



# Kinetic Studies on the Oxidation of Aniline by N-Chlorosaccharin

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**Abstract—** The kinetics of oxidation of aniline by N-chlorosaccharin (NCSA) in acetonitrile-water medium has been studied iodometrically at 303 K in the presence of perchloric acid. The ionic strength of the medium was maintained by using sodium perchlorate. The reaction is first order with respect to both aniline and NCSA and is catalyzed by  $H^+$  ion and the order of the reaction with respect to  $[H^+]$  is also one. It has been observed that the reaction rate is not affected by changes in ionic strength of the reaction medium or by the addition of acrylonitrile and potassium chloride. However, addition of saccharin causes a decrease in the rate of reaction. An increase in the water content of the solvent mixture decreases the rate of reaction. Substituent effects have been studied by invoking Hammett plots. Thermodynamic and activation parameters have also been evaluated. Based on the kinetic results a suitable mechanism has been proposed for the oxidation of anilines by NCSA.

**Index Terms—**Oxidation, Kinetics, Mechanism, Aniline, N-chlorosaccharin

## I. INTRODUCTION

Aromatic amines exhibit a complex behavior with different oxidants and yield a variety of complex and polymeric products. These products find application in drug and dye-stuff industries. Kinetics of oxidation of aromatic amines by a variety of oxidants has been studied extensively with N-halocompounds such as, N-bromoacetamide[1], N-bromosuccinimide[2], chloramine-T[3], N-chlorosuccinimide[4], and N-bromophthalimide[5] and other oxidants such as peroxydisulfate[6], hexacyanoferrate[7], pyridiniumchlorochromate[8], sodiumiodate[9], isoquinolinium bromochromate[10], imidazolium fluorochromate[11], etc.

Among the various oxidants, the N-halo compounds get much attraction due to their ability to act as sources of halonium ions, hypohalite species and nitrogen anions, which act as both bases and nucleophiles.

N-Chlorosaccharin has been introduced as an oxidimetric titrant for use in aqueous acetic acid medium. Both direct and potentiometric titrations have been developed for a variety of substrates using NCSA as the titrant. It is very stable in solid state and its solution in anhydrous acetonitrile has better keeping qualities. Investigations on kinetics of oxidation of polyhydroxy alcohols[12], benzaldehyde[13], (phenylthio)acetic acids[14], etc., using NCSA are available in the literature. There seems to be no report on the oxidation of aniline by NCSA. Hence, in the present work, the kinetics of oxidation of aniline in acetonitrile-water mixture by NCSA has been investigated to get a clear picture of mechanism of oxidation.

## II. EXPERIMENTAL

All the chemicals used were of AR Grade. Anilines were distilled before use. AR grade NCSA (Aldrich), perchloric acid (E.Merck) and GR grade sodium perchlorate were used as received. All the solutions used in the study were made in distilled acetonitrile or double distilled water.

### Kinetic measurements

The reactions were carried out under pseudo first order conditions by keeping an excess of substrate over NCSA. The kinetic runs were carried out in 50% acetonitrile-50% water (v/v) solvent mixture in acid medium, the acid strength being maintained by the addition of  $HClO_4$  and the ionic strength by  $NaClO_4$ . The progress of reaction was followed by monitoring the decrease in concentration of NCSA iodometrically at suitable intervals of time. The rate constants were determined by least square method from the linear plots of  $\log [NCSA]$  versus time. Replicate runs showed that the rate constants were reproducible to within  $\pm 5\%$ .

### Product analysis

In a typical experiment, solutions of aniline and NCSA in 1:2 molar ratio were mixed and kept aside for 2 to 3 days. The resulting precipitate was filtered off and washed with

distilled water until free from NCSA. TLC of the precipitate using benzene as an eluent revealed the presence of two compounds. The major product (85%) was identified as azobenzene by mixed melting point determination with an authentic specimen.

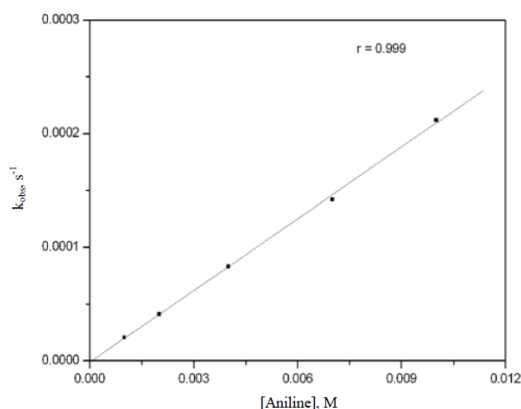
### Stoichiometry

In a typical experiment, a reaction mixture containing 10 times excess of NCSA over aniline was prepared and allowed to react overnight. Then the unreacted NCSA was estimated, which established a 1:1 stoichiometry between NCSA and aniline, as represented in the following scheme.

## III. RESULTS AND DISCUSSION

Oxidation of aniline by NCSA has been conducted in 50% acetonitrile and 50% water medium at 303 K, under pseudo first-order conditions. As it was found that ionic strength of the reaction medium had no significant effect on reaction rate, constancy of ionic strength was not maintained throughout the present study.

The values of  $k_{\text{obs}}$  were calculated for different concentrations of NCSA by maintaining other parameters at constant values. The data in Table 1 show that the rate constant remains almost constant on varying the concentration of NCSA, revealing that the reaction follows a first-order kinetics with respect to [NCSA]. The  $k_{\text{obs}}$  values calculated for different concentrations of aniline by keeping the concentrations of NCSA and  $\text{H}^+$  at constant values are also included in Table 1. The data establishes that the rate increases with increase in [aniline] in a first-order fashion. Further, the plot of  $k_{\text{obs}}$  versus [aniline] is excellently linear passing through origin (Figure 1;  $r = 0.999$ ). Also, the  $k_2$  values remain constant when [aniline] is varied (Table 1); this result, coupled with the nearly unit slope value of the double logarithmic plot between  $k_{\text{obs}}$  and [aniline] ( $r = 0.999$ ; slope =  $0.998 \pm 0.006$ ) confirms the first-order nature of the reaction with respect to [aniline].



**Figure 1.** Direct plot of  $k_{\text{obs}}$  versus [aniline] for the oxidation of aniline with NCSA

The  $k_{\text{obs}}$  values measured at different initial concentrations of  $\text{H}^+$  by keeping the [NCSA] and [aniline] at constant values. The  $k_{\text{obs}}$  value increases linearly with increase in  $[\text{H}^+]$  (Table 1), establishing the catalytic behavior of perchloric acid. The double logarithmic plot of  $k_{\text{obs}}$  versus  $[\text{H}^+]$  is excellently linear ( $r = 0.998$ ; slope =  $1.03 \pm 0.03$ ) with a slope value very equal to one, establishing that the reaction is first-order with respect to  $[\text{H}^+]$ .

**Table 1.** Pseudo first-order and second-order rate constants for the oxidation of aniline by NCSA in 50:50 acetonitrile-water (v/v) mixture at 303 Ka

$10^3[\text{NCSA}]_0, \text{M}$	$10^3[\text{Aniline}]_0, \text{M}$	$10^3[\text{H}^+], \text{M}$	$10^3 k_{\text{obs}}, \text{s}^{-1}$	$10^3 k_2, \text{M}^{-1} \text{s}^{-1}$
1.0	1.0	1.0	$1.59 \pm 0.13$	$1.59 \pm 0.13$
2.0	1.0	1.0	$1.54 \pm 0.12$	$1.54 \pm 0.12$
3.0	1.0	1.0	$1.58 \pm 0.13$	$1.58 \pm 0.13$
5.0	1.0	1.0	$1.66 \pm 0.14$	$1.66 \pm 0.14$
10.0	1.0	1.0	$1.63 \pm 0.14$	$1.63 \pm 0.14$
5.0	2.0	1.0	$3.21 \pm 0.37$	$1.61 \pm 0.14$
5.0	4.0	1.0	$6.21 \pm 0.53$	$1.55 \pm 0.13$
5.0	7.0	1.0	$11.4 \pm 1.0$	$1.63 \pm 0.14$
5.0	10.0	1.0	$17.2 \pm 1.5$	$1.72 \pm 0.15$
5.0	1.0	0.5	$3.19 \pm 0.28$	$3.19 \pm 0.28$
5.0	1.0	2.0	$5.12 \pm 0.47$	$5.12 \pm 0.47$
5.0	1.0	3.0	$8.47 \pm 0.78$	$8.47 \pm 0.78$
5.0	1.0	5.0	$17.3 \pm 1.6$	$17.3 \pm 1.6$

As determined by iodometrically following the disappearance of NCSA; the error quoted in  $k$  values is the 95% confidence limit of 'Student  $t$  test'. b Estimated from pseudo first order plots over 80% reaction. c Individual  $k_2$  values estimated as  $k_{\text{obs}}/[\text{Aniline}]$ .

The effect of ionic strength of the reaction on the reaction rate was studied by varying the ionic strength of the medium by adding different quantities of  $\text{NaClO}_4$ , maintaining other parameters constant (Table 2). The data reveal that variation of ionic strength of the medium has no significant effect on reaction rate. This result shows the participation of a neutral species as a reactant in the rate-determining step. The kinetic runs carried out in the presence of acrylonitrile (Table 2) establish that the reaction fails to initiate the polymerisation of added acrylonitrile, which rules out the involvement of free radical intermediates. The kinetic runs carried out in the presence of  $\text{NaCl}$  (Table 2) establish that the reaction rate does not change significantly with increase in concentration of added  $\text{NaCl}$ . This result rules out the participation of  $\text{Cl}^-$  or  $\text{Cl}_2$  as reactive species in the present reaction.

**Table 2.** Influence of ionic strength, acrylonitrile (AN) and  $\text{NaCl}$  on reaction rate for the oxidation of aniline by NCSA in 1:1 acetonitrile-water (v/v) mixture at 303 Ka

[I], M	$10^4 k_{\text{obs}}, \text{s}^{-1}$	[AN], M	$10^4 k_{\text{obs}}, \text{s}^{-1}$	[NCSA], M	$10^4 k_{\text{obs}}, \text{s}^{-1}$
0.30	$1.66 \pm 0.14$	0	$1.66 \pm 0.14$	0	$1.66 \pm 0.14$
0.50	$1.68 \pm 0.15$	0.001	$1.51 \pm 0.14$	0.001	$1.71 \pm 0.13$
0.75	$1.72 \pm 0.15$	0.003	$1.29 \pm 0.11$	0.003	$1.68 \pm 0.11$
1.00	$1.77 \pm 0.16$	0.006	$0.99 \pm 0.10$	0.006	$1.69 \pm 0.12$

<sup>a</sup> General conditions: [NCSA] = 0.0002 M; [aniline] = 0.001 M; [H<sup>+</sup>] = 0.001 M

a. General conditions: [NCSA] = 0.0002 M; [Aniline] = 0.001 M; [H<sup>+</sup>] = 0.001 M; Solvent = 1:1 acetonitrile-water (v/v) mixture unless otherwise stated. b. Rest = water

The rate constant values measured for the oxidation of aniline with NCSA in presence of differing amounts of saccharin are listed in Table 3. The data show that the rate of reaction decreases significantly with increasing concentration of added saccharin. This result establishes that the reaction step in which saccharin is formed as one of the products is reversible in nature.

The effect of the solvent composition on the reaction rate was studied by varying the acetonitrile content in the solvent mixture from 50% to 80% and the measured  $k_{\text{obs}}$  values (Table 3) show that the rate of the reaction increases remarkably with increase in the percentage proportion of acetonitrile in the solvent medium, establishing that the reaction between aniline and NCSA is favoured by a solvent of low dielectric constant. The plot of  $\log k_{\text{obs}}$  versus  $1/D$  is linear, with positive slope, indicating that the reaction is of ion-dipole type.

Table 3. Influence of added saccharin and solvent polarity on reaction rate for the oxidation of aniline by NCSA at 303 K

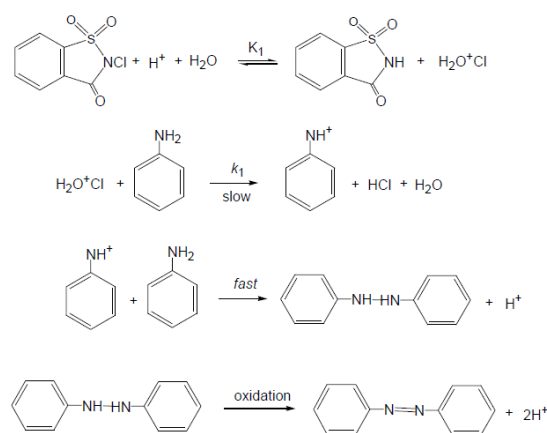
[Saccharin], M	$10^4 k_{\text{obs}}, \text{s}^{-1}$	%CH <sub>3</sub> CN, v/v <sup>b</sup>	$10^4 k_{\text{obs}}, \text{s}^{-1}$
0	$1.66 \pm 0.14$	50	$1.66 \pm 0.14$
0.001	$1.51 \pm 0.14$	60	$2.09 \pm 0.17$
0.003	$1.29 \pm 0.11$	70	$2.99 \pm 0.22$
0.006	$0.99 \pm 0.10$	80	$4.39 \pm 0.41$

a. General conditions: [NCSA] = 0.0002 M; [Aniline] = 0.001 M; [H<sup>+</sup>] = 0.001 M; Solvent = 1:1 acetonitrile-water (v/v) mixture unless otherwise stated. b. Rest = water

The reaction was carried out at three other temperatures (298, 313 and 323 K) keeping other experimental conditions constant. From the Arrhenius and Eyring plots, the thermodynamic parameters for the oxidation of aniline were found to be  $E_a = 53.4 \pm 1.4$  kJ/mol,  $\Delta H^\ddagger = 50.9 \pm 1.4$  kJ/mol,  $\Delta G^\ddagger$  (303 K) =  $84.7 \pm 2.8$  kJ/mol and  $\Delta S^\ddagger = -111.6 \pm 4.6$  JK<sup>-1</sup> mol<sup>-1</sup>.

## Mechanism

The reactive species that can be formed [15] from N-halo compounds (N-X) in acidic solutions are HOX, H<sub>2</sub>O<sup>+</sup>X and >N<sup>+</sup>HX. The first-order dependence of present reaction on hydrogen ion concentration excludes the possibility of >N<sup>+</sup>HCl or HOCl being the reactive species and establishes the involvement of H<sub>2</sub>O<sup>+</sup>Cl, a stronger electrophile than HOCl, as reactive species [16]. The hypohalous acidium ion, H<sub>2</sub>O<sup>+</sup>X is the reactive species in the present study, is further evidenced by the retarding effect shown by added phthalimide. The participation of H<sub>2</sub>O<sup>+</sup>X in many electrophilic and oxidation reactions has well been documented [17]. Based on the foregoing kinetic results, the following mechanism has been proposed.



The mechanism accounts for the decrease in rate of oxidation with increasing saccharin concentration. Equilibrium shifts to the right with increasing [saccharin], decreasing the concentration of the active species, H<sub>2</sub>O<sup>+</sup>Br.

The rate law can be given as

$$\text{Rate} = \frac{K_1 k [\text{NCSA}] [\text{Aniline}] [\text{H}^+]}{[\text{Saccharin}]}$$

This rate law explains first-order dependence of the reaction on [aniline], [NCSA], and [H<sup>+</sup>] and the retarding effect of saccharin.

$$k_{\text{obs}} = \frac{K_1 k [\text{Aniline}] [\text{H}^+]}{[\text{Saccharin}]}$$

$$k_2 = \frac{K_1 k [\text{H}^+]}{[\text{Saccharin}]}$$

This equation explains the linear plot of  $k_2$  versus [H<sup>+</sup>] which passes through origin (Figure 2).

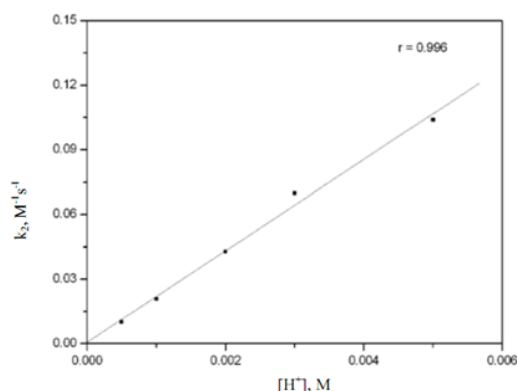


Figure 2. Plot of  $k_2$  versus  $[H^+]$  for the oxidation of aniline with NCSA

#### IV. CONCLUSIONS

The NCSA oxidation of aniline involves hypohalous acidium ion,  $H_2O^+Cl$  as reactive species which attacks aniline electrophilically to give azobenzene as product. This mechanism is supported by the experimental data such as the reaction stoichiometry, the oxidation products and the activation parameters.

#### V. ACKNOWLEDGEMENT

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