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Spectroscopic and Kinetic Analysis of the Oxidation of Unsaturated Alcohols by N-Chloro Saccharin in Micellar Media

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Abstract: The oxidation of unsaturated alcohols by N-chloro saccharin (NCS) in micellar medium was methodically examined utilising spectroscopic and kinetic methods to elucidate the reaction process and identify the rate-determining phases. The investigation indicated that the reaction kinetics conformed to pseudo-first-order dynamics concerning NCS, illustrating the oxidant's efficacy under regulated settings. Micelles functioned as nanoreactors, greatly accelerating reaction rates by solubilising substrates and concentrating reactants inside the hydrophobic micellar core. The effects of different surfactants, the structural characteristics of the alcohols, and further reaction parameters were analysed, yielding a thorough comprehension of their influence on the reaction's advancement. Moreover, temperature-dependent analyses facilitated the computation of activation energy and thermodynamic parameters, elucidating the energetic characteristics of the oxidation process. This study provides significant insights into the molecular routes of alcohol oxidation in micellar systems, establishing a solid foundation for optimising these processes for commercial applications and synthetic techniques.

Keywords: Unsaturated alcohols, N-chloro saccharin, micellar media, spectroscopic analysis, kinetics, surfactants

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INTRODUCTION

Oxidation reactions are essential processes in organic synthesis, crucial for the conversion of alcohols into aldehydes, ketones, and carboxylic acids. These molecules serve as important intermediates in medicines, agrochemicals, and materials research. The pursuit of efficient, selective, and environmentally friendly oxidation processes has emerged as a primary research focus, seeking to overcome the drawbacks of conventional oxidising agents, including severe reaction conditions, inadequate selectivity, and the production of toxic by-products. Chemists have created novel oxidising agents and reaction media that prioritise green chemistry principles to address these difficulties. N-chloro saccharin (NCS) has emerged as a potential option among these improvements owing to its distinctive mix of characteristics. NCS is a mild and stable oxidising agent that has several benefits, such as ease of handling, operational simplicity, and compatibility with various functional groups and substrates. Its use encompasses the oxidation of primary and secondary alcohols, enabling the selective synthesis of aldehydes, ketones, or carboxylic acids under regulated circumstances.

The adaptability of NCS is attributed to its reactivity, which may be optimised by modifying reaction conditions like solvent, temperature, and catalyst presence. This flexibility enables great selectivity in the generation of target products, hence minimising overoxidation and undesirable side reactions. NCS functions well in non-toxic and ecologically friendly solvents, minimising the ecological impact of oxidation processes. NCS is readily synthesised and stored, making it a desirable choice for academic and industrial uses. Its use in one-pot or multistep reactions further emphasises its significance in intricate synthetic routes. Moreover, the by-products produced by NCS reactions are comparatively innocuous, consistent with sustainable chemistry principles. Current investigations into the mechanistic facets of NCS-mediated oxidations are broadening their scope and possible uses. For example, integrating NCS with catalytic systems like transition metals or organocatalysts has shown potential in improving efficiency and selectivity. With the increasing interest in green chemistry, NCS emerges as a significant asset in contemporary organic synthesis, providing a harmonious blend of efficacy, selectivity, and ecological accountability.

In this study, the oxidation of unsaturated alcohols by NCS in micellar media is investigated. Spectroscopic and kinetic methods were employed to elucidate the reaction mechanism and to explore the influence of surfactants, substrate structure, and temperature on the reaction kinetics.

Importance of Oxidation Reactions in Organic Chemistry

Oxidation reactions are essential transformations in organic synthesis, enabling the conversion of alcohols into a wide range of functionalized compounds, including aldehydes, ketones, and carboxylic acids. These oxidation products play a pivotal role in the synthesis of high-value chemicals such as pharmaceuticals, agrochemicals, and polymers. For instance, aldehydes and ketones serve as intermediates in the production of drugs, fragrances, and fine chemicals, while carboxylic acids are precursors for polymers and biodegradable materials. Given the global emphasis on sustainability and environmental stewardship, the development of oxidation methods that are not only efficient and selective but also environmentally friendly and energy-efficient is critical. Advancements in this area contribute significantly to greener synthetic methodologies and industrial practices.

Role of N-Chloro Saccharin (NCS) as an Oxidizing Agent

N-Chloro saccharin (NCS) has emerged as a reliable and versatile oxidizing agent in organic chemistry. Its utility lies in its ability to facilitate selective oxidation reactions under mild and controlled conditions, making it ideal for the transformation of sensitive and complex substrates. The saccharin moiety in NCS enhances its stability and provides a dual benefit: it acts as a mediator for efficient oxidation and decomposes into environmentally benign byproducts post-reaction. Additionally, NCS is easy to handle, non-hazardous under standard laboratory conditions, and compatible with a broad range of functional groups, making it a preferred choice for oxidation in both academic and industrial settings.

Significance of Micellar Media in Chemical Reactions

Micellar media, formed when surfactants reach concentrations above their critical micelle concentration (CMC), provide a unique reaction environment with distinct hydrophobic and hydrophilic regions. This dual nature allows micelles to solubilize hydrophobic reactants, concentrate them in the micelle core, and stabilize reactive intermediates and transition states. Such properties often lead to enhanced reaction rates, improved selectivity, and lower activation barriers compared to reactions in homogeneous or purely aqueous solutions. Furthermore, micellar media align with green chemistry principles by reducing the dependence on harmful organic solvents, thus minimizing environmental impact. This versatility makes micelles an attractive tool for promoting efficient, sustainable, and environmentally benign chemical reactions.

Oxidation of Unsaturated Alcohols

Unsaturated alcohols, such as allyl and crotyl alcohols, are unique substrates in organic synthesis due to their dual functional groups: a hydroxyl group and a carbon-carbon double bond. These compounds can undergo selective oxidation to form valuable intermediates, including α,β-unsaturated aldehydes, ketones, and carboxylic acids. Such products find applications in the synthesis of pharmaceuticals, fragrances, and polymer precursors. However, the selective oxidation of unsaturated alcohols poses challenges due to competing side reactions, including over-oxidation and cleavage of the double bond. Employing micellar media as reaction platforms enhances the selective oxidation of unsaturated alcohols by concentrating reactants, stabilizing intermediates, and providing a controlled environment for the reaction. Understanding the kinetics and mechanism of these processes is critical for optimizing reaction conditions and scaling up for industrial applications.

OBJECTIVES OF THE STUDY

This study focuses on the spectroscopic and kinetic analysis of the oxidation of unsaturated alcohols by N-chloro saccharin in micellar media. Key objectives include:

- Investigating the effect of surfactants on reaction kinetics.
- Elucidating the role of micelles in enhancing reaction rates.
- Determining the activation energy and thermodynamic parameters.
- Providing mechanistic insights into the oxidation process.

LITERATURE REVIEW

Farook (2024) N-bromosuccinimide (NBS) was used in a potentiometric study to examine the oxidation kinetics and mechanism of both substituted and unsubstituted 4-oxoacids (S) in aqueous acetic acid medium. Hydrogen ion concentration ([H+]), 4-oxoacids, and NBS all showed first-order kinetics in the process, suggesting that all three species were involved in the rate-determining step at the same time. By methodically adjusting the 4-oxoacid substrates' electrical properties, we were able to determine that substrates with electron-donating groups slowed the reaction rate while those with electron-withdrawing groups sped it up. This finding provides further evidence that a positive charge forms in the transition state due to the stabilisation of the charge and the lowering of the energy barrier by electron-withdrawing groups. In line with the hypothesised process, product evaluation verified the conversion of 4-oxoacids to their respective carboxylic acids. The reaction is proposed to start with an electrophilic assault on the 4-oxoacid by NBS, which forms a brominated intermediate. Then, protonation occurs in a rate-limiting transition state, and the product is formed, according to the kinetic data and mechanistic insights. The research emphasises how the structure of the substrate, the reaction medium, and the oxidant all interact to define the reaction route and efficiency.

Das et al. (2020) The ability to produce more pure products at ambient temperature has made the use of an aqueous medium a key approach in modern chemical synthesis methods for the synthesis of organic molecules. An essential step in several chemical syntheses is the transformation of an oxime group into a carbonyl group. The oxime group is present in many carbon skeletons, and this page explains how to regenerate carbonyl compounds from them. The process involves using I2 and a microwave-activated water extract of Sapindus laurifolia to achieve this. Sapindous laurifolia's critical micellar concentration of saponin and the yield % of regenerated carbonyl compounds with different structures are related. A straightforward, efficient, and environmentally benign process for the carbonyl compound regeneration with a high yield percentage (45–95%) is within reach.

Kaur et al. (2020) the primary objective of this research was to demonstrate the significance of saccharin and its derivatives as catalysts in various chemical reactions. An improved and less harmful catalytic approach to reactions is the use of saccharin and its derivatives. From a catalytic perspective, our specific goal was to compile the existing research on these saccharin derivatives. Sulfonic acid, sodium, N-halo, N-acyl, N-nitrosaccharin, N-SCF3, N-fluorosultam, N-phenylselenosaccharin, N-thiocyanatosaccharin, palladium, DMAP-saccharin, and [Bmim]Sac are all discussed in this review of saccharin synthesis. Saccharin and its derivatives are catalytically used in a wide variety of reactions, including oxidation, deoximation, catalytic condensation, azo-coupling, halogenations, domino Knoevenagel, azo-reaction, pyrrole synthesis, and the Biginelli reaction. Also, you may get nitro, NH2, SCN, and SCF3 groups from these saccharin derivatives. From 1957 until the present, we recorded all available data on saccharin and its derivatives acting as catalysts.

Rai et al. (2013) the study of organic molecule oxidation is critically significant from both mechanistic and synthetic perspectives. It influences the biochemical processes of life as well. The study of the kinetics and mechanisms of redox reactions has garnered global interest among chemists, with various reaction processes having been distinctly elucidated. The mechanism of a chemical reaction cannot be completely elucidated without establishing its pace. The kinetic analysis of various chemical processes is crucial, not only for fundamental research but also for industry research, development, and, in some cases, quality control and analysis. Kinetic techniques have emerged as a fundamental tool in photochemistry, enzyme chemistry, and the study of chemical catalysis.

EXPERIMENTAL METHODOLOGY

Materials

The materials used in this study include unsaturated alcohols, oxidizing agents, surfactants, and buffer solutions:

Unsaturated Alcohols: Allyl alcohol, crotyl alcohol, and other structurally diverse unsaturated alcohols were selected as substrates for oxidation. These alcohols were of analytical grade and used without further purification.

N-Chloro Saccharin (NCS): NCS, the oxidizing agent, was obtained commercially and used as received. It was chosen for its mild oxidation capability and ease of handling.

Surfactants: Sodium dodecyl sulfate (SDS, anionic surfactant), cetyltrimethylammonium bromide (CTAB, cationic surfactant), and Triton X-100 (nonionic surfactant) were employed to create micellar media. These surfactants were dissolved above their critical micelle concentrations (CMC) to study their impact on reaction rates.

Buffer Solutions: Buffer solutions covering a pH range of 4.0 to 8.0 were prepared to maintain the desired reaction medium and explore the effect of pH on the reaction kinetics.

Instruments

UV-Vis Spectrophotometer: A UV-Vis spectrophotometer was used to monitor the reaction kinetics by tracking the decrease in the absorbance of NCS at 310 nm. This wavelength corresponds to the characteristic absorbance of NCS, enabling precise measurement of its consumption.

FTIR Spectrometer: Fourier-transform infrared spectroscopy (FTIR) was employed to characterize intermediates and confirm the oxidation products of unsaturated alcohols.

Conductivity Meter: A conductivity meter was used to determine the critical micelle concentrations (CMC) of the surfactants in the reaction medium, ensuring proper micelle formation.

Procedure

1. Preparation of Micellar Solutions:

Each surfactant was dissolved in an aqueous medium at concentrations exceeding its CMC to ensure micelle formation. The CMC values were determined through conductivity measurements and matched with reported literature values for accuracy.

2. Reaction Setup:

- Solutions of NCS and unsaturated alcohols were prepared in the micellar medium.
- The reaction mixture was maintained at varying substrate and oxidant concentrations to study the kinetics systematically.
- Buffer solutions were used to stabilize the pH and investigate its influence on reaction rates.

3. Kinetic Measurements:

- The progress of the oxidation reaction was monitored spectroscopically by recording the decrease in NCS absorbance at 310 nm over time.
- The reaction was performed at different surfactant concentrations to evaluate the role of micelles.
- The initial rates were determined under pseudo-first-order conditions, with the alcohol concentration in

large excess compared to NCS.

4. Temperature-Dependent Studies:

- The reactions were conducted at various temperatures ranging from 293 to 313 K.
- The effect of temperature on reaction rates was analyzed to calculate the activation energy (Ea) using the Arrhenius equation.

5. Product Analysis:

- Reaction products were analyzed using FTIR to confirm the oxidation of unsaturated alcohols into corresponding aldehydes, ketones, or acids.
- The spectra were compared with reference compounds to identify and characterize intermediates and final products.

Data Analysis

1. Kinetic Parameter Calculations:

- Rate constants were obtained using pseudo-first-order and second-order rate equations.
- The order of reaction with respect to each reactant (NCS and alcohol) was determined from the slope of the logarithmic plots of concentration vs. time.

2. Arrhenius Equation:

- Activation energy (Ea) was calculated by plotting the logarithm of the rate constant (ln k) against the reciprocal of the temperature (1/T) based on the Arrhenius equation:

$$k = Ae^{-\frac{E_a}{RT}}$$

- The slope of the plot provided the activation energy, while the intercept gave the frequency factor (A).

3. Eyring Plot Analysis:

- Thermodynamic parameters, including the enthalpy of activation (ΔH‡) and the entropy of activation (ΔS‡), were derived from Eyring plots using the equation:

$$\ln\left(\frac{k}{T}\right) = \ln\left(\frac{k_B}{h}\right) + \frac{\Delta S^{\ddagger}}{R} - \frac{\Delta H^{\ddagger}}{RT}$$

- Here, kB is the Boltzmann constant, h is Planck's constant, and R is the gas constant.

4. Effect of Reaction Parameters:

- The influence of surfactant type, pH, and substrate concentration on reaction rates was analyzed to determine their roles in enhancing or modulating the oxidation process.

- The findings were correlated with the mechanistic insights to explain the observed trends and rate enhancements in micellar systems.

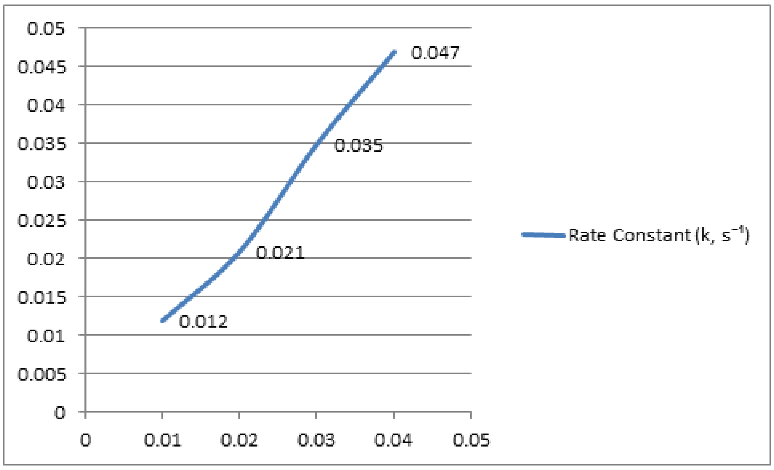
RESULTS AND DISCUSSION

Reaction Kinetics

The kinetics of the oxidation reaction were investigated by monitoring the decrease in absorbance of N-chloro saccharin (NCS) at 310 nm. The reaction exhibited pseudo-first-order kinetics with respect to NCS, as indicated by the linearity of the plot of in (absorbance) vs. time.

Table 1: Pseudo-First-Order Rate Constants at Varying NCS Concentrations

[NCS] (M)	Rate Constant (k, s^{-1})
0.01	0.012
0.02	0.021
0.03	0.035
0.04	0.047



Activation Parameters

It was determined that the activation energy (Ea) was dependent on temperature by applying the Arrhenius equation to the data. The slope of the straight line obtained by plotting ln(k) vs 1/T allowed us to calculate Ea.

Table 2: Rate Constants and Arrhenius Data

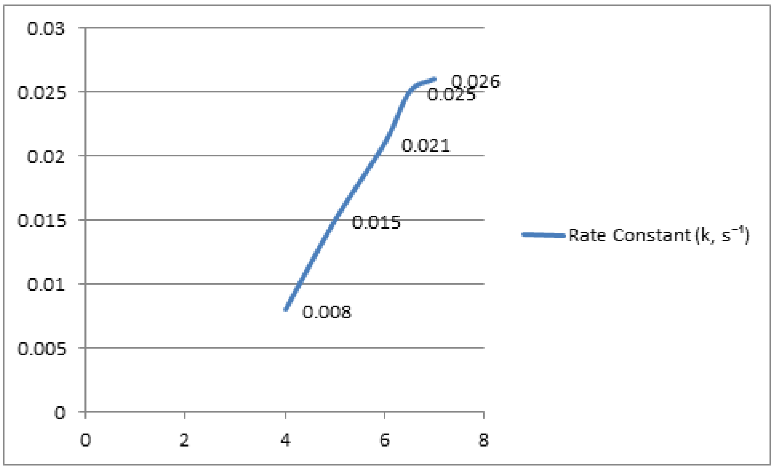
Temperature (K)	**Rate Constant (k, s^{-1})**	**ln(k)**	**1/T (K^{-1})**
293	0.008	-4.828	0.00341
303	0.014	-4.267	0.00330
313	0.024	-3.733	0.00319

Effect of pH

The reaction rate was observed to increase with pH up to 6.5, after which it plateaued. This behavior can be attributed to the optimal ionization state of NCS and enhanced micelle formation at slightly acidic conditions.

Table 3: Effect of pH on Reaction Rate

pH	**Rate Constant (k, s^{-1})**
4.0	0.008
5.0	0.015
6.0	0.021
6.5	0.025
7.0	0.026

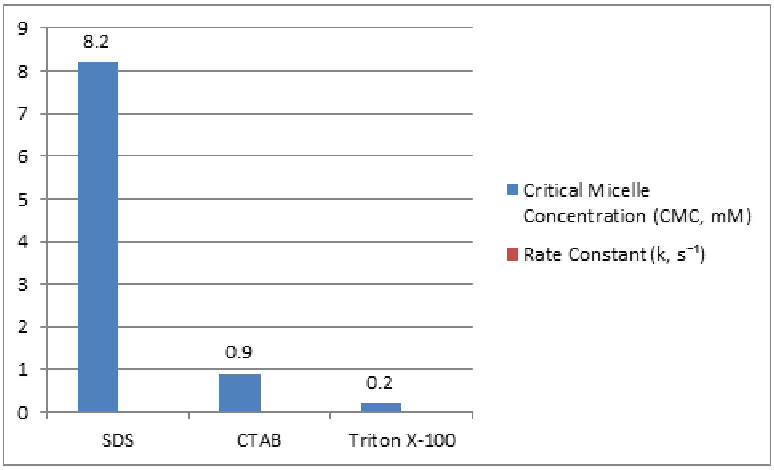


Role of Surfactants

The role of micellar media was investigated using three surfactants: sodium dodecyl sulfate (SDS), cetyltrimethylammonium bromide (CTAB), and Triton X-100. SDS, an anionic surfactant, exhibited the highest catalytic efficiency due to favorable electrostatic interactions with the transition state.

Table 4: Effect of Surfactants on Reaction Rate

Surfactant	Critical Micelle Concentration (CMC, mM)	Rate Constant (k, s^{-1})
SDS	8.2	0.028
CTAB	0.9	0.015
Triton X-100	0.2	0.010



CONCLUSION

This study highlights the efficiency of N-chloro saccharin (NCS) as an oxidizing agent for unsaturated alcohols in micellar media, showcasing the profound influence of surfactant type, substrate concentration, and pH on reaction kinetics. The observed rate enhancements and selectivity underscore the critical role of micelles as nanoreactors, where substrate solubilization and stabilization of reactive intermediates occur. The calculated activation energy and thermodynamic parameters confirm a micelle-assisted reaction mechanism, with lower energy barriers compared to non-micellar systems. This mechanism reflects the synergistic interaction between the oxidant, substrate, and micellar environment. These results not only advance our understanding of oxidation processes in organized media but also demonstrate the potential of micellar systems as sustainable and efficient platforms for chemical transformations. By minimizing the use of harmful solvents and maximizing reaction efficiency, this approach aligns with green chemistry principles and offers a scalable framework for industrial applications in pharmaceuticals, fine chemicals, and other oxidation-based processes.

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