

Kinetics and Mechanism of Oxidation of L-Lysine by Chloramine-T in Acidic Medium: Effect of Sodium Dodecyl Sulphate Micelles

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Abstract

The kinetics of oxidation of L-lysine by chloramine-T (CAT) were investigated in acidic medium in the presence of sodium dodecyl sulphate (SDS). The reaction was studied under pseudo-first-order conditions with L-lysine in excess. The observed rate constant increased with increasing L-lysine concentration and temperature, whereas it decreased with increasing hydrogen ion concentration. SDS was associated with significant rate enhancement, consistent with the role of an organized surfactant medium in concentrating and orienting reacting species. The kinetic observations support a mechanism involving acid-base equilibria of the amino acid and oxidant followed by electron transfer. Summary tables and graphs prepared from the kinetic data reported in the dissertation are included to present the concentration and temperature effects clearly.

L-lysine; Chloramine-T; SDS; oxidation kinetics; micellar catalysis; amino acid oxidation.

1. Introduction

Oxidation of amino acids is important in chemical and biochemical systems because oxidative modification can alter molecular structure and reactivity. Chloramine-T is a useful oxidizing reagent whose reactive form depends on the reaction medium. Surfactants such as SDS provide organized environments that may modify reaction rates through association, concentration and orientation of reactants. The present work examines the oxidation of L-lysine by chloramine-T in acidic medium and the influence of SDS on the reaction kinetics.

2. Experimental

2.1 Materials

Chloramine-T and freshly prepared L-lysine solutions were used for kinetic measurements. SDS was employed as the anionic surfactant. Reagents were prepared in doubly distilled water, and CAT concentration was checked iodometrically.

2.2 Kinetic Measurements

Kinetic experiments were performed under pseudo-first-order conditions using excess amino acid over CAT. The reaction was followed by iodometric determination of residual oxidant. The effects of L-lysine concentration, hydrogen ion concentration and temperature were examined. The dissertation reports kinetic experiments at 30, 35 and 40 °C.

3. Results and Discussion

3.1 Effect of L-Lysine Concentration

The reported values of k_{obs} increased with increasing L-lysine concentration at all three temperatures. The increase was also greater at higher temperature, demonstrating the combined effects of substrate concentration and temperature on the reaction rate.

Table 1. Effect of L-lysine concentration on the observed rate constant

[L-Lysine] (M)	k_{obs} at 30 °C (10^{-4} s^{-1})	k_{obs} at 35 °C (10^{-4} s^{-1})	k_{obs} at 40 °C (10^{-4} s^{-1})
0.02	4.45	6.13	8.03
0.04	6.15	12.18	16.13
0.06	8.5	18.25	24.25
0.08	12.5	24.3	31.58

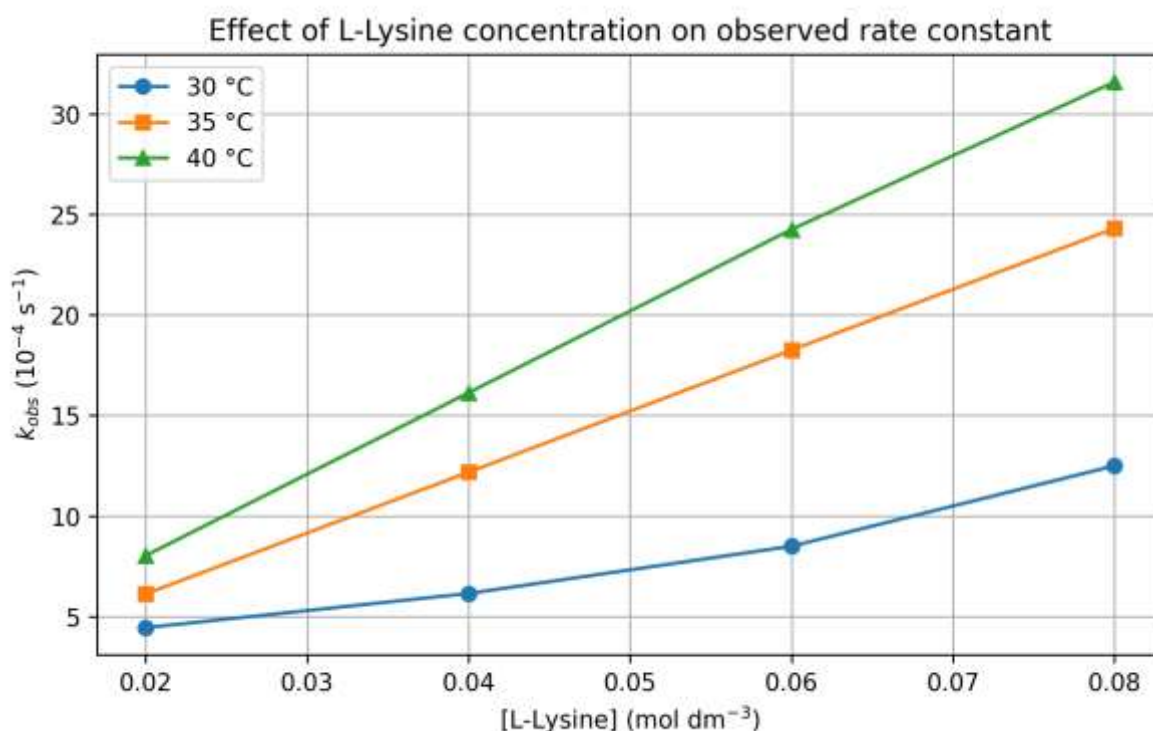


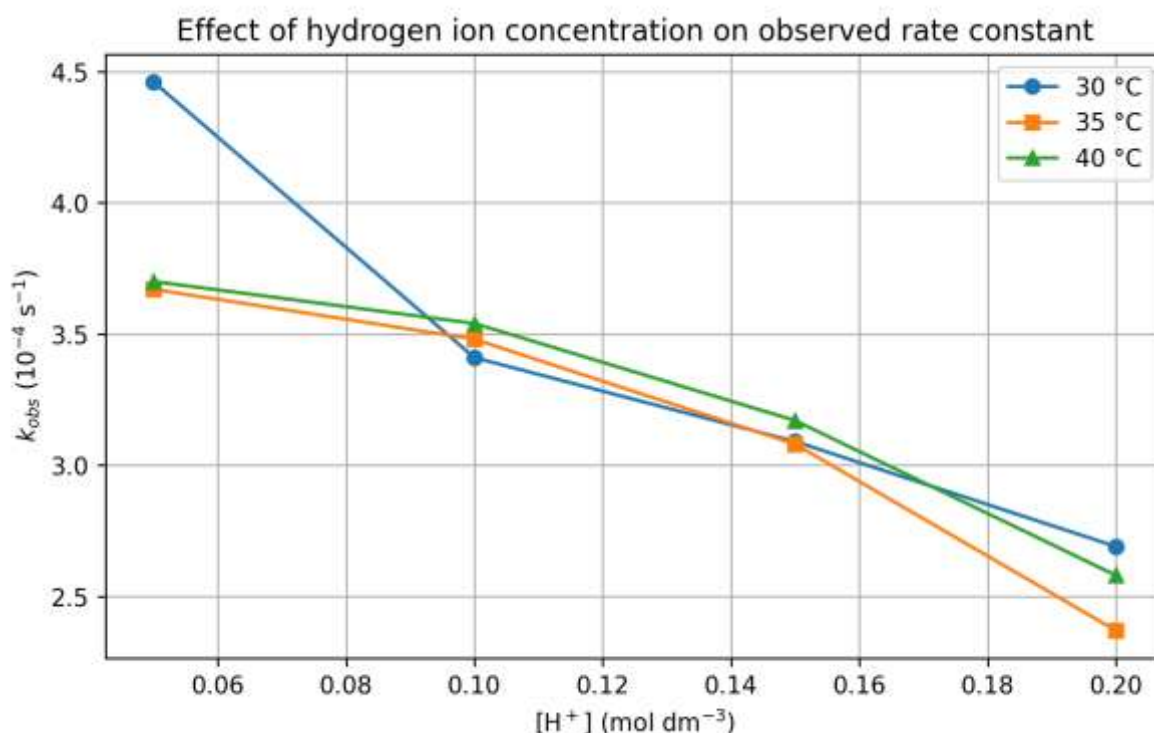
Figure 1. Variation of observed rate constant (k_{obs}) with L-lysine concentration at different temperatures.

3.2 Effect of Hydrogen Ion Concentration

The observed rate constant decreased as hydrogen ion concentration increased from 0.05 to 0.20 M. This trend was observed at 30, 35 and 40 °C and supports the proposed involvement of hydrogen-ion-dependent equilibria in determining the concentration of the reactive species.

Table 2. Effect of hydrogen ion concentration on the observed rate constant

[H ⁺] (M)	k _{obs} at 30 °C (10 ⁻⁴ s ⁻¹)	k _{obs} at 35 °C (10 ⁻⁴ s ⁻¹)	k _{obs} at 40 °C (10 ⁻⁴ s ⁻¹)
0.05	4.46	3.67	3.7
0.1	3.41	3.48	3.54
0.15	3.09	3.08	3.17
0.2	2.69	2.37	2.58


Figure 2. Variation of observed rate constant (k_{obs}) with hydrogen ion concentration at different temperatures.

3.3 Effect of Temperature

For the L-lysine concentration series, the reported k_{obs} values increased progressively from 30 to 40 °C. For example, at 0.02 M L-lysine, k_{obs} increased from $4.45 \times 10^{-4} \text{ s}^{-1}$ at 30 °C to $8.03 \times 10^{-4} \text{ s}^{-1}$ at 40 °C. At 0.08 M L-lysine, the corresponding values increased from $12.50 \times 10^{-4} \text{ s}^{-1}$ to $31.58 \times 10^{-4} \text{ s}^{-1}$. These data demonstrate a clear temperature dependence of the reaction.

3.4 Effect of SDS and Proposed Micellar Role

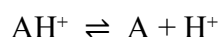
The dissertation reports enhancement of the oxidation rate in the presence of SDS. The kinetic behaviour was interpreted in terms of association of reactants with surfactant aggregates and facilitated electron transfer in the organized micellar environment. The negatively charged SDS interface may promote favourable localization of suitable lysine species and reactive oxidant species, increasing their effective local concentration.

4. Proposed Reaction Mechanism

The kinetic results reported in the dissertation indicate that the oxidation of L-lysine by chloramine-T in acidic medium does not proceed through a single simple elementary step. The proposed mechanism is based on: (i) acid-base equilibria of L-lysine, (ii) equilibria involving the reactive oxidizing species derived from chloramine-T, (iii) parallel hydrogen-ion-dependent and hydrogen-ion-independent reaction pathways, and (iv) association of reacting species with SDS aggregates in the surfactant medium.

4.1 Speciation of L-Lysine in Acidic Medium

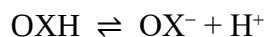
L-Lysine contains two amino groups and one carboxylic acid group and therefore exists in different protonation states depending on the acidity of the medium. Under the acidic experimental conditions, protonated forms of lysine are expected to be important. The dissertation represents the kinetically relevant acid-base equilibrium in a simplified form as:



where AH^+ represents a protonated form of the amino acid and A represents the corresponding less protonated reactive form. The equilibrium determines the concentration of the species A available for oxidation. Since the concentration of A is related to the hydrogen ion concentration, increasing acidity reduces the contribution of the pathway involving this reactive form.

4.2 Formation of the Reactive Chloramine-T Species

Chloramine-T can exist in more than one form in acidic aqueous medium. The dissertation considers equilibria involving the oxidant and represents the relevant reactive species in a generalized form. One such acid-base equilibrium may be written as:



The kinetic interpretation is based on the availability of a reactive oxidizing form of CAT whose concentration is governed by the acidity of the solution. Thus, the observed reaction rate depends not only on the analytical concentration of CAT but also on the equilibrium concentration of the kinetically active oxidant species.

4.3 Hydrogen-Ion-Independent Pathway

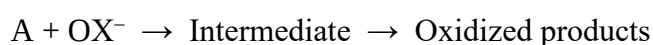
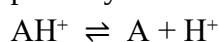
One component of the observed rate is independent of hydrogen ion concentration. This pathway is represented by direct oxidation of a kinetically active lysine species by the reactive CAT species:



The contribution of this route is represented by the k_2 term in the proposed rate expression. It accounts for the non-zero intercept obtained in the kinetic treatment of the hydrogen ion effect.

4.4 Hydrogen-Ion-Dependent Pathway

A second pathway depends on the concentration of the less protonated amino acid species generated through acid-base equilibrium. As the equilibrium concentration of this species increases when the inhibitory effect of hydrogen ion decreases, the contribution of this route is inversely related to $[H^+]$. The pathway can be represented in simplified form as:



Consequently, the rate contribution from this route is proportional to $k_1/[H^+]$. Combining both pathways gives the experimentally proposed rate law:

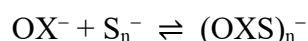
$$-d[CAT]/dt = (k_2 + k_1/[H^+])[LYS][CAT]$$

This expression explains why the observed rate decreases as the hydrogen ion concentration is increased: the hydrogen-ion-dependent contribution becomes progressively smaller, while the hydrogen-ion-independent pathway remains.

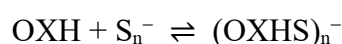
4.5 Role of SDS in the Organized Reaction Medium

The presence of SDS introduces an additional organized environment for the reaction. SDS is an anionic surfactant, and its negatively charged aggregates can associate with suitably charged or polar reacting species. The dissertation interprets the rate enhancement in terms of premicellar or micellar association and increased effective concentration of reactants at the aggregate interface.

The association of the oxidant with SDS aggregates is represented in generalized form as:



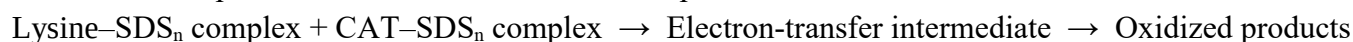
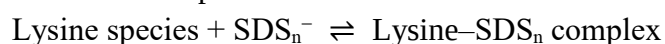
and



where S_n^- represents an SDS aggregate and the right-hand species represent oxidant-associated surfactant aggregates. Similar association of the substrate or its kinetically relevant ionic form with the micellar interface can bring the reactants into closer proximity.

4.6 Electron-Transfer Step in the Micellar Environment

After localization of the reacting species at or near the SDS interface, electron transfer is facilitated because the reactants are concentrated within a restricted interfacial region. The overall sequence may therefore be represented as:

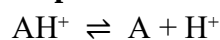


The micellar environment is therefore proposed to enhance the rate by providing reactant association, favourable localization and an increased effective local concentration. The saturation-type behaviour discussed in the dissertation is consistent with a pre-equilibrium association of reactants with the organized surfactant medium before the rate-determining oxidation step.

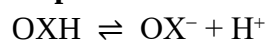
4.7 Overall Mechanistic Scheme

The complete proposed mechanism may be summarized as the following sequence:

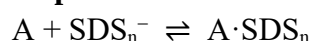
Step 1: Acid-base equilibrium of L-lysine



Step 2: Formation/interconversion of the reactive oxidant species



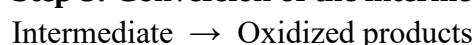
Step 3: Association of reactive species with SDS aggregates



Step 4: Rate-determining electron-transfer oxidation



Step 5: Conversion of the intermediate into oxidized/decarboxylated products



Thus, the overall mechanism combines bulk-phase and surfactant-associated pathways. The experimentally observed kinetics are accounted for by parallel hydrogen-ion-dependent and hydrogen-ion-independent contributions, while the acceleration in SDS medium is attributed to organized association of reactants and facilitated electron transfer at the surfactant interface.

Mechanistic Note

The detailed elementary structures of every intermediate and the exact stoichiometric identity of the final oxidation products should be retained exactly as established in the original experimental dissertation. The present elaborated scheme expands the kinetic mechanism already used in the paper and does not introduce additional experimentally verified intermediates beyond the generalized species required to explain the reported rate law and surfactant effect.

5. Conclusions

1. The reaction was studied under pseudo-first-order conditions with L-lysine in excess.
2. The observed rate constant increased with increasing L-lysine concentration.
3. The observed rate constant decreased with increasing hydrogen ion concentration.
4. The reaction showed a clear dependence on temperature, with higher rates observed in the L-lysine concentration series at higher temperature.
5. SDS was associated with enhancement of the oxidation rate, indicating the importance of surfactant-mediated reactant association.
6. The kinetic behaviour supports a mechanism involving acid-base equilibria and electron-transfer oxidation in aqueous and organized surfactant environments.

Data Source Note

The numerical values in Tables 1 and 2 and Figures 1 and 2 were prepared directly from the kobs values reported in the uploaded dissertation. The graphs are newly formatted visualizations of those reported experimental data and are not additional experimental measurements.

Table 3. Summary of the principal kinetic observations

Parameter examined	Observation	Kinetic interpretation
[CAT]	Pseudo-first-order behaviour; identical k_{p} values at different initial CAT concentrations.	First order with respect to CAT.
[L-Lysine]	Rate increases with substrate concentration; reciprocal kinetic plots indicate saturation-type behaviour in surfactant medium.	Substrate association/binding with organized surfactant medium.
[H ⁺]	Rate decreases as hydrogen ion concentration increases; plots against $1/[\text{H}^+]$ are linear with positive intercept.	Two concurrent pathways: one H ⁺ -independent and one inversely dependent on [H ⁺].
Ionic strength	No discernible effect on observed rate constant.	Simple ionic-strength effects are negligible.
SDS concentration	Strong enhancement at low surfactant concentration; constancy at concentrations at or above CMC.	Premicellar/substrate-induced aggregation and micellar association.
Temperature	Rates measured between 30 and 40 °C; activation parameters	Temperature dependence of the rate and activated complex.

	evaluated.	
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Placement note: Tables 1 and 2 and Figures 1 and 2 are retained in the Results and Discussion section immediately after the corresponding discussion of L-lysine concentration and hydrogen ion concentration. Table 3 summarizes the remaining qualitative kinetic observations derived from the source dissertation.

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