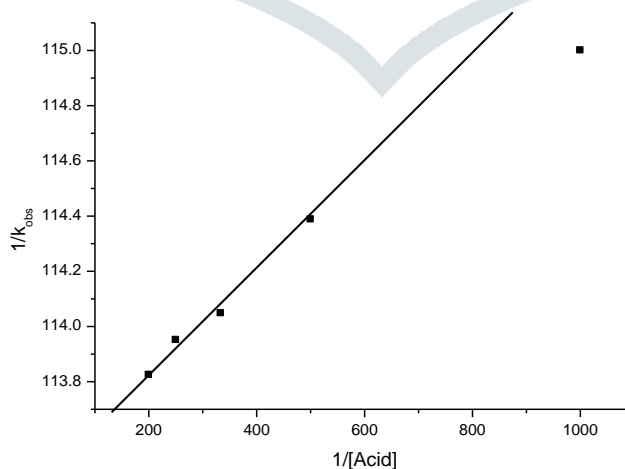
**Figure No.2 : Graph of log[NCS] Vs log K<sub>obs</sub>.**

### Effect of variation of concentration of H<sup>+</sup>

In order to study the effect the H<sup>+</sup> ion concentration on the rate of oxidation reaction of Benzyl alcohol, the dependence of reaction rate has been investigated at different initial concentration of H<sub>2</sub>SO<sub>4</sub>. The rate of reaction increases with increase in [H<sub>2</sub>SO<sub>4</sub>]. The plot of log k<sub>obs</sub> verses log [H<sup>+</sup>] are also straight line with slope less than unity[19], indicating a fractional order dependence on [H<sub>+</sub>]. (Table-3)

**Table No.3 : Effect of variation of concentration of H<sub>2</sub>SO<sub>4</sub>**

[H <sub>2</sub> SO <sub>4</sub> ]	K <sub>obs</sub>
0.001	0.00869562
0.002	0.00874217
0.003	0.00876823
0.004	0.00877568
0.005	0.00878541



**Figure No.3 : Graph of 1/[H<sub>2</sub>SO<sub>4</sub>] Vs 1/K<sub>obs</sub>.**

### Effect of ionic strength

In the present investigation effect of salt on the rate of reaction is carried out. The salts selected are KCl, KBr, and KI. These will give effect of anion particularly halides on the rate of reaction. The divalent and trivalent cationic salt were also used. The experiments were carried out under pseudo[20] first order condition. These results were used to determine first order rate constant. The rate constants for the oxidation of Benzyl alcohol in presence of different salt are shown in table. From table it is clear that, the rate increases with increase in cationic charge and decreases with increase in anionic charge. In case of KCl the rate of reaction decreases with the addition of KCl, this is due to the formation of less reactive species [21] by interaction between Cl-ion and protonated NCS.

**Table 4: Effect of variation of [KCl] on reaction rate**

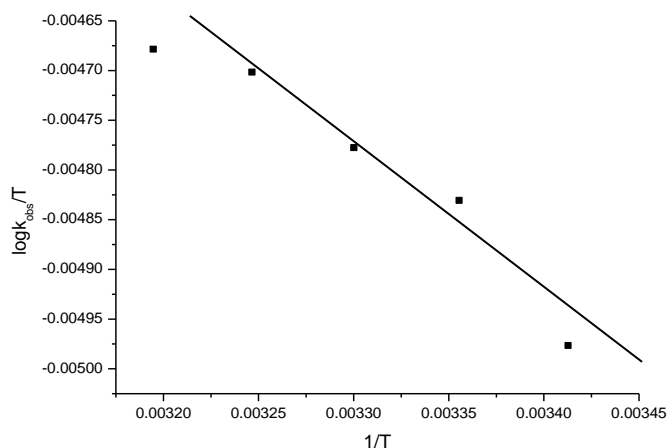
[KCl]	$k_{obs}$
0.001	0.014358756
0.002	0.014373162
0.003	0.014215267
0.004	0.014326400
0.005	0.014381900

### Effect of temperature

The study of effect of temperature on rate of oxidation of Benzyl alcohol by NCS has been subjected to different temperature range 293K to 313K by keeping the concentration of Benzyl alcohol and reagent constant. Rate constants are given in table 5. The plots of log of  $K_{obs}$  Vs  $1/T$  are linear. Activation parameters are presented in table. The negative values of entropy of activation reflect that the transition state is more rigid than initial state. The nearly constant  $\Delta G$  value indicates that similar mechanism is operative for the oxidation of Benzyl alcohol [22].

**Table No.5 : Effect of variation of temperature**

Temperature K	$k_{obs}$
293	0.00575268
298	0.00588421
303	0.00591381
308	0.00597233
313	0.00598049



**Figure No.4 : Graph of 1/T Vs logK<sub>obs</sub>./T**

### Thermodynamic parameters

Thermodynamic parameters are presented in (Table 6). The negative values of entropy of activation reflect that the transition state is more rigid than initial state. The nearly constant  $\Delta G^\ddagger$  value indicates that similar mechanism is operative for the oxidation of 2-Phenylethanol

**Table No.6: Thermodynamic Parameters**

Temperature	Ea	$\Delta H^\ddagger$	$\Delta S^\ddagger$	$\Delta G^\ddagger$
293K-303K	2.0396 kJmol <sup>-1</sup>	-0.47985kJmol <sup>-1</sup>	-289.59JK <sup>-1</sup> mol <sup>-1</sup>	87.26633kJmol <sup>-1</sup>
303K-313K	0.8843 kJmol <sup>-1</sup>	-1.71826 kJmol <sup>-1</sup>	-293.54JK <sup>-1</sup> mol <sup>-1</sup>	90.15902kJmol <sup>-1</sup>

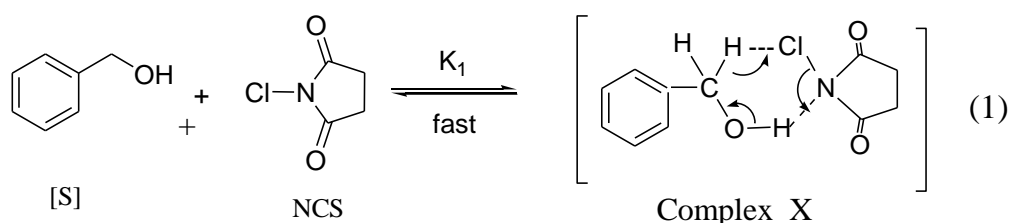
### Energy-Entropy relationship

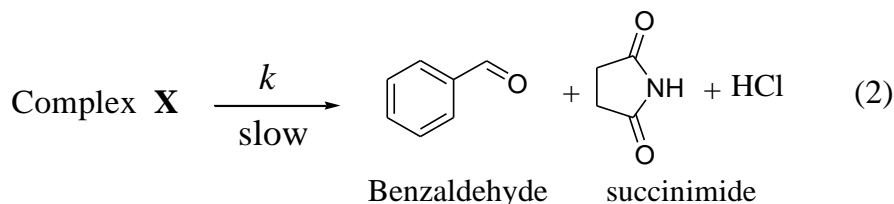
The entropy of activation and heat of reaction are correlated by equation

$$\Delta H^\ddagger = \Delta H^\ddagger + \beta \Delta S^\ddagger \dots\dots(1)$$

Where  $\beta$  is the isokinetic temperature, the isokinetic temperature for the reactions between benzyl alcohol and NCS in aqueous acetic acid is 303K, which is greater than experimental temperature [23]. The values of entropy of activation also suggested that the reaction is entropy as well as controlled. The values of free energies of activation of reaction were found to be more or less similar. These trends also support the identical reaction mechanism being followed in these reactions [24].

### Mechanism of oxidation of Benzyl alcohol by NCS and rate law:





$$-\frac{d[\text{NCN}]}{dt} = \text{rate} = \frac{kK_1[\text{S}][\text{NCN}]}{1+K_1[\text{S}]} \quad (3)$$

$$k' = \frac{kK_1[\text{S}]}{1+K_1[\text{S}]} \quad (4)$$

Reciprocal of eq<sup>n</sup> (4) gives,

$$\frac{1}{k'} = \frac{1}{kK_1[\text{S}]} + \frac{1}{k} \quad (5)$$

The kinetics results suggest the possibility of formation of binary complex involving oxidant and substrate is strongly favored. However, such a binary complex is undergoes redox decomposition to the end of products intramolecularly. Such complex formation was also proved kinetically by the non-zero intercept of the double reciprocal plot of  $1/k'$  Vs  $1/[\text{S}]$ . Evidence is also provided by the fractional order found in substrate. The spectral evidence for complex formation between oxidant and substrate was obtained of the mixture. As per double reciprocal plot of  $1/k'$  Vs  $1/[\text{S}]$  eq<sup>n</sup> (5), the decomposition rate constant  $k$  and formation constant  $K_1$  was find out.

## Conclusion

The active species of NCS is understood to be for the said reaction. The rate constants of the slow step involved in the mechanism were evaluated and activation parameters were also computed. The negative value of  $\Delta S$  provides support to the formation of rigid transition state. The kinetics results suggest the possibility of formation of binary complex involving oxidant and substrate is strongly favored. The overall mechanism described here is consistent with product and kinetic studies.

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