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Oxidation of 3-Carboxy-3-Hydroxy Pentane dioic Acid by N-Chlorosuccinimide in alkaline medium –kinetics and mechanism

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Abstract: The oxidation of α- hydroxy acid, 3-carboxy-3-hydroxy pentanedioic acid (CA) by N-chlorosuccinimide (NCS) was carried out in alkaline medium under pseudo first order conditions. It was followed up to 50% conversation of [NCS] and above that condition, it showed curvature due to the formation of less reactive form of citric acid. The reaction was said to be first order in [NCS], [CA] and [NaOH]. The reaction was carried out at different temperatures and the thermodynamic parameters were calculated. The rate constants involved in the different steps of the reactions were calculated. The product was analyzed by IR spectra by comparing with the authentic sample. Based on the results obtained, a suitable mechanism was proposed.

Keywords: Kinetics; Mechanism; Oxidation; Citric acid; N-chlorosuccinimide

1. Introduction

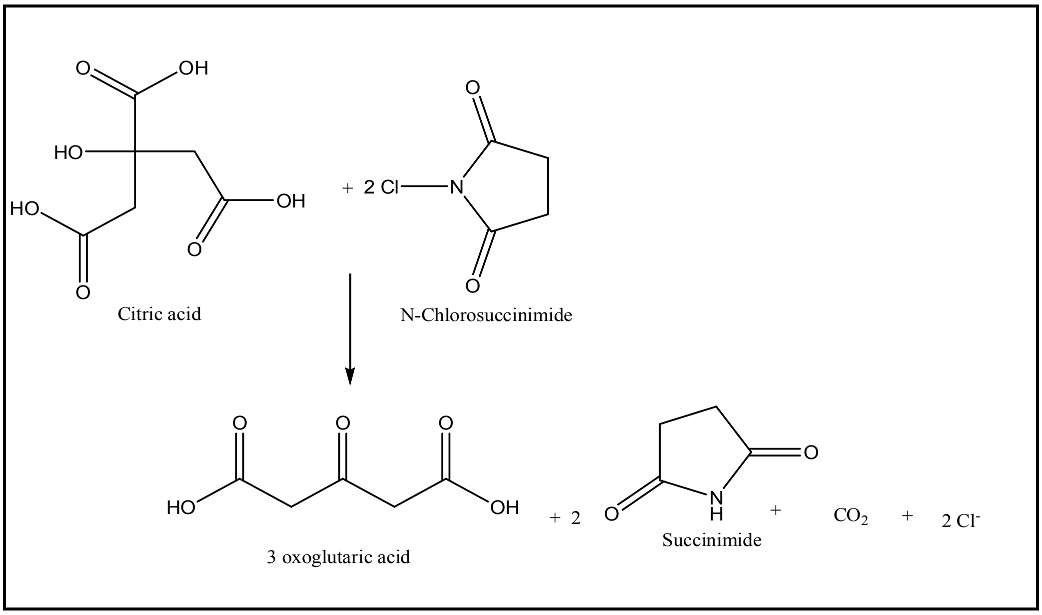
Citric acid is a weak organic acid, occurs naturally in citrus fruits. It is an excellent chelating agent in binding metals. It is used to remove lime scale from boilers and evaporators. It can be used to soften water, which makes it useful in soaps and laundry detergents. In biochemistry, the conjugate base of citric acid, citrate, is important as an intermediate in the citric acid cycle, which occurs in the metabolism of all aerobic organisms. Further it is a successful alternative to nitric acid passivation of stainless steel. Hydroxy acids are naturally occurring organic acids which can act both as an antioxidants and antiflammating agents. This will also be used as a natural preservative in some of the food industries. The oxidation products depend on the nature of oxidant and on the medium as well. Kinetic studies on the oxidation of α-hydroxy acid with several oxidants such as N-bromophthalimide[1-7], N-bromoacetamide[8], silver(II)[9], N-bromosuccinimide[10], Cr(VI) in aqueous perchloric acid medium[11], alkaline hexacynoferrate(III)[12], alkaline iodate[13] and chloramines-T[14-16] have been reported. Literature studies revealed that the oxidation of α- hydroxy acids by various oxidants produced keto acids/ carbonyl compounds and CO_2. Oxidation of α-hydroxy acid by $KBrO_3$ in the presence of Ru(III) and $Hg(OAC)_2$ in acidic medium were also reported[17]. Studies on the kinetics of oxidation of citric acid and tartaric acid by N-bromoacetamide in perchloric acid and iridium trichloride as catalyst was reported[18]. However the kinetics of oxidation of citric acid by NCS has not yet been studied. This has initiated us to do the present study. The study reports on the kinetics of oxidation of citric 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 citric acid by NCS in alkaline medium was investigated under pseudo first order conditions, i.e., [citric acid] > [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 CA. Simultaneously, a blank solution of the reaction mixture was also prepared by adding all the solutions without citric 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. After making correction for the self-decomposition of [NCS], the observed stoichiometry of the reaction was calculated as [CA] : NCS = 1:2.



2.2 Product analysis

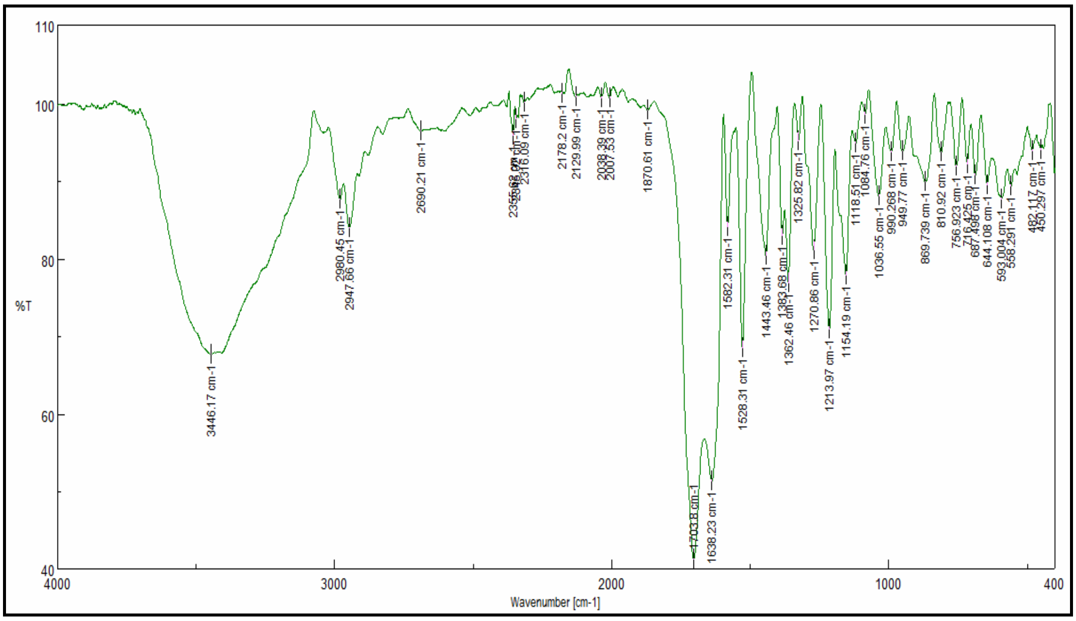


Figure 1: IR spectrum of 3 -oxoglutaric acid

The reaction mixture containing a large excess of [NCS], i.e., 3 times over CA in a blackened vessel was allowed to stand for 48 hours at room temperature for completion of the reaction and sodium bisulphite 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 one prominent spot. The reaction mixture was purified by column chromatography. The separated products were analyzed by IR spectroscopy. IR spectral data of main product of citric acid showed absorption at 3446.17 cm^{-1} , 17038 cm^{-1} & 1638.23 cm^{-1} which might be due to OH group, carbonyl group peak due to carboxylic acid and carbonyl group peak due to ketone respectively . The product was identical to an authentic sample of 3 oxoglutaric acid (Figure 1).

2.3 Spectral Analysis

The reaction mixture was scanned in the Ultra-Violet and visible regions on a Perkin-Elmer LS 25 spectrometer to unravel the intermediate formed during the course of the reaction. The reaction mixture was prepared by adding NCS ($2.5x10^{-5}$ mol dm^{-3}) to CA ($5x10^{-2}$ mol dm^{-3}) in alkaline medium. The spectra was taken immediately after preparing the reaction mixture in1 cm cell at room temperature (298K). A peak was observed at λ_{max} 290 nm which disappeared during the course of the reaction. This might be due to the formation of hypochlorite and it would be consumed to give the products. The reaction between hypochlorite and citric acid lead to the formation of an intermediate which has an absorption at 230 nm (Figure 2).

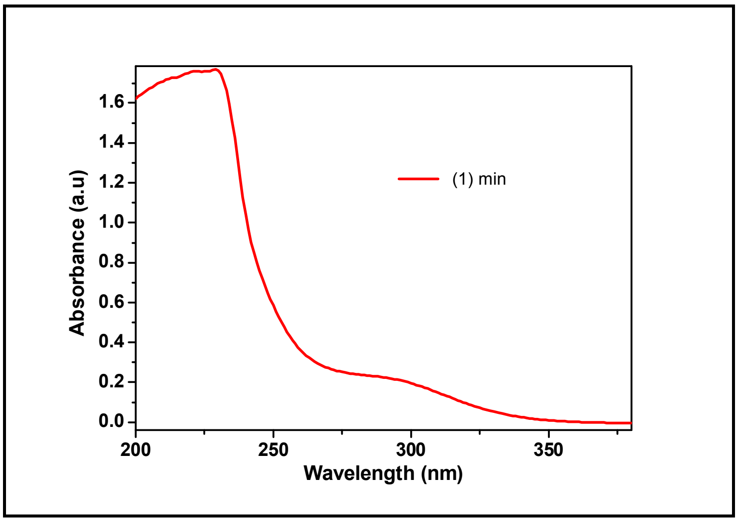


Figure 2. UV absorption spectra of the reaction mixture at various time intervals [citric acid] = 0.005 mol dm^{-3}; [sodium hydroxide] =0.01 mol dm^{-3}; [N-Chloro succinimide] = 0.008 mol dm^{-3}.

3. Results and discussion

The oxidation of citric 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 CA by NCS in an alkaline medium are given below. The rate constant obtained for the variation of reactants, temperature and ionic strength for citric acid is tabulated in Table 1.

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

10^3[NCS] mol dm^{-3}	10^2[CA] mol dm^{-3}	10^2 [NaOH] mol dm^{-3}	T (k)	10^5 $k_{obs}s^{-1}$
		[NCS] variation		
2.00	5.00	15.00	308	24.18
4.00	5.00	15.00	308	12.21
6.00	5.00	15.00	308	08.29
8.00	5.00	15.00	308	06.90
		[TA] variation		

4.00	2.50	15.00	308	26.86
4.00	5.00	15.00	308	15.35
4.00	7.50	15.00	308	10.36
4.00	10	15.00	308	08.44
		[NaOH] variation		
4.00	5.00	05.00	308	03.83
4.00	5.00	10.00	308	09.21
4.00	5.00	12.50	308	10.75
4.00	5.00	15.00	308	22.26
4.00	5.00	20.00	308	33.00
		Temperature variation		
4.00	5.00	15.00	301	04.61
4.00	5.00	15.00	307	06.52
4.00	5.00	15.00	315	16.50
4.00	5.00	15.00	322	47.98

3.1 Effect of [NCS] on k_{obs}

The oxidation of citric acid 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 50% conversion of [NCS] (Figure 3). Further, the values of k_{obs} calculated from the different concentration of NCS decreases with increase in $[NCS]_0$, indicating the formation of dimer of the intermediate (Figure 4).

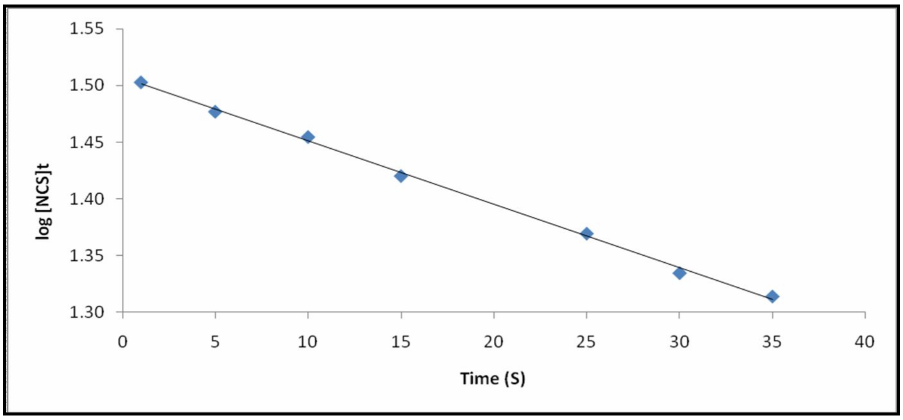


Figure 3. Plot of log $[NCS]_t$ versus time at 308 K. [Citric acid = 0.05 mol dm^{-3}]; [sodium hydroxide] =0.1 mol dm^{-3}; [N-Chloro succinimide] = 0.004 mol dm^{-3}.

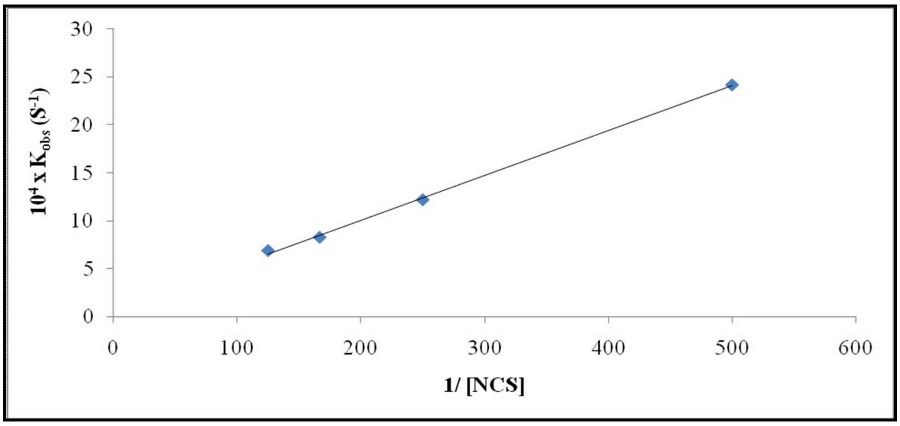


Figure 4. Plot of 1/[NCS] versus k_{obs} at 308 K. [Citric acid = 0.05 mol dm^{-3}]; [sodium hydroxide] =0.1 mol dm^{-3}; [N-Chloro succinimide] = 0.004 mol dm^{-3}.

3.2 Effect of [CA] on k_{obs}

By keeping all parameters at constant values, the values of k_{obs} for different concentration of [citric acid] is found to decrease with increase in [CA] This reveals that a less active form of citric acid was produced and hence the rate was also decreased. Further the plot of k_{obs} v_s 1/[CA] was linear (Figure 5) .

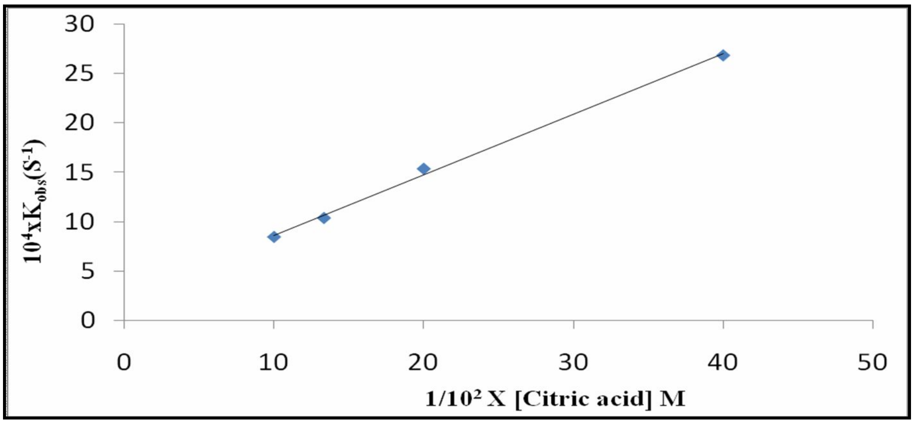


Figure 5. Plot of k_{obs} versus 1/ [citric acid] at 308 K. [Citric acid = 0.05 mol dm-3]; [sodium hydroxide] =0.1 mol dm-3; [N-Chloro succinimide] = 0.004 mol dm-3.

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} increases with increase in [NaOH]. The concentration of NaOH was varied from 0.05M to 0.20 M i.e., [NaOH]$_f$ =0.1M. Further the plot of k_{obs} v_s $[OH]^2$ is linear with positive intercept.

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 was 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 ($5x10^{-2}$M to $20x10^{-2}$M) with NaOH concentration of 0.15M 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 K, 307 K, 315 K and 322 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 (Table2). Negative values of entropy of activation suggested that the formation of a rigid transition state with a reduction of the degree of freedom of the molecules involved than the reactants.

Table 2: Kinetic and Activation Parameters for the oxidation of [CA] by [NCS]

Activation parameters	Citric acid
10^4 Ea (J/mol)	3.74
10^4 ΔH*(J/mol)	3.65
ΔS*(J/mol)	-134.41
10^4 ΔG*(J/mol)	7.79
kK_1	30.43
K_2	110

3.7 Test for free radicals

To test the intervention of the free radical during the course of the reaction, freshly distilled acrylonitrile monomer was added to the reaction mixture and kept for 2 hours under nitrogen atmosphere. No precipitate was obtained, when adding methanol which revealed that the oxidation of CA 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.

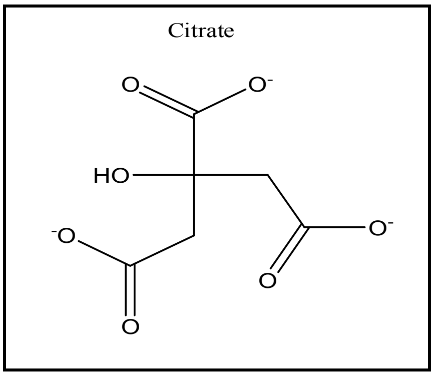
3.8 Effect of polarity on the rate constant

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

Citric acid is a slightly stronger acid than typical carboxylic acids because the anion can be stabilized by intramolecular hydrogen-bonding from other protic groups on citric acid. The pK_a values of citric acid are 3.13, 4.76 and 6.39.

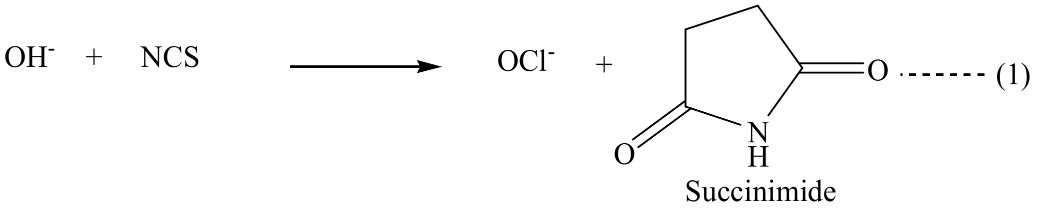
At the given experimental condition, citric acid exists as

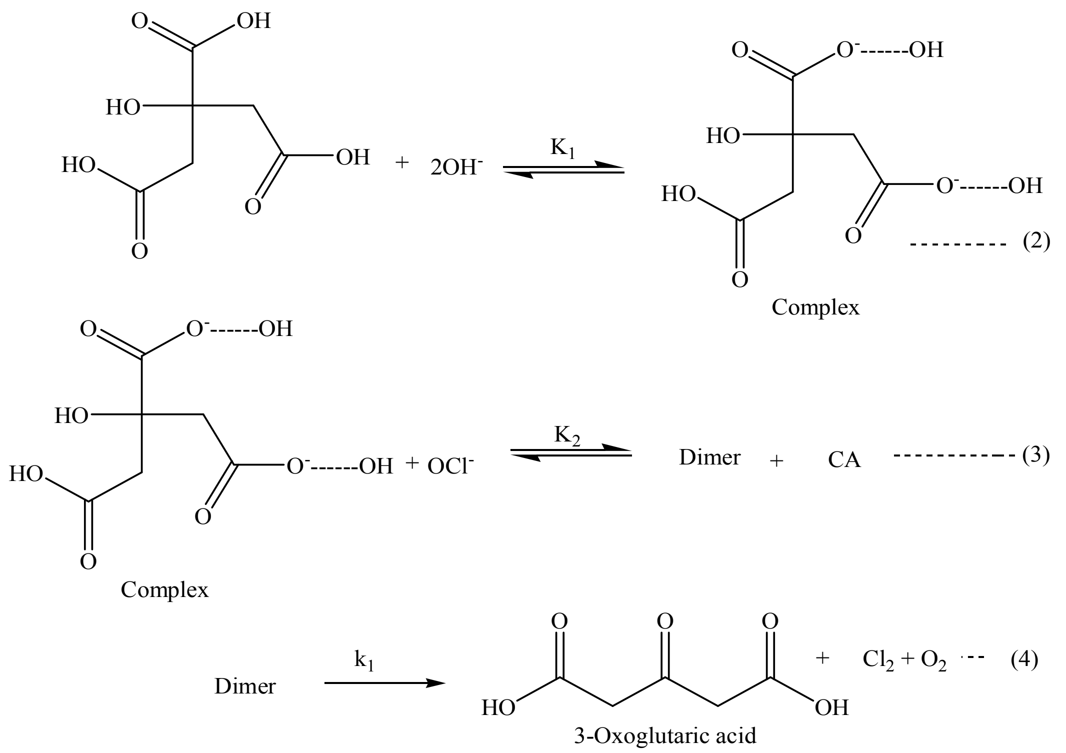


In alkaline medium NCS will react with OH^- to give OCl^-

NCS + NaOH → OCl^-

Based on the above mechanism, the following mechanism is proposed





$$\frac{-d[OCl^-]}{dt} = k_1[\text{Complex}]\,[OCl^-] \quad \text{------------------ (5)}$$

$$= \frac{k_1K_1[CA][OH]^2}{[NCS] + K_2[CA]} \quad \text{------------------(6)}$$

$$2OCl^- \xrightarrow{k_2} Cl_2 + 2NCS \quad \text{----------------------(7)}$$

$$k_{obs} = \frac{k_1K_1K_2[CA][OH]^2}{K_2[NCS] + 4[CA]} + k_2 \quad \text{------------------ (8)}$$

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