Journal of Advances in Science and Technology
Vol. 22, Issue No. 1, March-2025, ISSN 2230-9659

DOI: https://doi.org/10.29070/3razbr88

Experiment of Kinetics Oxidation of Substituted 3'-4'-Dimethylphenyl by N-chlorosaticarin in Acetic-acid Reaction

Ranjan Kumar [1] * , Dr. Ajendra Kumar [2]

1. Research Scholar, Dept. of Chemistry, Magadh University, Bodh Gaya, Bihar, India
ranjasondiha@gmail.com ,
2. Assistant Professor, Dept of Chemistry, S.M.S.G.College Sherghati (Gaya), Bihar, India

Abstract: The oxidation process of 3'-4'-dimethylphenyl time and butanoic acid using N-chlorosaccharin in an acetic acid medium, with perhydrochloric acid as a catalyst, was investigated. The reaction followed a primary order with respect to [ka], [NCSA], and [H+]. The sole oxidation product identified was 3,4-dimethylbenzoic acid. To regulate the reaction rate involving the acid and its products, saccharin formed as a byproduct was introduced. The dissociation of ionic forces within the reaction site had minimal influence on oxidation speed across various conditions. However, a slight reduction in the dielectric constant led to a moderate increase in reaction rate. Hypochlorous acid (H_2O^+Cl) was proposed as the primary oxidizing agent. A reaction mechanism was suggested, aligning with experimental observations, and activation parameters were determined for the rate-limiting steps.

Keywords: Kinetic energy, Oxidation, Dimethylphenyl, NCSA, N-Chlorosaccharin

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INTRODUCTION

The kinetic reactions of N-halo compounds play a crucial role in synthetic chemistry, contributing to the development of various chemical pathways. Chemical kinetics, a branch of physical chemistry, focuses on understanding reaction rates and their influencing factors. While thermodynamics explains energy transformations within a process, it does not provide insights into reaction speed. In this analogy, thermodynamics serves as the "arrow of time," while chemical kinetics acts as the "clock," measuring how fast reactions occur.

Chemical kinetics is an interdisciplinary field that connects scientific principles with practical applications in multiple domains. It provides a framework for analyzing both the qualitative and quantitative aspects of chemical and physical processes. The study of reaction kinetics is essential for understanding reaction mechanisms, which in turn help in predicting the behavior of chemical systems[1].

The significance of kinetic reactions lies in their ability to explain the underlying mechanisms of chemical transformations. By gaining insights into reaction pathways, scientists can determine not only fundamental principles of nature but also optimize reaction conditions for industrial and commercial applications. Many industrial processes rely on alternative reaction routes, and a thorough understanding of mechanisms allows for the selection of conditions that enhance efficiency and yield.

Thus, we know chemical kinetics as reaction kinetics, chemical kinetics investigates the rate of processes.

The measure on this research on secondary experiment like A3 or A4 reaction and its conditions should be affect the rate of chemical reactions, and information on the mechanisms and transitional states of reactions, as well as how they affect the construction of mathematical models that can explain the properties of chemical reactions.[2]

The N-Halo compounds were used in detail as oxidizers for organic substrates. The N-Halo compounds were the source of positive halogens and were used as oxidants for various substrate in acid-base concentration.[3] The nature and mechanism of active oxidation vary depending on the specific species involved, with the functional group attached to the nitrogen playing a crucial role in determining reaction pathways. Numerous studies have documented the oxidation of organic compounds using N-halo compounds under different reaction conditions. It has been observed that the oxidation and decomposition of N-chloroacetylcysteine, an active compound in this context, have not been systematically studied in motor-based testing[4].

In acidic aqueous acetic acid medium, the presence of perchloric acid facilitates the formation of N-chloroacetic acid, which contains a 3'-4' dimethylphenyl group. This reaction has been shown to influence the oxidation kinetics of butanoic acid, with kinetic results providing valuable insights into the underlying oxidation mechanisms.

Experimental Research- 3'-4'dimethylphenyl such as N-chlorosaticarine and butanoic acid were prepared using the reported methods. ouble-distilled water and purified acetic acid were used in the experimental setup. Perchloric acid served as the primary source of hydrogen ions, ensuring a controlled acidic environment for the reaction. The concentration of hydrogen ions remained constant throughout the process, maintained by the addition of sodium perchlorate as a stabilizing agent[5].

The reactions were conducted under pseudo-first-order conditions, where [KA] was significantly higher than [NCSA]. Following the reaction, potentiometric measurements were carried out by immersing platinum and reference electrodes in the reaction mixture to stabilize the ion-cell response. The experiments were performed using an Equip-Tronic potentiometer, specifically designed for thermodynamic assessments. The time constant was periodically measured, while continuous stirring ensured uniform mixing of the reaction components. The reaction rate constant, determined through logarithmic calculations, exhibited reproducibility within ±5%,[6] following a pseudo-first-order kinetic model over time.

The oxidation reaction of acetoacetic ester with N-chlorosaccharin in aqueous acetic acid has been a subject of extensive investigation, particularly in mechanistic studies. This reaction has attracted significant research interest over the years due to its implications in kinetic modeling and chemical transformation processes. Notably, this reaction was also explored in the work of German chemists, further emphasizing its significance in the field of reaction kinetics[7].

Long before Wilhelmy did his job, some measurements, reaction kinetics, and reaction mechanisms were made. Still, the mechanism cannot be reliably derived, as subsequent testing may indicate unexpected complications. Kinematic studies can refute mechanisms, but certainly cannot create mechanisms. Kinematic studies cover a wide range of areas from several perspectives.

Arrhenius conducted a quantitative analysis of fundamental reactions by studying the relationship between reaction rates and temperature, expressed by the equation k=Ae−Ea/RTk = Ae^{-E_a/RT}k=Ae−Ea/RT, where AAA is the pre-exponential factor, EaE_aEa is the activation energy, RRR is the universal gas constant, and TTT is the absolute temperature. This equation establishes a direct correlation between temperature and reaction rate. Additionally, the Eyring–Polanyi equation provides an alternative approach to reaction rate theory, which is derived from statistical mechanics and transition state theory.

This formulation is represented by the equation kr=kBT/h·e−ΔG‡/RTk_r = k_B T/h \cdot e^{-\Delta G^\ddagger/RT}kr=kBT/h·e−ΔG‡/RT, where krk_rkr is the reaction rate constant, kBk_BkB is the Boltzmann constant, hhh is Planck's constant, and ΔG‡\Delta G^\ddaggerΔG‡ is the Gibbs free energy of activation. These equations highlight the role of temperature and molecular energy in determining reaction kinetics.

Regarding research developments, one of the earliest kinetic studies involved N-chlorosaccharin. It was observed that benzoyl alcohol oxidation was catalyzed by an NCSA derivative, where saccharin served as a stabilizing agent[8]. The oxidation process was influenced by both NCSA and hydrogen ion concentration, indicating that the reaction followed a specific order with respect to these components.

Further investigations proposed hypochlorous acid (HOCl) as the active oxidant in the reaction. The kinetic studies revealed that alcohol oxidation proceeded via CH bond fragmentation, ultimately leading to the formation of hydroxyl acid[9]. The role of NCSA in facilitating this oxidation was confirmed through controlled experiments, demonstrating its effectiveness in promoting the reaction mechanism.

RESULTS AND DISCUSSION

The obtained results that the stoichiometry and reaction products are different reaction mixtures containing different amounts of NCSA and Ka with constant concentrations of perchloric acid and sodium perchlorate were reacted at 30°C for 24 hours. The remaining NCSAs were estimated. The oxidation products were identified as 3.4-dimethylbenzoic acid and saccharin. Products were identified by determining melting points, chemical tests, and TLC. The results are consistent with a 1:01 stoichio-metry:-

$$(CH_3)_2\ C_6H_3COCH_2CH_2COOH + C_6H_4SO_2\ CONCI + 5\ H_2O$$
$$H^+$$
$$(CH3)_2\ C_6H_3COOH + C_6H_4SO_2CONH + 3\ CO_2 + 6\ H_2 + HCI \qquad \ldots\ldots(1)$$

Experimental results of NCSA: The reaction order was determined by analyzing the slope of a double logarithmic plot, obtained by dissolving one of the reactants (KA) in perchloric acid while maintaining the concentration of other reactants constant. The plot of log K against log KA exhibited linearity with a correlation coefficient of r=0.991r = 0.991r=0.991, while log KA against log KA followed a similar linear trend with r=0.993r = 0.993r=0.993. These results support the conclusion that the reaction follows a first-order dependence on KA, NCSA, and H^+. The linearity of the log-NCSA plot as a function of time further confirms the primary order of the reaction with respect to [NCSA].

Effect of Added Saccharin

The impact of saccharin on the reaction rate was examined by varying its concentration between 0.02 and 0.1 mol dm−3^{-3}−3. It was observed that the presence of saccharin led to a decrease in the oxidation rate of keto acid, indicating its inhibitory effect on the reaction.

Effect of Ionic Strength and Dielectric Constant

The influence of the reaction medium's dielectric constant on the reaction rate was assessed by conducting the reaction in solvents of varying compositions. The results demonstrated a significant increase in reaction rate with an increasing proportion of acetic acid in the solvent mixture. The effect of ionic strength was further investigated by varying the concentration of sodium perchlorate ($NaClO_4$) in the reaction medium. It was found that changes in ionic strength had no significant impact on the reaction rate of NCSA, suggesting that the oxidation process is independent of ionic strength[10].

Additionally, the reaction was carried out in the presence of acrylonitrile, a well-known free radical scavenger. The absence of any observable radical formation confirmed that the oxidation reaction does not proceed via a free radical mechanism.

Table-1

Rate constants for oxidation of 4-oxo4-(3’-4”-dimethylphenyl) butanone acid on NCSA in aqueous acetic acid 30°.

10^3 [KA] mol dm^{-3}	10^3 [NCSA] mol dm^{-3}	[H^{+3}] mol dm^{-3}	10^3 k_1bs^{-1}	10^3 k_2c dm^{-3}mol^{-3} s^{-1}
2.0	2.0	0.5	5.35±0.13	26.70±0.13
4.0	2.0	0.5	9.73±0.53	24.35.35±0.13
6.0	2.0	0.5	15.5±0.1	25.80±0.2
8.0	2.0	0.5	21.0±1.4	26.30±1.08
2.0	2.0	0.8	7.70±0.37	0.96±0.0.05
2.0	2.0	1.2	12.00±0.7	1.00±0.06
2.0	2.0	1.6	13.30±0.9	0.95±0.07
2.0	1.5	0.5	5.26±0.19	5.35±0.13
2.0	1.0	0.5	5.37±0.23	5.35±0.13

2.0	0.5	0.5	5.38±0.25	5.35±0.13

General conditions: [Nacio4] = 1.5 mol+ dm*, solvents compositions: 50.00% acetic-acid 50.00% water B (V/V); Errors specified with AI values estimated from the pseudo-primary diagram are 95% confidentiality limit for the "student T" test.[7] Individual K2 values estimated as K1/$[H^+]$.

Effect of Temperature: Reaction kinetics were measure on the different temperature. Activations parameter of the oxidations of keto-acids by NCSA were evaluating for the gradient on Arrheniu's diagram. The obtained $\Delta H^{\#}$ and $\Delta S^{\#}$ obtained values were 22.1 KJ mol^{-1} or -202.1 JK^{-1} mol^{-1}.

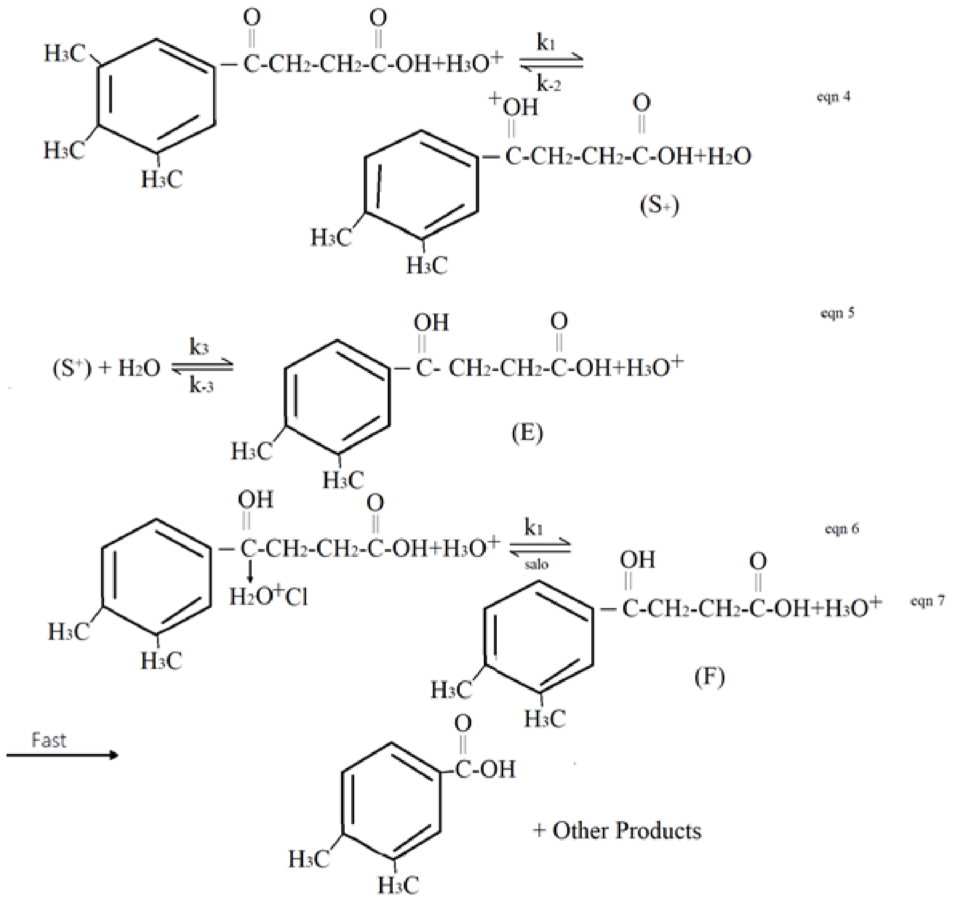
Mechanism: The literature shows that potential reactive species of NCSA are present in acidic solutions. This response is primary in [NCSA], KA, and H^+. This rate of the reaction increase with the increase on H^+ at a constants -ionic strengths. This indicates on masure reactions passes completely' throughs the acid catalysed pathway's. Changes on media polarity have a major effect on reaction rate. The observed trends can be attributed to multiple factors. It may be due to a decrease in the dielectric medium and prefers to react with protonation. Furthermore, the enolation of keto acids can be catalysed by acetic-acid, which can also contribute to fractional reinforcement. The diagram for log-k_1 compared to 1/d is a linear has been positives gradient (r = 0.987), indicating the interaction between positive ions and dipol molecules. It support the assumption of H_2O^+Cl as a reactivate species. The delay in reaction-rate when adding saccharin indicates that the iso-weight step affects the process of which saccharin is a products.

$$\mathrm{NCSA} + H_3O^+ \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} H_2O^+Cl + \mathrm{Saccharin}$$ eqn…2

If it is an equilibrium oxidation process, then the rate of oxidation should be the inverse function of saccharin concentration. This is obtained due to the observation that the rate of oxidation is the inverse of a constant and has a linear center (r = 0.999) diagram i.e., Saccharin.

$$\mathrm{NCSA} + H_3O^+ \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} H_2O^+Cl + \mathrm{Saccharin}$$ eqn………..3

The mechanism was proposed and influence attack on $[H_2O+Cl]$ on -enol for these substrates (E) in the rate determination step.[11] Enolation is known to have been proposed as a necessary step prior to substrate oxidation.



Eqn-(7) it clearly shows the observed results. H. in reverse order in [KA], [NCSA], [H$^+$] and Saccharin. Khan et al. analyzed the oxidation process, identifying its kinetic characteristics in the formation of benzilic acid and oxidanedicarboxylic acid by N-chlorosaccharin in an aqueous acetic acid medium. The study examined the effect of substrate concentration on reaction rates, confirming that the reaction follows first-order kinetics with respect to both the substrate and NCSA. Additionally, it was observed that the presence of perchloric acid ($HClO_4$) exhibited an inhibitory effect on the reaction.

The study also revealed that variations in the dielectric constant of the reaction medium led to a decrease in the reaction rate. The active oxidant species involved in the process were identified, supporting the proposed reaction mechanism. Based on kinetic data, a plausible mechanistic pathway was suggested to explain the observed results.

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