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Research Articles

REACTION KINETICS AND MECHANISM OF BUTANE-2-OL OXIDATION USING N-CHLOROPICOLINAMIDE

Sanjay K Singh[1], Deepti Pandey[2*], Ritika yadav[3]

1. Department of Chemistry Govt.T.R.S. College Rewa

2. Department of Chemistry, Govt PG College Rampur Naikin

3. Department of Chemistry, Govt Girls Degree College Rewa

** Corresponding author: pandeydeepti23@gmail.com*

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ABSTRACT:

The oxidation of butane-2-ol by a mild and selective oxidizing agent N-chloropicolinamide (NCPA) leads to the formation of corresponding substituted but-2-one. The reaction found first order in NCPA. The reaction follows Arrhenius relationship with respect to butane-2-ol. A retarding effect of acetic acid is observed. Various thermodynamic parameters have been computed. No evidence of Polymerization of acrylonitrile showed any effect of free radical on the rate of reaction. Stoichiometric study revealed 1:1 mole ratio. On the basis of thermodynamic parameters and stoichiometry a feasible mechanism has been proposed and rate law has been derived.

Keywords: Kinetics, butane-2-ol, Mechanism, NCPA, Oxidation.

1. INTRODUCTION

N-halo oxidants have a long history of acting as oxidants on a variety of substrates.[1–11] A recent addition to the N-halo family is N-chlorophthalimide

(NCPA). This study focuses on the synthesis and characterization of N-chloropicolinamide for the rapid oxidation of organic substrates.[12–14] NCPA, a phthalimide derivative, is a cheap, effective, stable, and gentle oxidant for organic materials. The existence of the N-X bond is confirmed by the elemental analysis and physical characteristics of NCPA. Because of this, the molecule might be a useful source of halonium ions.

Numerous studies have been conducted on the oxidation kinetics of secondary alcohol. They have significantly improved our comprehension of the reaction's mechanistic mechanism. Secondary alcohols follow first order kinetics and are investigated with a variety of oxidants [15–26].

The oxidation of butane-2-ol with NCPA has not been documented, according to a general assessment of the literature, which led to the current inquiry and evaluation of kinetic parameters and correlation analysis.

2. MATERIALS AND METHODS

2.1. Chemicals

Chemicals employed in this study were of A.R. grade. Double distilled water used throughout the study. The solutions were prepared without any further purification of chemicals. The solution of NCPA prepared by reported method.

2.2. Kinetic experiment

The experiments were performed under pseudo-first-order conditions by keeping an excess of the substrate over NCPA. The experiments were carried out in a black-coated stopper glass vessel to avoid any photochemical effect. A thermo-stated water bath maintained the desired temperature within ± 0.1K (308K).Requisite volumes of all reagents, except NCPA, were introduced into a reaction vessel and equilibrated at 308K. A measured volume of NCPA, equilibrated separately at the same temperature, was rapidly poured into the reaction vessel. The progress of the reactions was monitored by examining aliquots of the reaction mixture for unconsumed NCPA iodometrically using starch as the indicator.

2.3. Product analysis

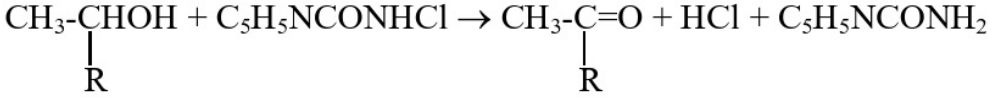
The end product from the oxidation of butane-2-ol was **But-2-one** and its presence confirm by existing conventional methods. The analysis of end product was carried out under kinetic conditions i.e., with the excess of butane-2-ol was taken over NCPA. After completion of reaction the solution is treated with an excess (200ml) of saturated solution of 2,4- dinitrophenylhydrazine (DNPH) in 2 mol/dm^3 HCl and kept in refrigerator for 24 hours. The precipitate of 2,4- dinitrophenylhydrazone (DNP) filtered, dried and weighed respectively. recrystallize the crystal of DNP with ethanol and weighed again. The DNP was found identical (m.p. and mixed m.p.) with DNP of butane-2-ol.

3. RESULT AND DISCUSSION

The oxidation of butane-2-ol was carried out by NCPA at 308K under pseudo first order condition. The rate of butane-2-ol and other experimental data were obtained. Oxidation of butane-2-ol by NCPA under the condition [NCPA] << [butane-2-ol] had the following kinetic feature.

3.1. STOICHIOMETRIC STUDIES

The stoichiometric studies of oxidation of butane-2-ol by NCPA were carried out with excess of oxidant (NCPA) and maintaining other parameters constant (HOAc-H_2O = 30 % (v/v), Temperature = 308K).The stoichiometric results indicated 1 mole of substrate consumes 1 mole oxidant as represented by the following empirical equation:



Where R = CH_2-CH_3 for butan-2-ol

There is first order rate constant is unchanged with an increase in the NCPA.

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3.1.1. Order with respect to [oxidant] [substrate]

The plots of log (a-x) vs. time (Figure 1) show first-order dependence on NCPA when the substrate (SA2) is in significant excess. It is discovered that the pseudo first-order rate constants in NCPA computed at various reactant starting concentrations are independent of the substrate concentration. Initially linear, the plot of k1vs [substrate] passes through the origin before bending toward the horizontal axis to reach a limiting value (Figure 2). As a result, the reaction exhibits fractional order behavior in relation to the concentration of the substrate.

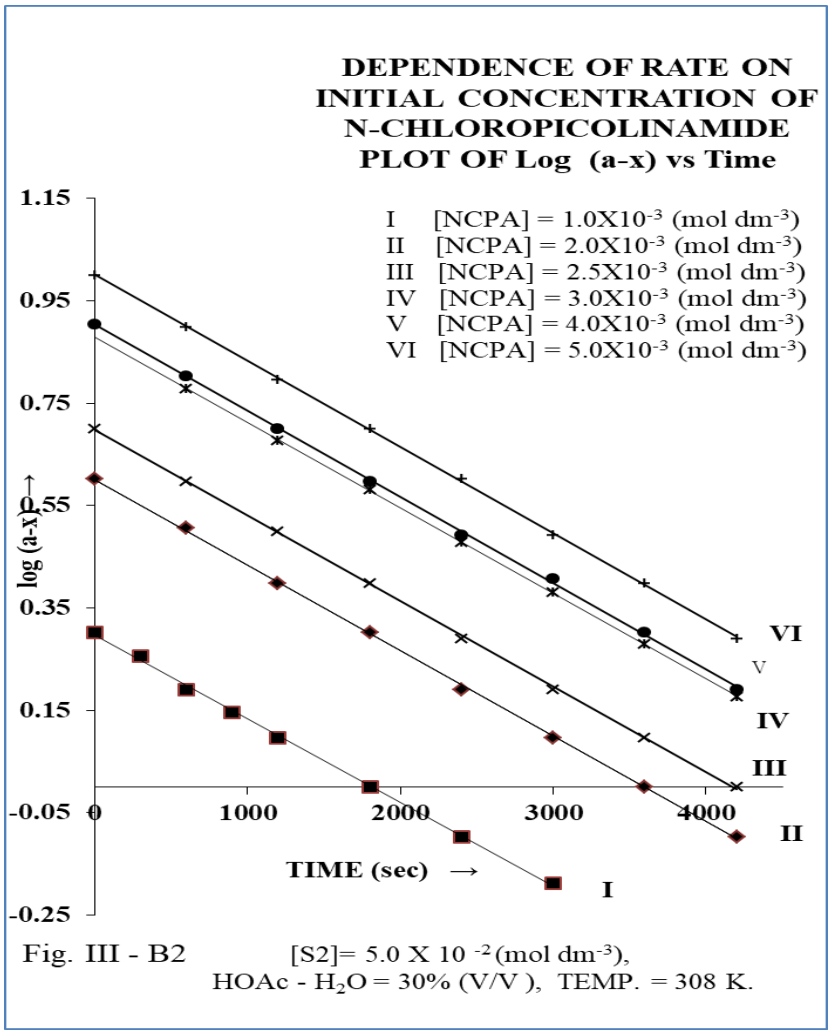

Figure 1: The plot of log (a-x) versus time. Conditions are given in Table 1.

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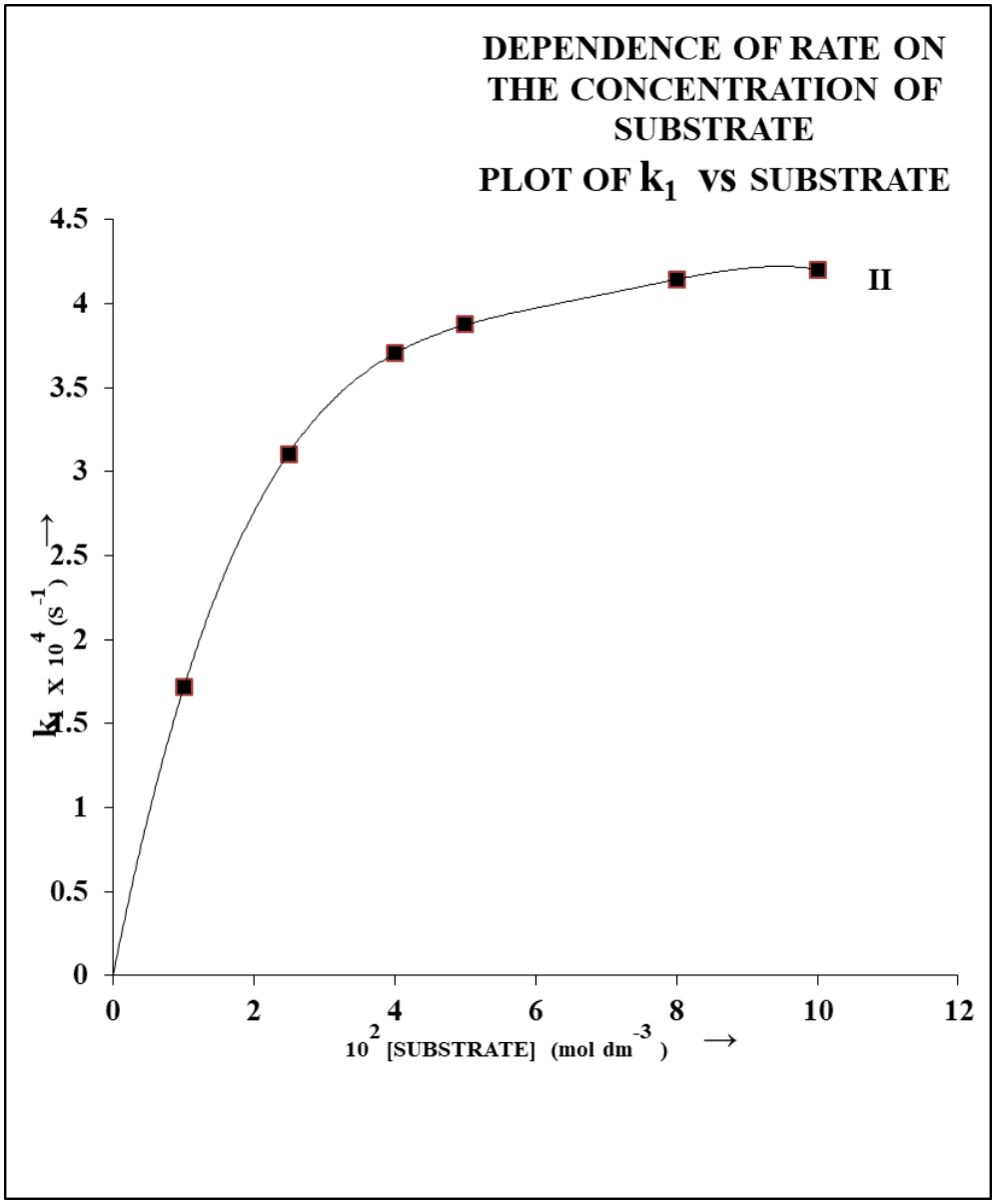

Figure 2: Dependence of k_1 on [Substrate]. Conditions are given in Table

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Table 1: Effect of variation of reactants on pseudo-order rate constant k_1 at 308K

10^2 [Substrate] (mol dm^{-3})	10^3 [NCPA] (mol dm^{-3})	$[H^+]$ (mol dm^{-3})	% HOAc - H_2O	k_1x10^4 (s^{-1})
1.00	2.50	-	30	1.717
2.50	2.50	-	30	3.104
4.00	2.50	-	30	3.706
5.00	2.50	-	30	3.878
8.00	2.50	-	30	4.142
10.00	2.50	-	30	4.203
5.00	1.50	-	30	3.589
5.00	2.00	-	30	3.538
5.00	2.50		30	3.878
5.00	3.00	-	30	3.559
5.00	4.00	-	30	3.587
5.00	5.00	-	30	3.579
5.00	7.50	-	30	3.540
5.00	2.50	0.00	30	3.878
5.00	2.50	0.10	30	4.147
5.00	2.50	0.15	30	4.406
5.00	2.50	0.20	30	4.725
5.00	2.50	0.25	30	5.142
5.00	2.50	0.30	30	5.436
5.00	2.50	0.40	30	5.703
5.00	2.50	0.50	30	6.021
5.00	2.50	-	10	4.414
5.00	2.50	-	20	4.135
5.00	2.50	-	30	3.878
5.00	2.50	-	40	3.486
5.00	2.50	-	50	3.213

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3.1.2. Effect of variation of $[H^+]$:

The catalysed kinetics was observed by the addition of perchloric acid. On varying perchloric acid concentration there is an increase in reaction rate (**Table 1**). The plot of log k_1 versus $[H^+]$ (**Figure 3**) gave a straight line with positive intercept, suggesting that acid plays a complex role in the reaction system.

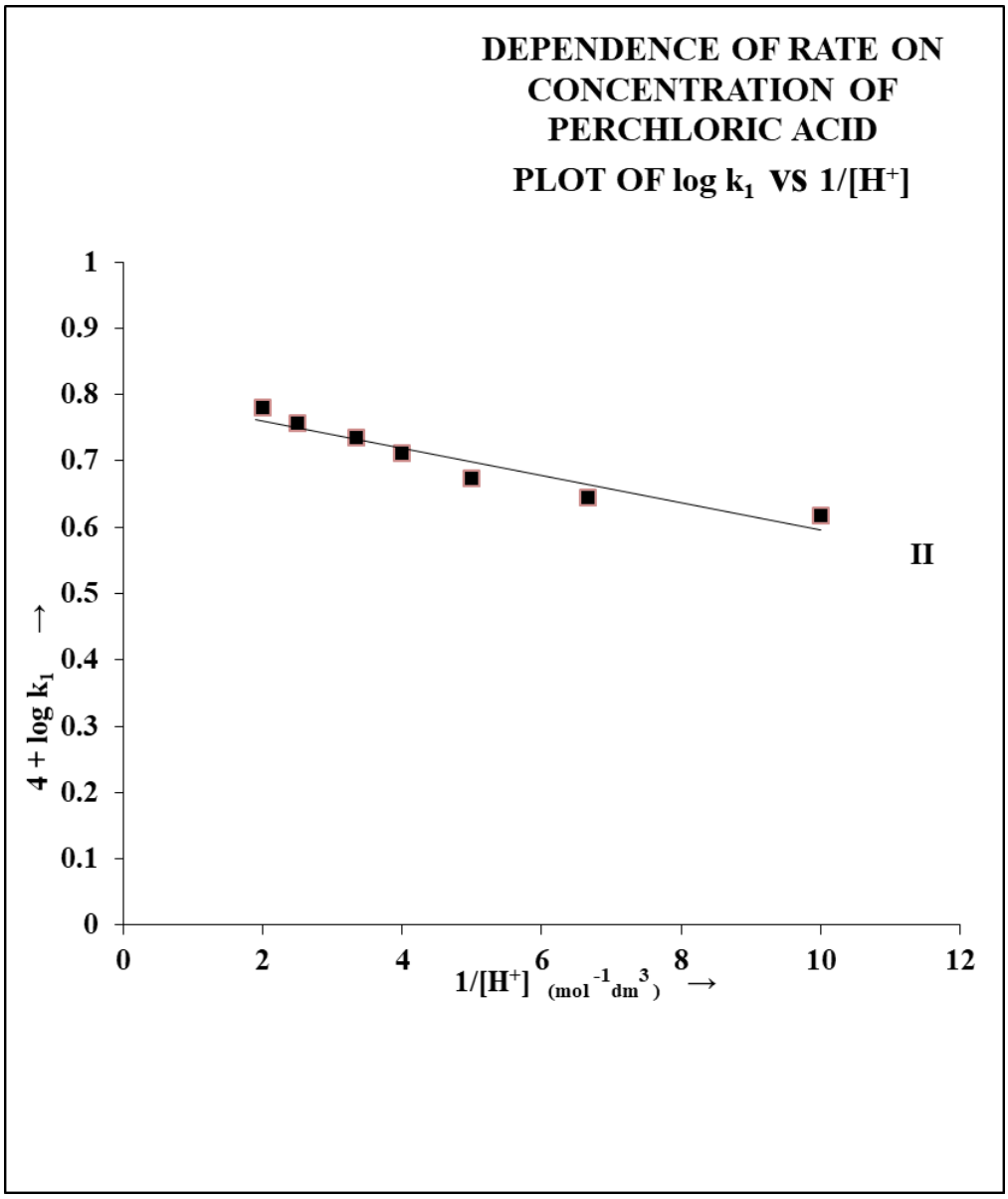

Figure 3: Dependence of k_1 on $[H^+]$. Conditions are given in Table 1.

3.1.3. Effect of solvent on reaction velocity:

The rate was studied at different concentrations of the solvent. It is observed that the rate decreases with increasing concentration of acetic acid.

3.1.4. Effect of ionic strength and Picolinamide:

The reaction rate was not influenced by the addition of chemically neutral salt. Hence the ionic behavior on slow step in the reaction mechanism is ruled out. Addition of picolinamide (one of the reaction products), at constant NCPA and substrate concentration, decreases the rate of reaction. The retardation of reaction rate on the addition of picolinamide suggests a pre-equilibrium step that involves a process in which picolinamide is one of the products. If this equilibrium is involved in the oxidation process the retardation should be an inverse function of picolinamide concentration.

3.1.5. Effect of Product and Free Radical Inhibitor:

The reaction under study failed to induce polymerization of added acrylonitrile discarding the presence of free radicals and free radical path.

3.1.6. Effect of temperature:

The effect of temperature on the reactions of butane-2-ol with NCPA in was also studied. The value of energy of activation, ΔS, ΔH & ΔG were computed. These values are summarized in **Table 2** along with the other parameters.

Table 2: Thermodynamic parameters Butane-2-ol-NCPA system

Substrate	Ea (kJ mol^{-1})	A (s^{-1})	ΔH* (kJ mol^{-1})	ΔG* (kJ mol^{-1})	-ΔS* (JK^{-1} mol^{-1})
Butane-2-ol	**71.637**	**1.05 x10^{8}**	**66.551**	**89.732**	**73.083**

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4. MECHANISM

The concentration of NCPA was found to be constant over a period of time. So, it was found that there was no appreciable reaction between acid and NCPA.

Retarding effect of picolinamide & solvent and positive effect of H+ clearly ruled out the NCPA, CH3COOCl, CH3COO+HOCl are not prime reactive species from the list of possible reactive species. Thus, the only choice and possibility that is left as a remote prime active species more probable is for HOCl. Our kinetic finding also suggests to us to assume that HOCl is to be considered as the most predominant, fertile reacting species. This leads to the postulation of the following overall mechanism and rate law.

$$NCPA + H_2O \quad HOCl + Picolinamide$$

$$NCPA + H^+ \rightleftharpoons NCPAH^+$$

$$NCPA + H^+ \rightleftharpoons Picolinamide + Cl^+$$

$$NCPA + H_2O \rightleftharpoons HOCl + Picolinamide$$

$$HOCl + H^+ \rightleftharpoons H_2O^+Cl$$

$$NCPAH^+ + H_2O \rightleftharpoons H_2O^+Cl + Picolinamide$$

$$NCPA + CH_3COOH \rightleftharpoons Picolinamide + CH_3COOCl$$

$$CH_3COOCl + H^+ \rightleftharpoons CH_3COO^+HCl$$

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$$NCPA + H_2O \overset{K_1}{\rightleftharpoons} HOCl + \text{Picolinamide (PA)} \quad (1)$$

$$HOCl + H^+ \overset{K_2}{\rightleftharpoons} H_2O^+Cl \quad (2)$$

$$NCPA + H^+ \rightleftharpoons NCPAH^+ \quad (3)$$

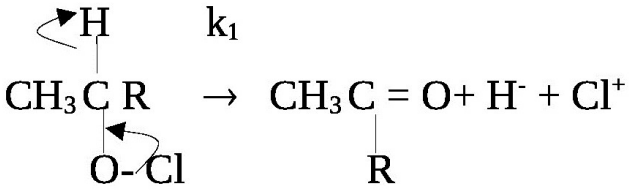
$$NCPAH^+ + H_2O \rightleftharpoons H_2O^+Cl + \text{Picolinamide (PA)} \quad (4)$$

$$CH_3\underset{\underset{OH}{|}}{CH}R + HOCl \overset{K_3}{\rightleftharpoons} CH_3\underset{\underset{O\text{-}Cl}{|}}{CH}R + H_2O \quad (5)$$

$X_1^{\#}$

$$CH_3\underset{\underset{OH}{|}}{CH}R + H_2O^+Cl \overset{K_4}{\rightleftharpoons} CH_3\underset{\underset{O^+HCl}{|}}{CH}R + H_2O \quad (6)$$

$X_2^{\#}$



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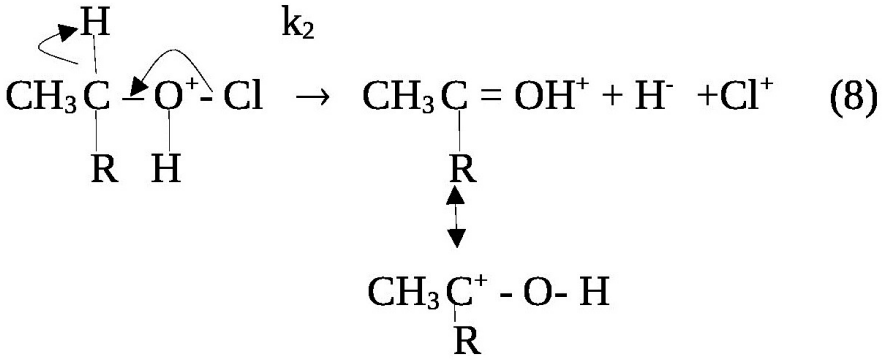

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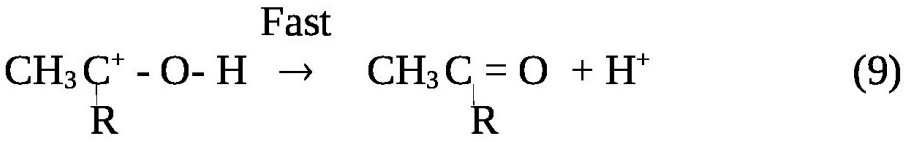

(9)

On the basis of the aforementioned steps involved in the proposed mechanism and at steady state approximation condition, the final rate law is derived as;

$$k_{obs} = \frac{[SA]\ (k_1K_3 + k_2K_4\,K_2\,[H^+])\,K_1}{[PA] + K_1 + K_3\,[SA]\,K_1 + K_2\,K_1\,[H^+]\,(1+K_4\,[SA])}$$

This proposed rate law explained all experimental facts.

5. CONCLUSION

A particular type of secondary alcohol is prop-2-ol. Initially, the substrate generated a complex that HOCl, an active species of NCPA, attacked. The kinetics of NCPA's oxidation with various other substrates is similar to those of the oxidation of several other compounds with N-halo oxidants [27–30]. An intermediate complex is created, which then breaks down at a gradual rate to produce the final result. The Arrhenius

relationship is obeyed by the reaction. The results of the experiments are consistent with the suggested mechanism.

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