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REACTIVITY OF 2-HYDROXY ETHANOIC ACID TOWARDS N-CHLOROSUCCINIMIDE OXIDATION

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Abstract:

Kinetics and mechanism of oxidation of 2-hydroxyethanoic acid (glycolic acid-GA) with N-chlorosuccinimide (NCS) has been studied in alkaline medium at 308K under pseudo first order conditions. The results revealed that the rate of the reaction was zero with respect to [hydroxy acid]. The rate of the reaction remained constant with increase in [NaOH] and increases with increase in concentration of substrate. Glycolic acid is oxidized to give glyoxylic acid which is confirmed by IR spectral studies. Increase in ionic strength of the medium does not show any appreciable change in the rate. The reaction does not induce the polymerization of acrylonitrile. The effect of temperature is quite marked in all these reactions and activation parameters have been determined. A mechanism consistent with the observation was proposed and the related rate law deduced.

Key Words: Kinetics; Mechanism; Oxidation; Glycolic Acid & N-Chlorosuccinimide

1. Introduction:

Glycolic acid finds applications in textile industry as a dyeing and tanning agent, in food processing as a flavoring agent and as a preservative, and in the pharmaceutical industry as a skin care agent. It is also used in adhesives and plastics. It is often included into emulsion polymers, solvents and additives for ink and paint in order to improve flow properties and impart gloss. It is used in surface treatment products that increase the coefficient of friction on tile flooring. Due to its excellent capability to penetrate skin, glycolic acid finds applications in skin care products, most often as a chemical peel performed by a dermatologist. It is used to improve the skin's appearance and texture. It is also a useful intermediate for organic synthesis, in a range of reactions including: oxidation-reduction, esterification and long chain polymerization. It is used as a monomer in the preparation of polyglycolic acid and other biocompatible copolymers. The oxidation products depend on the nature of oxidant and on the medium as well.

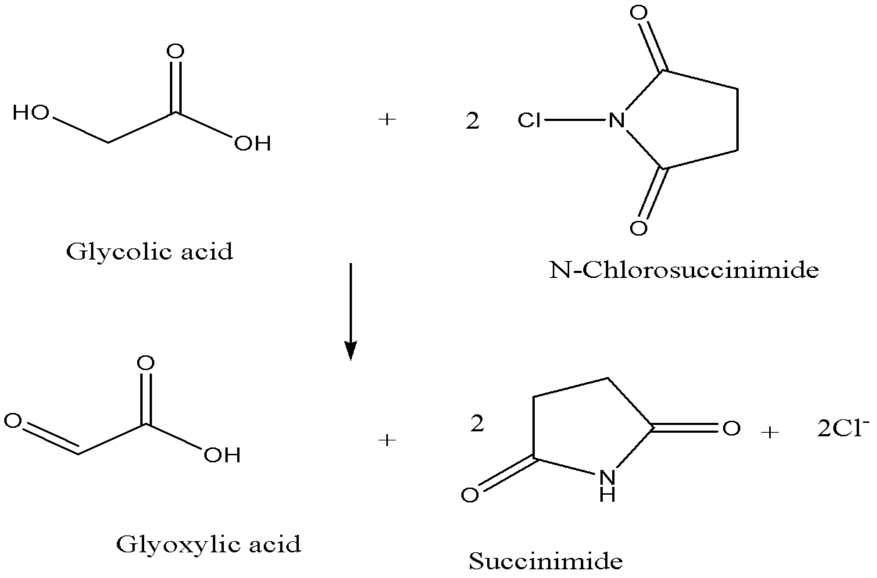
Kinetic studies on the oxidation of hydroxy acids with several oxidants such as N-bromophthalimide [1-2], silver(II) [3], N-bromosuccinimide [4], Cr(VI) in aqueous perchloric acid medium, alkaline hexacynoferrate(III) [5], N-bromoacetamide [6] have been reported. The oxidation of glycolic acid by cerium (IV) in aqueous nitric acid has been studied [7]. The kinetics and mechanism of glycolic acid by N- bromosuccinimide oxidation in presence of Ir(III) catalyst[8], pyridinium fluorochromate oxidation [9], piperidium chlorochromate [10], hexamethylenetetramine-bromine [11] in aqueous acetic acid medium, Quinoxalinium Chloro chromate [12], PMS- System[13] in the presence of Fe(II), Tripropylammonium Fluorochromate[14] in aqueous acetic acid medium, Quinolinium chlorochromate [15] has been studied. Literature study revealed that the oxidation of hydroxy acids by various oxidants produced keto acids/carbonyl compounds and CO_2. However the kinetics of oxidation of glycolic acid (GA) by NCS has not yet been studied. This prompted us to undertake the present study on the kinetics of oxidation of glycolic acid by NCS in alkaline medium and also to propose the reaction mechanism.

2. Experimental Methods:

A fresh solution of NCS was prepared every time before starting the experiment. Other chemicals used in this study were of analar grade and used as such without any further purification. Double distilled water was used throughout this study. The kinetics and oxidization of glycolic acid by NCS in alkaline medium was investigated under pseudo first order conditions, i.e., [hydroxy acids] > [NCS]. The rate of the reaction was determined from the concentration of the unreacted [NCS] at different time intervals by iodometry.

2.1 Stoichiometry:

The stoichiometry of the reaction was determined by allowing the reaction mixtures containing three times excess of [NCS] over [GA]. Simultaneously, a blank solution of the reaction mixture was also prepared by adding all the solutions without hydroxy acid. Both the reaction mixtures were allowed to stand for 48 hours and the excess of [NCS] in both the solution was estimated by iodometry. Correction for the self-decomposition of [NCS] was made. The observed stoichiometry of the reaction was calculated as [GA] : NCS = 1:2. The stoichiometric equation is given as follows.



2.2 Product Analysis:

The reaction mixture containing a large excess of [NCS], i.e., 3 times over [GA] in a blackened vessel was allowed to stand for 48 hours at room temperature for completion of the reaction and sodium bisulphate was added to destroy the remaining [NCS]. The reaction mixture was then extracted with dichloromethane and the sample was analyzed by TLC (thin layer chromatography) and it showed two prominent spots. The reaction mixture was purified by column chromatography. The separated products were analyzed by IR spectroscopy. IR spectral data of the product of glycolic acid showed absorption at 3329 cm^{-1}, 2932 cm^{-1} & 1750cm^{-1} which might be due to glyoxylic acid. Another product showed absorption due to succinimide.

3. Results and Discussion:

The oxidation of glycolic acid was studied in perchloric acid medium and also in acetic acid/sodium acetate buffered medium. However the reaction was very sluggish in the above medium and did not proceed at all even after 4hours. Hence the reaction was studied in alkaline medium. The results obtained for the oxidation of GA by NCS in an alkaline medium are given below. The rate constant obtained for the variation of reactants, temperature and ionic strength for GA are tabulated in Table 1.

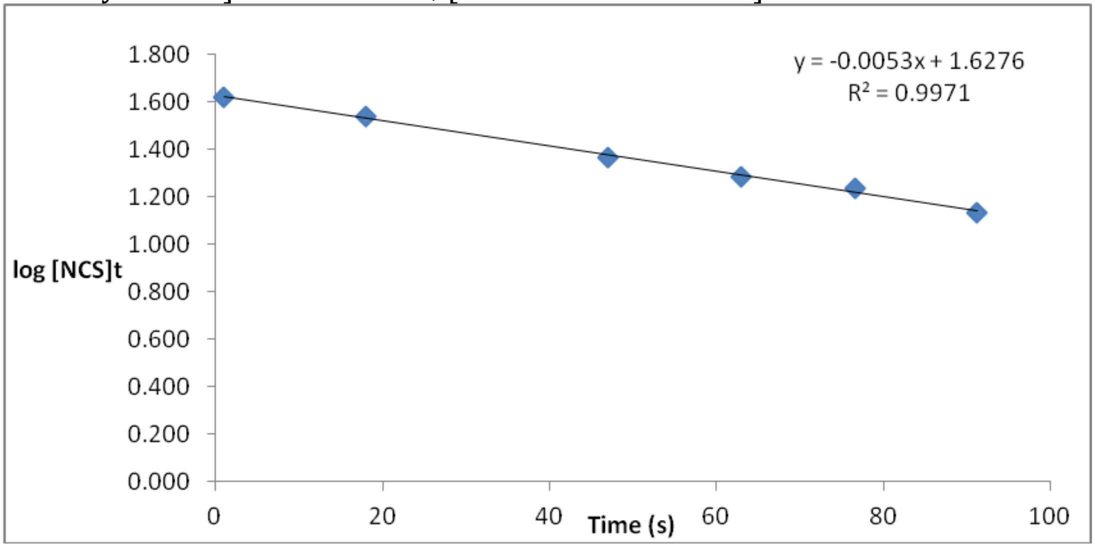
Table 1: Effect of the variations of NCS, Sodium hydroxide on the reaction rate of GA at 308K and temperature effect on the reaction rate of GA at various temperatures.

10^3[NCS]mol dm^{-3}	10^2[GA]mol dm^{-3}	10^2[NaOH]mol dm^{-3}	T (K)	10^4 k_{obs} s^{-1}
2.00	5.00	15.00	308	2.89
4.00	5.00	15.00	308	2.78
6.00	5.00	15.00	308	2.90
8.00	5.00	15.00	308	2.87
4.00	2.50	15.00	308	2.40
4.00	3.75	15.00	308	2.65
4.00	5.00	15.00	308	2.70
4.00	6.25	15.00	308	2.69
4.00	7.50	15.00	308	2.72
4.00	10.0	15.00	308	2.80
4.00	5.00	05.00	308	2.05
4.00	5.00	10.00	308	2.18
4.00	5.00	15.00	308	2.03
4.00	5.00	20.00	308	2.07
4.00	5.00	15.00	301	1.01
4.00	5.00	15.00	306	2.03
4.00	5.00	15.00	311	3.34
4.00	5.00	15.00	316	6.37

3.1 Effect of [NCS] on k_{obs}

The oxidation of GA by NCS in alkaline medium was investigated under pseudo-first order conditions. The oxidation followed first order with respect to NCS as evidenced by the linear of log $[NCS]_t$ v_s time upto 80% conversion of [NCS] (Figure 2). Further, the values of k_{obs} calculated from the different plots were independent of $[NCS]_0$, indicating that the rate of reaction was first order in [NCS].

Figure 2: Plot of log $[NCS]_t$ versus time at 308 K. [glycolic acid] = 0.05 mol dm^{-3}; [sodium hydroxide] =0.1 mol dm^{-3}; [N-Chloro succinimide] = 0.004 mol dm^{-3}.



3.2 Effect of [GA] on k_{obs}

By keeping all parameters at constant values, the values of k_{obs} for different concentration of [GA] were found to be constant with increase in [GA]. The reaction between active form of NCS and the hydroxy acid was very fast and hence the rate was independent of [hydroxy acid]. This showed that the order of the reaction was zero in the acid.

3.3 Effect of [NaOH] on k_{obs}

The effect of [NaOH] on k_{obs} was studied by varying [NaOH] and keeping the other parameters at constant values. The rate constant k_{obs} did not alter with increase in [NaOH] in GA. The concentration of NaOH was varied from 0.15M to 0.20 M i.e., $[\text{NaOH}]_f$ =0.1M.

3.4 Effect of [succinimide] on k_{obs}

By keeping all parameters at constant values, the values of k_{obs} for different concentrations of succinimide, the reduction product of the oxidant were determined. The rate of the reaction remained constant ruling out the dimerisation of NCS.

3.5 Effect of ionic strength (μ) on k_{obs}

The effect of ionic strength on the reaction rate was studied by the addition of sodium perchlorate (5×10^{-2}M to 20×10^{-2}M) with NaOH concentration of 0.15M in the case of GA by maintaining other parameter at constant values. It was observed that the k_{obs} value had a negligible effect on the reaction rate, which may be attributed to the involvement of neutral species in the rate determining step. Since [NaOH] was kept at predetermined values so pH remained constant throughout the study.

3.6 Effect of Temperature:

The oxidation was carried out at four different temperatures, namely 301, 306, 311 and 316 K. The k_{obs} values increased with increase in the temperature. Further the plot of log k_{obs} Vs 1/T were straight lines. The thermodynamic parameter ΔH^*, ΔS^* and ΔG^* were calculated from the Eyring plot of log k_{obs} /T Vs 1/T and tabulated (Table3). Negative values of entropy of activation suggested the formation of a rigid transition state with a reduction of the degree of freedom of the molecules involved than the reactants.

Table 3: Kinetic and Activation Parameters for the oxidation of [GA] by [NCS]

Activation Parameters	Glycolic Acid
10^4 Ea (J/mol)	4.02
10^4 ΔH^*(J/mol)	3.98
ΔS^*(J/mol)	-98.18
10^4 ΔG^*(J/mol)	7.00

3.7 Test for Free Radicals:

To test the intervention of the free radical during the course of the reaction, acrylonitrile monomer was added to the reaction mixture and kept for 2 hours under a nitrogen atmosphere. No precipitate was obtained, which revealed that the oxidation of GA by NCS did not involve a free radical. Further ESR study confirmed that the reaction did not proceed through free radical as intermediate since no signal was obtained in the study.

3.8 Effect of Polarity on the Rate Constant:

By keeping all parameters at constant values, the values of k_{obs} were calculated by changing the polarity of the solvent. The rate of the reaction was studied by varying the composition of acetonitrile-water mixture. The result revealed that k_{obs} did not change with respect to the change in the solvent composition (0-20%) ruling out the formation of more polar intermediate than the reactants.

4. Discussion:

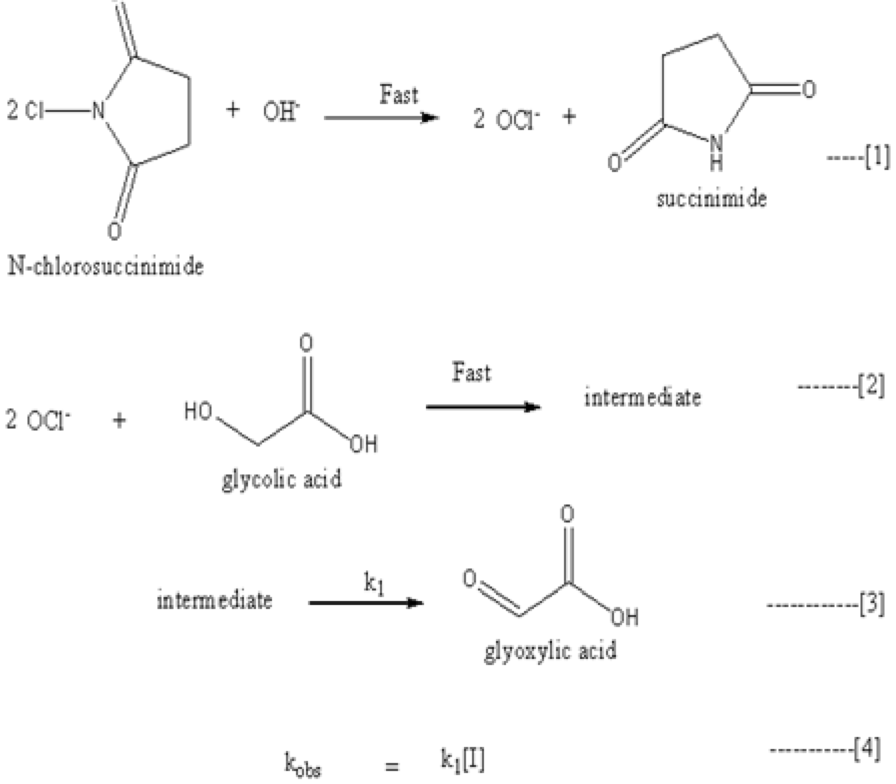
In alkaline medium NCS will react with OH^- to give OCl^-

$$NCS + NaOH \rightarrow OCl^-$$

UV-Visible spectral studies revealed that there were two absorptions maximum for the reaction mixtures, one at 290nm and the other at 209nm in glycolic acid. Time history of the spectrum revealed that absorbance at 290nm decreased within 15 minutes. However the absorbance at 209 nm also decreased with increases with time. The peak at 290nm was due to the formation of hypochlorite. The effect of hydroxy acid on the rate of the reaction revealed that the rate of the reaction was zero order with respect to [hydroxy acid]. Moreover the reaction between hypoclorite and hydroxy acid was fast and hence the rate did not depend on the concentration of hydroxy acid.

Based on the above results the following mechanism was proposed.

Scheme I: Glycolic Acid



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