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KINETIC STUDY OF CIPROFLOXACIN HYDROCHLORIDE WITH BASIC SODIUM P-TOLUENESULFOCHLORAMIDE

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ABSTRACT
The kinetic studies of Ciprofloxacin hydrochloride by sodium N-chloro toluene sulfonamide were assessed by spectrophotometric means in an alkaline aqueous system. The oxidation process proceeds with first-order kinetics for both Chloramine-T and [CPH]. Equimolar quantities of reactants and products are involved in the reaction. Studies revealed that the reaction proceeds with first-order kinetics concerning both Ciprofloxacin hydrochloride and Chloramine-T. The study also includes the effect of altering substrate and oxidant concentrations. The oxidized compound was determined to be Ciprofloxacin oxide, based on GC-MS and FTIR results. The rate constant, along with activation parameters, has been estimated. A higher concentration of alkali led to an enhancement in the reaction rate. $NaClO_4$-induced ionic strength exerts a minor effect on the reaction rate. The impact of halide ions and medium polarity (relative permittivity) on reaction rate was analyzed. Thermodynamic variables were also computed and studied.

Keywords: Chemical Kinetics, Oxidative Process, Thermal Investigation, Sodium P-Toluenesulfonchloramide.
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INTRODUCTION

Ciprofloxacin (CIP), a Second-generation fluoroquinolone, is noted for its wide therapeutic coverage. Active against a broad array of bacteria, including both Gram types, aerobic and anaerobic bacterial pathogens. It is widely used in treating various infections. Ciprofloxacin has been used in the treatment of a wide range of infections. It is a faintly yellowish to light yellow crystalline substance. Fluoroquinolones are considered among the top significant Groups of antibacterial drugs worldwide. The compound is notable for its therapeutic value and strong global sales performance range. Fluoroquinolones are a class of Non-natural, broad-spectrum bacterial growth inhibitors employed in various medicinal and animal healthcare applications. The two major elements of this class, mentioned as CAT and CAB, widely recognized for their oxidative properties, play an essential role in driving the reaction.[1] However, CIP is a hypoglycemic drug, has morphology as a colorless crystalline powder of shows hygroscopic nature, and is highly soluble in water. The analytical reagent CAT is reported for its mechanistic characteristics in various reactions.[2] The inherent properties of CAT significantly show such as its competence, stability in the reaction, nontoxic nature, and sustainable oxidant. Nevertheless, significant exploitation of CAT has not been much studied or reported. As, valuable Constituent of the haloamine group, which functions as an excellent oxidant in protonic and hydroxide-rich media, CAT needs to be meaningfully exposed for more significant reactions. The variable reaction kinetics with adapting nature, low cost, and non-toxicity, all these properties make the CIP more interesting to study and report its activity for the large-scale product.[3]

EXPERIMENTAL

Materials and Methods

The chemical is used as provided by the industry. The pure Ciprofloxacin hydrochloride is used in the experiment as per the requirements.

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General Procedure

The fresh stock solution was prepared as per the required concentration. The pure chemicals were dissolved in the distilled water for the preparation of the stock solution as well as the reagents. A CAT solution with the desired concentration was prepared with the help of a stock solution and experimented, analyzed, and reported in the present work.

Kinetic Measurements

Kinetic investigations of the aqueous-phase Reactions of ciprofloxacin hydrochloride with the oxidizing agent Chloramine-T were systematically carried out under conditions of excess substrate and Ionic environment kept unchanged, employing UV–Vis spectrophotometry. Kinetic observations were recorded at ambient laboratory conditions to maintain experimental consistency and reliability 4,5. We tracked the course of the reaction spectrophotometrically after preparing the reaction mixture containing ciprofloxacin hydrochloride, Chloramine-T, sodium hydroxide, and sodium perchlorate. Substrate, NaOH, and water were combined to maintain a total reaction volume of 50 mL, and the system was brought to thermal equilibrium at 303 K. An appropriate volume of Chloramine-T solution, pre-adjusted to a uniform temperature, was swiftly Poured, and the reaction solution was shaken well to achieve complete mixing to ensure homogeneity. Five milliliters of the mixture were immediately transferred into a cuvette, and recorded absorbance was recorded using a SHIMADZU UV-1800 UV-Vis instrument at the characteristic wavelength of ciprofloxacin over exceeding twice the half-life duration. As evidenced by the linear dependence of log (absorbance ratio) on time, Rate constants assuming pseudo-first-order conditions (k/s^{-1}) were derived.

Stoichiometric Evaluation and Product Confirmation

The concentration ratio of CAT to CIP was calculated, and the reaction mixture underwent additional analysis. At the initial concentration, CAT, $[CAT]o = 5.0 \times 10^5$ mol per liter, and concentration of CIP, $[CIP]o = 5.0\times10^{-4}$ mol dm^{-3} was combined with 1.0 M sodium hydroxide solution for 48 h. Iodometric titration was employed to assess the residual oxidant. It was established that each mole of CIP necessitates two moles of oxidizing agent for complete oxidation, in line with stoichiometric principles. At the equilibrium time, the product was washed with dilute hydrochloric acid till a neutral pH was attained. The reaction of the products underwent a Chromatographic techniques and spot test evaluation, which exposed the development of Ciprofloxacin oxide under basic conditions.

Detection Method

GC-MS analysis confirmed that the oxidized product of CIP was Ciprofloxacin N-oxide. A base peak corresponding to the molecular ion was recorded at 145 amu, providing clear evidence for the presence of Ciprofloxacin. GC-MS instrumentation comprised a Shimadzu 17A GC instrument equipped with a QP-5050A MS detector, for compound identification was employed. No Additional oxidation of the product was observed under the current kinetic conditions.[6] The oxidized compound of CIP was identified by FT-IR spectroscopy (KBr), showing peaks at 1560 cm^{-1} ($–NH_2$), 1621 cm^{-1} (C=O), 3059 cm^{-1} (=NH), and 3500 cm^{-1} (–OH).[7]

$$2C_7H_7ClN{\cdot}NaO_2S + C_{17}H_{18}FN_3O_3HCl + 4H_2O \xrightarrow{NaOH} C_{17}H_{18}FN_3O_4 + 2C_7H_7SO_2NH_2 + 2NaCl + NH_3 + 2CH_3COOH$$

CAT CIP HCL Ciprofloxacin N-oxide

RESULTS AND DISCUSSION

The solid hydroxide was used to provide the alkaline media for the oxidation of Ciprofloxacin hydrochloride using Chloramine T. The oxidation kinetics were studied and reported. It was observed that with the only varying concentration of Ciprofloxacin hydrochloride, the rate of reaction increases, so the kinetics rise was observed with the constraint of all other parameters will be constant. The parameters, such as concentration of Chloramine T and sodium hydroxide constant result in a significant rise in the rate of the Kinetic oxidation reaction. The pseudo-first-order reaction conditions were observed during the oxidation reaction at a constant proportion of Chloramine-T and NaOH in the system, along with the temperature of the process. This condition will express as [CIP] >> [CAT]. The observed linearity in the Graphs of log-transformed absorbance against time supports a Single-exponential reaction behavior on [CIP]. Unreacted

CIP was quantified using spectrophotometry, based on its absorbance decrease at 276 nm.[8,9] The variation in the second individual parameter, i.e., Chloramine T [CAT] concentration variation, will serve as the second case study of the work. The remaining parameters, along with the temperature, will be constant till the end of the reaction. The reaction order concerning CAT was validated by varying its concentration from [CAT] = 5.0 to 25 $\times 10^{-5}$ mol dm^{-3}. A Reaction exhibits first-order reliance on chloramine-T-T-T. Table-1 provides the quantities of Pseudo-unimolecular rate constants (k/s^{-1}). The data for k/s^{-1} show no dependence on [CAT]. The rate initially depends on CAT in a first-order manner but shifts toward zero-order kinetics as the concentration increases. In its reactions, CAT Goes through a two-electron oxidation, generating PTS and sodium chloride.[10] Study of varying concentration of [NaOH] 5.0 to 25 $\times 10^{-5}$ mol dm^{-3} and with fixed levels of all remaining substances, Ciprofloxacin hydrochloride, [CAT], and NaClO4 constant. The observed linear plot of log k′ against the increase in [NaOH]. The observed slope of –1, implies a first-order inverse dependency of the rate upon [NaOH] concentration, with the rate initially increasing and then decreasing as [NaOH] increases.[11] An oxidation process involving CAT and CIP was studied at temperatures ranging within the interval 308–318 ^{0}K, with Analyte, Chemical oxidizer, Alkali-rich solution, and Total ion content held Steady. Elevating the temperature caused a corresponding rise in the kinetic constant of the reaction. The Arrhenius relationship between log k′ and 1/T was employed to determine activation and transition state parameters. The findings are systematically listed in Table-2. Enthalpic and entropic components of activation were calculated using the linear form of the Eyring Expression, while the Gibbs function of activation (ΔG) was determined using the Gibbs energy expression. The positive values of (ΔG). Suggest that the reaction is thermodynamically unfavorable, and the numerical value represents the minimum amount of energy required to make the reaction occur. and (ΔH) indicates that an addition of energy from the reaction (and from the surroundings), resulting in an endothermic reaction. A large negative value of (ΔS) indicates a decrease in entropy, which reflects a transition to a more ordered state.[12]

Table-1: Variation in Reaction Rate with Changing [CAT], [CIP], and [NaOH]
[CAT] = 0.000020 M; [CIP] = 0.0005 M; [NaOH] = 1.0 × 10^{-4} M; [$NaClO_4$] = 1.0 mol per liter

[CAT] ($\times 10^{-5}$ mol·dm^{-3})	[CIP] ($\times 10^{-4}$ mol·dm^{-3})	[NaOH] ($\times 10^{-4}$ mol·dm^{-3})	k′ ($\times 10^{-2}$ s^{-1})
5	5	5	0.028814442
10	5	5	0.107068681
15	5	5	0.210542669
20	5	5	0.07556922022
25	5	5	0.074420256
5	5	5	0.03569
5	10	5	0.090884482
5	15	5	0.15221
5	20	5	0.73758
5	25	5	0.09302
5	5	5	0.038149991
5	5	10	0.05005425
5	5	15	1.269061989
5	5	20	0.066202271
5	5	25	0.025925624

To Evaluate the Influence of the Ionic Content of the Medium on Reaction Kinetics

1M $NaClO_4$ solution was introduced into the reaction mixture. At constant concentrations of reactants and other conditions. The rate constant, provided in Table-3, confirms that ionic strength has a negligible impact on the reaction rate. To explore the added salt on the kinetics, the salt concentration was varied, while the Content of the oxidant, substrate, and alkali was kept unchanged.[13]

Role of Dielectric Constant in the Reaction Rate

The study of the dielectric behavior of the medium was carried out by introducing methyl alcohol into the Solvent environment. It was observed that increasing the strength of methyl alcohol reduces the permittivity of the solvent, yielding a higher reaction speed. The existence of free radicals and their influence on the

reacting system were studied by adding acrylonitrile and maintaining the mixture in an inert atmosphere for 24 hours. The lack of precipitate formation after methanol dilution confirms that free radicals do not participate in the process.

Table-2: Thermal Effect on Reaction Kinetics and Analysis of Activation Energy and Transition-State Factors

Serial Number	Maintained at ^{0}C	Maintained at ^{0}K	10^2 k′ (s-1)	Activation parameter * 10^3
01	35 ^{0}C	308 Kelvin	0.445848589	Ea = 176.45 kJ/mol
02	40 ^{0}C	313 Kelvin	0.021638803	$\Delta H^{\ddagger}$ = 176.44 kJ/mol
03	45 ^{0}C	318 Kelvin	0.100270586	$\Delta G^{\ddagger}$ = 2.31 kJ/mol
				$\Delta S^{\ddagger}$ = –556 J mol^{-1} K^{-1}

Chloramine-T (1.0×10^{-5} mol·dm^{-3}), Ciprofloxacin (1.0×10^{-4} mol·dm^{-3}), Sodium hydroxide (1.0×10^{-4} mol·dm^{-3}), and Sodium perchlorate (1.0 mol·dm^{-3})

Table-3: Influence of Added Electrolyte on the CIP–CAT Oxidation Process

Entry No.	Concentration of $NaClO_4$ (mol dm^{-3})	Observed rate constant, k′ (s^{-1})
1	10	0.09.5993765
2	15	1.231326896
3	20	1.18881547882
4	25	1.12479382

Chloramine-T (1.0×10^{-4} mol dm^{-3}), Ciprofloxacin (1.0×10^{-3} mol dm^{-3}), and Sodium hydroxide (1.0×10^{-3} mol dm^{-3})., temperature (T)=303^{0}K

Table-4: Effect of Polar Medium on Kinetic Behavior of the Reaction

Item No.	Volume percent of MeOH	Observed rate constant (s^{-1})
1	0	-0.004010447
2	10	0.007543684
3	20	0.014873175
4	30	0.02108227

[CAT] = 1.0×10^{-4} M, [CIP] = 1.0×10^{-3} M, [NaOH] = 1.0×10^{-3} M, at T = 303^0 K

Effect of Salt

The reaction rate was determined using KI, ensuring that [CAT], [substrate], and [NaOH] remained at constant levels. The reaction rate constant exhibited minimal fluctuation with changes in [KI], indicating its independence from ionic strength. The impact of additional salts on the oxidation of CIP has been analyzed. The results are given in Table-5. No systematic trend in the rate constant was observed with changes in the added salt concentration. The lower reaction rate constant for KI may be explained by the involvement of iodide ions, as both iodide and chloride ions participate in oxidation. (ii) $CaCl_2$. This behavior reveals that the rate constant is affected by the charge on the cations and increases as the Chloride ion content increases. (iii) Al $(NO_3)_3$. The observed rate constant initially decreases with increasing anion charge at low concentrations (up to 5 x 10^{-4} M), then shows an inverse trend at higher salt concentrations.

Table-5: Impact of Varying the Solvent Polarity on Reaction Kinetics

S.No.	10×10^{-2} mol dm^{-3}	KI k′ (s^{-1})	$Cacl_2$k′ (s^{-1})	$Al(NO_3)^3$ k′ (s^{-1})
1	1	0.0975	-0.01860	0.0977
2	3	0.167	0.0333663	0.13952
3	5	1.3972	0.0453217	0.1436
4	7	0.0555	0.07913	0.0836
5	9	-0.0911	-0.12276	0.0723

[Chloramine-T] = 0.0001 M, [Ciprofloxacin] = 0.001 M, and [NaOH] = 0.001 M; T = 303 ^{0}K

CONCLUSION

An investigation confirms that the oxidation of ciprofloxacin hydrochloride by N-chloro-p-toluenesulfonamide sodium in a basic Reaction environment follows first-order Time-course analysis, as verified through spectrophotometric analysis. The reaction exhibits an inverse-first-order dependence on [NaOH], and FT-IR analysis identifies the oxidized product as ciprofloxacin N-oxide. Calculations of thermodynamic parameters and rate constants further characterize the process. The reaction remains unaffected by variations in Ion-rich conditions, and investigation of the reaction environment dielectric

constant reveals no meaningful influence on the reaction kinetics. These findings highlight the potential of Chloramine-T as an efficient and soft oxidizing agent for diverse chemical transformations.

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CONFLICT OF INTERESTS

The authors declare that there is no conflict of interest.

AUTHOR CONTRIBUTIONS

The present work is related to *SDG-3: Good Health and Well-being*. All the authors contributed significantly to this manuscript, participated in reviewing/editing and approved the final draft for publication. The research profile of the authors can be verified from their ORCID ids, given below:

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