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Review on Kinetic and Thermal Study of Oxidation and Degradation of Medicinal Drug

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***Abstract:** Kinetic and thermal methods became of great interest in chemical and pharmaceutical analyses. Chemical kinetics is the study and discussion of chemical reactions with respective to reaction rate, effect of various variables, rearrangement of atoms and formation of intermediates. A development of medicinal drug brought revolution in human health. There is huge role of pharmaceutical drugs in diagnose. This paper reviews novel kinetic approaches to the determination of various types of drugs in pharmaceutical materials including chemiluminescent analysis. This review provides an overview of Kinetic and thermal study of various oxidation reaction, degradation of medicinal drug by using catalyst as reported over the past decades. This article also explains some analytical techniques for evaluation parameters of drug.*
***Keyword:** Kinetic; Thermal; Pharmaceutical drug; Oxidation; Degradation; Analytical method; etc.*

I. INTRODUCTION

Chemical kinetics is the study of the rates of transformation of chemical compounds from reactant species into products Chemical kinetics is concerned with understanding the rates of chemical reactions. It is to be contrasted with thermodynamics, which deals with the direction in which a process occurs but in itself tells nothing about its rate. fundamental concepts relating to rate coefficients, reaction order, the rate expression, reaction mechanisms, elementary reactions, third-body reactions, and steady-state concentration analysis are introduced. The main factors that influence the reaction rate include the physical state of the reactants, the concentrations of the reactants, the temperature at which the reaction occurs, and whether or not any catalysts are present in the reaction. Studying how enzymes and catalysts alter the rates of kinetic reactions is very important in manufacturing and biochemical fields. One reason for the importance of kinetics is that it provides evidence for the mechanisms of chemical processes. knowledge of reaction mechanisms is of practical use in deciding what is the most effective way of causing a reaction to occur. Many commercial processes can take place by alternative reaction paths, and knowledge of the mechanisms makes it possible to choose reaction conditions that favour one path over others. A description of a reaction mechanism must therefore deal with the movements and speeds of atoms and electrons. The rate of a reaction is defined in terms of the rates with which the products are formed and the reactants (the reacting substances) are consumed.

Oxidation is the loss of electrons during a reaction by a molecule, atom or ion.

Oxidation occurs when the oxidation state of a molecule, atom or ion is increased. While the addition of oxygen to a compound typically meets the criteria of electron loss and an increase in the oxidation state, Electrochemical reactions are great examples of oxidation reactions. pharmaceuticals drug would serve their intent only if they are free from impurities and are administered in an appropriate amount. To make drugs serve their purpose various chemical and instrumental methods were developed at regular intervals which are involved in the estimation of drugs. Impurity which makes the pharmaceutical risky to be administered thus they must be detected and quantitated. For this analytical instrumentation and methods play an important role. This review highlights the role of the Kinetic, thermal methods in assessing the quality of the drugs. The review highlights a variety of analytical techniques such as titrimetric, chromatographic, spectroscopic, electrophoretic, and electrochemical and their corresponding methods that have been applied in the analysis of pharmaceuticals.

Veeresh Tegginamath et al. were studied the kinetics of ruthenium (III) (Ru (III)) and osmium (VIII) (Os (VIII)) catalysed oxidation of neuroleptic drug, gabapentin (GBP) by diperiodatoargentate (III) (DPA) in alkaline medium. They found that reaction is of order first order and less than unit order. The main products were identified by spot test and spectroscopic studies. The reaction constants and catalytic constant (Kc) calculated for both catalysed reactions at different temperatures. Activation parameters were compared for both catalysed and uncatalyzed reactions. Catalytic constants were also computed. Main findings of work is Catalytic efficiency Ru (III) less than Os (VIII).

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Duy D. Do Pham et al. investigated on the oxidative N-demethylation of atropine, thebaine and oxycodone using a FeIII-TAML catalyst. The conversion of atropine in ethanol with aqueous H_2O_2 produces noratropine as the main product and N-formyl-noratropine and other atropine derivatives involving carbon-hydroxylated tropane species as minor by-products. the rate of H_2O_2 addition and the concentration of water, whereas temperature mainly affected the atropine conversion efficiency. It is clear from this current study that the catalytic selectivity of 15 for the N-demethylation of N-methylamine alkaloids is dependent on the substrate structure, with 15 providing greater N-demethylation selectivity for the tropane alkaloid. These results also highlight that further structural refinement of the FeIII-TAML catalyst. selective N-demethylation reactions to be used in the industrial-scale syntheses of active pharmaceutical ingredients (APIs).

Kirthi S. Byadagi et al. stated Catalytic Activity of Ruthenium (III) on the Oxidation of an Anticholinergic Drug-Atropine Sulfate Monohydrate by Copper (III) Periodate Complex spectrophotometrically in aqueous alkaline medium. The main oxidation products were confirmed by spectral studies. The reaction is first order with respect to [DPC] and [Ru (III)], while the order with respect to [ASM]and [OH–] was less than unity. The reaction rates revealed that Ru (III) catalyzed reaction was about seven-fold faster than the uncatalyzed reaction. Catalytic constants and the activation parameters with reference to catalyst were also computed. Plausible mechanisms and related rate laws have been designed. It can also be concluded that Ru (III) acts as an efficient.

M. S. Veena et al. described the kinetics and mechanism of oxidation of Phenylephrine (PHE) by Chloramine-T (CAT) in acid media by spectroscopic technique. It is found that the reaction is of first order with respect to PHE, fractional order with respect to CAT & inverse order with respect to H+. The reaction rate remained unchanged with the variation of ionic strength of the medium. The rate of reaction decreases with increase in concentration of dielectric constant. The major oxidation product of PHE has been identified by an UV, Cyclic voltammetry (CV), IR, H1 NMR and Mass spectroscopy. Thermodynamic parameters were computed from the Arrhenius plot. The observed results have been explained by the mechanism and the related rate equation has been deduced.

Blazheyevskiy Mykola et al. have been carried out the kinetic studies of Famotidine (FMT) pure substance and medicinal preparation in buffer solutions under second-order conditions by. New titrimetric procedures are described for the FMT determination. rate constant is in the interval from 14.49 to 32 min-1 L mol-1. FMT has been treated with a measured excess of standard potassium caroate in buffer solution with pH 7, the residual oxidant back has been determined by the iodometric titration method. The titrimetric method is applicable over 1-10 mg mL-1 concentration range and the reaction follows 1:2. (FMT: KHSO5) stoichiometry. The method has been validated for precision, accuracy, linearity, robustness and LOQ. The developed procedures are rapid, simple and inexpensive and could be applied to pharmaceutical preparation.

SAFWAN FRAIHAT The objective of this study is to develop and validate new selective kinetic methods for the determination of Gentamicin in pure and pharmaceutical preparations. The proposed methods (A and B) are based on the oxidation of Gentamicin drug with alkaline potassium permanganate at fixed temperature spectrophotometrically by measuring the increase in the absorbance owing to the formation of MnO42. The methods were linear in the concentration ranges 20–125 and 25-140 µg/ml with correlation coefficients of 0.995 and 0.988 and limits of detection LOD of 10.5 and 9.2 µg/ml for the two methods respectively. The proposed methods were applied for the determination of gentamicin in pharmaceutical formulations with recovery and relative standard deviations of 97%±8 and 98%±7 for the two methods. These methods (A) and (B) are based on initial-slope and fixed-time methods respectively. the developed methods were accurate, precise and reproducible compared to the official

I. O. OPEIDA et al. has been investigated the acenaphthene oxidation with molecular oxygen in the presence of N hydroxy phthalimide (NHPI). It is shown that the main oxidation product is acenaphthene hydroperoxide. The phthalimide-N-oxyl (PINO) radical has been generated in situ from its hydroxyimide parent, NHPI, by oxidation with iodobenzenediacetate. The rate constant of H-abstraction (kH) from acenaphthene by PINO has been determined spectroscopically in acetonitrile. The kinetic isotope effect and the activation parameters have also been measured. Obtaining the desired hydroperoxide in high yield. They also suggested a possible mechanism and kinetic model of this catalytic method. The activation parameters are determined for this reaction.

Margaret J. Sisley et al. have been developed Two methods of monitoring the chloride-catalysed oxidation of ascorbic acid by aqueous CuII and rate law for this system. They studied reaction over a wide concentration range. For the first time, it is shown that the ascorbic acid (H2asc)–CuII–chloride ion–CuI–dehydroascorbic acid (dha) system comes to equilibrium, under anaerobic conditions, It is interesting that our studies with $Co(NH_3)5(N_3)21$ have a formal analogy to the much studied autooxidation of ascorbic acid by CuII in which O_2 oxidizes CuI back to CuII. apparent order of the reaction can depend on the relative reagent concentrations and whether initial rates or the full reaction were used to determine the rate constant.

Jayadevappa H.P.* and Nagendrappa G. were studied the kinetics of lidocaine hydrochloride (LC) oxidation by sodium N-chloro p-toluenesulfonamide (CAT) in perchloric acid medium at 303K. The reaction stoichiometry oxidation products were identified. The

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reaction rate shows a first order dependence on [CAT] and fractional order on [LC] whereas inverse fractional order on [H+]. There is a slight negative effect by the dielectric constant. There were no free radicals during the course of reaction. thermodynamic parameters were computed. A mechanism consistent with observed parameters is proposed and rate law is derived.

Fathyah Oma and Co scientists has been investigated Kinetics of oxidation of amitriptyline hydrochloride drug (AMT) by chloramine-T (CAT) in alkaline buffer medium (9.3) at 306 K spectrophotometrically at λmax378 nm. The reaction showed first-order dependence on [CAT] and [AMT] o and inverse fractional-order dependence on [OH-] and [PTS]. Stoichiometry of the reaction was found to be 1:1 with respect to the substrate and oxidant respectively. Variation of ionic strength had no effect on the rate. Addition of p-toluene sulphonamide (PTS) retarded the rate of the reaction. Activation parameters have been computed. Probable mechanism and the relevant rate law have been deduced for the observed kinetic.

Bhagwat B. Nagolkar et al. reported the kinetics of oxidation of atenolol by 12-tungstocobaltate (III) in aquous acidic medium at a constant ionic strength of 0.25 mol dm-3 spectrophotometrically at λmax 624nm under pseudo first order conditions. The reaction between atenolol and 12-tungstocobaltate (III) in acidic medium exhibits 1:2 stoichiometry [atenolol:12-tungstocobaltate (III)]. The main oxidative products were identified by TLC spot test, FT-IR studies. The effect of [H+] ion, [Cl-] ion and ionic strength of the reaction medium have been investigated. The reaction constants involved in the different steps of the mechanism are calculated. The activation and thermodynamic parameters computed. A mechanism related to this reaction is proposed.

J.P. Shubha et al. studied A kinetic of oxidation of a potent local anaesthetic benzocaine hydrochloride by sodium N halo-p-toluene sulphonamides (chloramine-T and bromamine-T) in $HClO_4$ medium at 303 K. The rate shows a first-order dependence on both [oxidant]o, and [substrate]o, and a fractional-order dependence on acid concentration. Increase in the rate of reaction has been observed with decrease of dielectric constant of the medium. Variation of ionic strength and addition of p-toluene sulphonamide or NaCl have no significant effect on the rate. the activation parameters have been evaluated and probable mechanism and the associated rate law has been deduced. The stoichiometry of the reaction was found to be 1:1 and the oxidation products were identified by spectral analysis. The rate of oxidation of benzocaine hydrochloride is about three-fold faster with BAT as compared to CAT.

K. M. MEENAKSHI and K. VASANT KUMAR PAI were derived the kinetics of oxidation of metoclopramide hydrochloride (MCP) with sodium N-chloro p-toluenesulfonamide (CAT) in perchloric acid solution at 313K. The reaction rate shows a first order dependence on [CAT], fractional order on [MCP] and inverse fractional order on [H+]. There is a negative effect of dielectric constant of the solvent. The rate remained unchanged with the variation in the ionic strength of the medium. Thermodynamic parameters have been computed by Arrhenius plot. The stoichiometry of the reaction was found to be 1:2. The Michaelis-Menten type of kinetics has been proposed. Thermodynamic parameters were and A mechanism consistent with observed kinetics is proposed.

P. R. Rangaraju et al. designed the kinetics of oxidation of Metformin hydrochloride (MET) by bromamine-T (BAT) has been investigated in NaOH medium at 303 K. The reaction followed first-order kinetics with respect to [BAT], [MET] and fractional-order with [OH−]. First-order kinetics with respect to [BAT] was observed. An increase in medium concentration increased the rate of reaction. The effect of added halide ions, reduction product toluene sulphonamide (PTS), ionic strength (NaClO4) and dielectric constant of the medium was studied on the rate of reaction. The main products were identified by spot test, GC−MS spectral analysis. A mechanism was proposed and the activation parameters have been determined from the Arrhenius plots. the thermodynamic parameters were also determined and discussed.

Kudzanai Chipiso et al. reported the kinetics and mechanism of the oxidation of methimazole (1-methyl-3H-imidazole), MMI, by chlorite in mildly acidic environments. It is a complex reaction the stoichiometry is strictly 2:1. the sulfinic acid and sulfonic acid were observed as major intermediates. The sulfenic acid, which was observed in the electrochemical oxidation of MMI, was not observed with chlorite oxidations. Initial reduction of chlorite produced HOCl, an autocatalytic species in chlorite oxidations. HOCl rapidly reacts with chlorite to produce chlorine dioxide, which, in turn, reacts rapidly with MMI to produce more chlorite. The reaction of chlorine dioxide with MMI is competitive, in rate, with the chlorite-MMI and HOCl – ClO_2- reactions.

Neelaya Nanda et al. studied the oxidation of diazepam (DZ) by N-Bromosuccinimide (NBS) in aqueous acid medium follows a first-order kinetics in [NBS] and a fractional-order each on [HCl] and [DZ]. The reaction stoichiometry involves one mol NBS consumed by one mol DZ. The rate of the reaction increases with the decrease in dielectric constant of the medium. Added products and the variation of ionic strength have no significant effect on the rate of the reaction. The oxidation products were identified by spectral analysis. A mechanism involving the formation of an intermediate NBS-DZ complex has been proposed. The solvent effect is consistent. The activation parameters for the reaction have been determined.

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Khattak, et al. investigated the effect of pH, media, phosphate concentration and ionic strength on the kinetics of thermal degradation of betamethasone valerate and betamethasone dipropionate. A validated HPLC method has been used to determine the parent compounds and their major thermal degradation products identified in the reaction. Betamethasone-17-valerate gave rise to two major products, namely, betamethasone-21-valerate and betamethasone alcohol, and betamethasone dipropionate degraded into three major products, namely, betamethasone-17-propionate, betamethasone-21-propionate and betamethasone alcohol, in different media. Betamethasone valerate showed maximum stability at pH 4-5 while betamethasone dipropionate was maximally stable at pH 3.5-4.5. The degradation of betamethasone valerate and betamethasone dipropionate was found to follow first-order kinetics and the apparent first-order rate constants (k obs). The values of the rate constants decrease with increasing solvent polarity, phosphate concentration and ionic strength.

Aftab Aslam Parwez khan et al studied the reactions of Cefuroxime (CFA) by hexacyanoferrate (III) (HCF(III)) in alkaline medium at a constant ionic strength spectrophotometrically. It is a first order reaction, but fractional order in both CFA and alkali. Decrease in dielectric constant of the medium decreases the rate of reaction. A mechanism involving free radicals is proposed. In a composite equilibrium step, CFA binds to HCF(III) to form a complex that subsequently decomposes to the products. The main two products were separated and identified by column chromatography, TLC and FT-IR. The reaction was studied at different temperatures and activation parameters were computed.

Urszula Hubicka et al developed A simple, sensitive, and reproducible ultra-performance LC method for the determination of moxifloxacin (MOXI) oxidation stability under permanganate treatment in acidic conditions. The highest reaction rate constant was observed at pH 3.0, and this value decreased as the pH was increased to 6.0. The oxidation products were characterized, and their fragmentation pathways, derived from MS/MS data, were proposed. The process followed kinetics of a second-order reaction for the substrate, and the reaction rate constant depended on the solution pH.

Qasim Yahya Mohammed are described Three simple and sensitive methods for the determination of Ampicillin. The first method is based on investigation of the oxidation reaction of the drug with alkaline potassium dichromate, where sodium hydroxide used as an alkaline media. The absorbance of the coloured dichromate ions is measured at 369 nm. The second method is based on the oxidation reaction of Ampicillin with acidic potassium dichromate by Spectrophotometric analysis. The third method is based on the oxidation reaction of Ampicillin with alkaline hydrogen peroxide; all procedures were achieved at room temperature. All variables that affecting the procedures were investigated and the conditions were optimized. Calibration graphs were constructed; mean and standard deviation were calculated.

M. Bakovic and H. B. Dunford et al. synthase prostaglandin H compounds I and II by using caffeic acid is a moderate stimulator of prostaglandin H cyclooxygenase activity and a good reducing substrate. The discrepancy between the two properties is explained by a specific peroxidative mechanism that includes the formation of an inhibitory complex of caffeic acid. The concentration of caffeic acid necessary to produce 50% stimulation of 0.2 mM arachidonic acid oxidation is 0.8 F 0.1 n & I. The rate constant for the reaction of prostaglandin H synthase-compound II with caffeic acid is (1.25 -t 0.1) x lo6 M-i s-l. The dissociation constant of caffeic acid from the inhibitory complex is 35 + 10 FM. The oxidation of caffeic acid could be important in the regulation of both prostaglandin H synthase and lipoxygenase activities and hence prostaglandin and leukotriene biosynthesis.

Amar K Durgannavar et. al investigated Kinetics and mechanism of oxidation of clindamycin phosphate by potassium dichromate in aqueous sulfuric acid medium spectrophotometrically at 25°C at a constant ionic strength. The stoichiometry of the reaction is determined (1:2). The oxidation products are characterized and confirmed by spectral studies such as IR, GC-MS and LC-MS. The reaction is first order each in chromium (VI) and clindamycin phosphate concentrations. An increase in the sulfuric acid concentration causes an increase of the reaction rate. From the results of kinetic studies, reaction stoichiometry and product analysis a suitable free radical mechanism is proposed. computation of the activation parameters with respect to the slow step of the proposed mechanism was evaluated.

SHAO XiaoLing et. reported Oxidation of estrone by permanganate: Reaction kinetics and estrogenicity removal. Kinetics was determined at pH 2.5−9.4 and temperature 15–40°C. It was found that the reaction is second-order overall and first-order with respect to both estrone and permanganate. The reaction rate first decreased with the increase of pH then increased greatly with the increase of pH. In addition, the rate constant exponentially increased with the increase of reaction temperature. Results show that the estrogenicity increased in the initial 15 min of reaction and then decreased fast, with a removal rate of 73.8%. Results also demonstrate that the reaction rate between estrone and permanganate is faster in natural water background than in the ultra-pure water system.

Jayachamarajapura PraneshShubha et. al were studied A kinetic study of oxidation of tetracaine hydrochloride by sodium N-chlorobenzene sulphonamide (chloramine-B or CAB) has been carried in $HClO_4$ mediumat303K.The rate shows first order

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dependence on [CAB]o, shows fractional–order dependence on [substrate]o, and is self-governing on acid concentration. Decrease of dielectric constant of the medium, by adding methanol, increased the rate. Variation of ionic strength and addition of benzene sulphonamide or NaCl have no significant effect on the rate. There action was studied at different temperatures and the activation parameters have been evaluated. The stoichiometry of the reaction was found to be1:5 and the oxidation products were identified by spectral analysis. The observed results have been explained by possible mechanism and the related rate law has been deduced.

Praveen N. Naik et al described the kinetics of the oxidation of Metronidazole by alkaline permanganate has been spectrophotometrically and at constant ionic strength. The stoichiometry was found to be i.e. one mole of Metronidazole reacted with one mole of manganese (VII). The reaction was first order with respect to manganese (VII) concentration. The order with respect to Metronidazole was found to be less than unity (0.65). Increase in alkali concentration increased the rate. The effect of added products, ionic strength and dielectric constant of the medium was studied on the rate of reaction. A suitable mechanism was proposed. The reaction constants involved in the different steps of the reaction mechanism were calculated. The activation parameters were determined.

Refaat Ahmed Saber et al.studied the thermal analysis of telmisartan and cilazapril. Thermogravimetry (TGA), derivative thermogravimetry (DTG) and differential thermal analysis (DTA) were used through the work to achieve the thermal analysis study of some antihypertensive drugs, telmisartan and cilazapril. The results led to thermal stability data and also to the interpretation concerning the thermal decomposition. Thermogravimetry data allowed determination of the kinetic parameters such as, activation energy and frequency factor. The simplicity, speed and low operational costs of thermal analysis justify its application in the quality control of pharmaceutical compounds for medications.

Ricardo Alves et al investigated the thermal behaviour of two polymorphic forms of rifampicin by DSC and TG/DTG. Polymorph I was the most thermally stable form, the DSC curve showed no fusion for this species and the thermal decomposition process occurred around 245 °C. The DSC curve of polymorph II showed two consecutive events, an endothermic event (Tpeak = 193.9 °C) and one exothermic event (Tpeak = 209.4 °C). Isothermal and non-isothermal thermogravimetric methods were used to determine the kinetic parameters of the thermal decomposition process. For non-isothermal experiments, the activation energy (Ea) was derived, yielding values for polymorph form I and II of 154 and 123 kJ mol-1, respectively. In the isothermal experiments, the Ea was obtained from the plot of lnt vs 1/T at a constant conversion level.

Zhimin Tao et al. have measured the influence of mesoporous silica (MCM-41 and SBA-15) nanoparticles and dense silica nanoparticles on epinephrine oxidation, a pH-dependent reaction, whose rate is small in acidic or neutral solutions but much greater at higher pH. The presence of MCM-41 or silica spheres does not accelerate the oxidation, but SBA-15 does, showing that the difference in the structures of nanomaterials leads to differing effects on the epinephrine oxidative process. a vital role of oxygen radicals (probably *O(2)(-)) in the oxidation of epinephrine. mesoporous SBA-15 and MCM-41 materials own much larger surface area than solid silica particles do, whereas MCM-41 possesses a much narrower pore size (0.4-fold) than SBA-15. It seems, therefore, that large surface area, characteristic mesoporosity, and surface structures aid in the deposit of oxygen radicals inside MSN particles, which catalyse the epinephrine oxidation in a favourable phosphate environment.

Electrochemical oxidation of acetaminophen (paracetamol) has been studied in various pHs using cyclic voltammetry and controlled-potential coulometry. The results indicate that electrochemically generated *N*-acetyl-*p*-benzoquinone-imine (NAPQI) participates in different type reactions based on solution's pH. It is hydrolyzed in strong acidic media and hydroxylated in strong alkaline media and also, it is dimerized in intermediate pHs. In addition, in various pHs, based on related mechanism, the observed homogeneous rate constants (k_{obs}) of hydrolysis, hydroxylation and dimerization reactions were estimated by comparing the experimental cyclic voltammetric responses with the digital-simulated results. The most amounts of k_{obs} are calculated in pHs less than 2 and more than 9. In this study, the least observed homogeneous rate constant (k_{obs}) belongs to pHs 5.0 and 9.0.

Feng Gao et al. performed the heterogeneous catalytic hydrogenation of acetophenone (Aceph) over Pt/Al_2O_3 in d8-toluene/h8-toluene at 273 K, using Fourier transform infrared (FTIR) spectroscopy measurements. The on-line FTIR measurements, with sensitivity on the order of 10−5mol/L, also lead to the following kinetic observations: (i) Water had a strong inhibiting effect on the hydrogenation rates. The latter included rapid initial hydrogenations on fresh catalyst (due to the presence of spill over hydrogen) and observable adsorption–desorption of other reactants. The reaction rates obtained from the well-defined experiments in h_8-toluene were fit to a number of Langmuir–Hinshelwood–Hougen–Watson (LHHW) models. The regression of the kinetic data suggested that water made a statistically significant contribution to the competitive adsorption on the catalyst surface.

Zohreh Abedizadeh et al. reported the oxidation kinetics of N-acetylcysteine (RSH) by hydrogen peroxide at neutral pH at different concentration ratios. In all the cases studied, N-acetylcystine (RSSR) is the only oxidized product formed. Our kinetic data have focused on the importance of the concentration ratio to reach the stoichiometric oxidation of N-acetylcysteine by hydrogen

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peroxide. Indeed, non-stoichiometric oxidation of RSH occurs at relatively low concentration ratios (R < 2.5) whereas stoichiometric oxidation is observed when R > 2.5. Moreover, it has been shown that in the first minutes of the reaction there is the formation of a complex between RSH and H_2O_2, the stoichiometry of the complex being RSH concentration-dependent for a given R (R > 2.5). Reaction mechanisms have been quantitatively established and the k values of each step determined.

Ravraj Kulkurni et al. studied the kinetics of the oxidation of sulfamethoxazole (SMZ) by permanganate in aqueous alkaline medium at constant ionic strength spectrophotometrically. The reaction is of first order in [permanganate ion] and has apparent less than unit order in both [SMZ] and [alkali]. However, increasing ionic strength and decreasing dielectric constant of the medium increase the rate. The oxidation in alkaline medium has been shown to proceed via an alkali-permanganate species, which forms a complex with SMZ. The reaction constants involved in the mechanism were evaluated. The activation parameters were computed with respect to the slow step of the proposed mechanism.

Fathyah Omar et al investigated the oxidation of amitriptyline (AMI) and nortriptyline (NOR), in ferrate (VI) (Fe (VI)) solution. The removal rate of AMI and NOR increased with increasing Fe (VI) dosage and was seen to be pH dependent in the order pH 7.0 < 10.0 < 8.0 < 9.0. UV irradiation at 254 nm was found to exert a synergistic effect on the Fe (VI) oxidation of AMI and NOR. By LC–ESI-MS/MS analysis, the main oxidation products of AMI and NOR by Fe (VI) have been identified. The exocyclic double bond is first oxidized to give the *exo*-epoxide, which is then hydrolyzed and finally oxidized to give dibenzosuberenone and 3-dimethylamino-propionaldehyde. The results suggest that Fe (VI) has a good ability to oxidize AMI and NOR in aqueous solution and for the purification of waters containing these particular antidepressants.

Virender K Sharma the kinetics of ferrate (VI) ($FeVIO4\ 2-$, Fe (VI)) oxidation of an antiphlogistic drug, ibuprofen (IBP), as a function of pH (7.75–9.10) and temperature (25–45C) were investigated to see the applicability of Fe (VI) in removing this drug from water. The rates decrease with an increase in pH and the rates are related to protonation of ferrate (VI). The rates increase with an increase in temperature. The E a of the reaction at pH 9.10 was calculated as 65.46.4kJmol−1. The rate constant of the $HFeO_4$ − with ibuprofen is lower than with the sulphur drug, sulfamethoxazole. The use of Fe (VI) to remove ibuprofen is briefly discussed.

Nagolkar B B and Chavan L D were studied Oxidation of the drug guaifenesin by a Ag (III) complex anion, [Ag (HIO6)2]5-, in aqueous alkaline medium by using spectrophotometry. The major oxidation product of guaifenesin was identified by mass spectrometry. The oxidation reaction displayed an overall second-order kinetics: first-order with respect to both Ag (III) and guaifenesin. Variations of [OH-] and [IO4-] tot had a significant influence on the reaction rates, where [IO4] tot denotes the total concentration of periodate added externally. An empirical rate expression, was derived, and ionic strength of 0.30 mol· L-1. Activation parameters associated with ka and kb were also derived. A mechanism involving the [Ag (HIO6) (OH) (H2O)]2- as the reactive species of the oxidant was proposed. Guaifenesin and the reactive species reversibly formed a complex, which decomposed by two parallel slow steps to give rise to the products.

Rajesh Hegade et al were studied the kinetics of oxidation of a hemorheologic drug, pentoxifylline by permanganate in alkaline medium at a constant ionic strength spectrophotometrically. The reaction between permanganate and pentoxifylline in alkaline medium exhibits 1:2 stoichiometry (pentoxifylline/permanganate). The reaction is of first order in [permanganate ion] and less than unit order dependence each in [PTX] and [OH (-)]. However, the orders in [PTX] and [OH (-)] changes from first order to zero order as their concentrations increase. A decrease in the dielectric constant of the medium increases the rate of the reaction. The effect of added products and ionic strength of the reaction medium have been investigated. A suitable mechanism is proposed. The main products were identified by TLC and spectral studies including LC-MS. The activation parameters are computed.

Shigang shen et al described Oxidation of mephenesin by bis (hydrogen periodato) argentite (III) complex anion, $[Ag\ (HIO_6)_2]^{5-}$, in aqueous alkaline medium. The major oxidation product of mephenesin has been identified as 3-(2-methylphenoxy) -2-ketone-1-propanol by mass spectrometry. An overall second-order kinetics has been observed with first order in [Ag (III)] and [mephenesin]. The effects of $[OH^-]$ and periodate concentration on the observed second-order rate constants k' have been analyzed, Activation parameters associated with k_a and k_b have been calculated. A mechanism has been proposed.

Shigang Shen, Hongmei Shi, Hanw has been studied the kinetics of oxidation of phenyldiethanolamine (PEA) by a silver (III) complex anion, [Ag (HIO6)2]5−, in an aqueous alkaline medium by conventional spectrophotometry. The main oxidation product of PEA has been identified as formaldehyde. In the temperature range 20.0–40.0 °C, through analyzing influences of [OH−] and [IO −4] tot on the reaction, it is pseudo-first-order in Ag (III) and ionic strength of 0.30 M. Activation parameters associated with k 1 and k 2 have also been derived. A reaction mechanism is proposed involving two pre-equilibria. The ternary complex undergoes a two-electron transfer from the coordination PEA to the metal center via two parallel pathways: one pathway is spontaneous and the other is assisted by a hydroxide ion.

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Nagaraj P. Shetti reported the oxidation L-tryptophan (L-trp) by diperiodatoargentate (III) (DPA) in alkaline medium at a constant ionic strength of 0.02 mol dm^{-3} spectrophotometrically. The reaction between L-trp and DPA in alkaline medium exhibits 1:2 stoichiometry (L-trp:DPA). Intervention of free radicals was observed in the reaction. a mechanism involving the monoperiodatoargentate (III) (MPA) as the reactive oxidant species has been proposed. The products were identified by spot test and characterized by spectral studies. The reaction constants involved in the different steps of mechanism were calculated. The activation parameters with respect to slow step of the mechanism were computed and discussed. The thermodynamic quantities were also determined for different equilibrium steps. Isokinetic temperature was also calculated and found to be 192.2 K

M R Gasco and M E Carlotti were investigated the equilibrium constants, kinetics, and mechanism of promazine and promethazine oxidation by ferric perchlorate at different temperatures and acidities using spectrophotometric technique. The overall reaction can be represented as follows: (formula: see text) where P+ represents the radical cation corresponding to the phenothiazine derivative. The equilibrium quotients were evaluated at 1.00 M HClO4, 25.0 degrees, and ionic strength 1.0 M. The kinetics of reaction follow the equation: -d[P] divided by dt = k1[Fe3+] [P]-k-1[Fe2+] [P+] The rate constants k1 and k-1 are independent of acidity and are related to the corresponding equilibrium quotients.

Sakia G Zimmermann et al were studied the kinetics and oxidation products (OPs) of tramadol (TRA), an opioid, for its oxidation with ferrate (Fe (VI)) and ozone (O (3)). The kinetics could be explained by the speciation of the tertiary amine moiety of TRA, in total, six OPs of TRA were identified for both oxidants using Qq-LIT-MS, LTQ-FT-MS, GC-MS. An oxygen transfer mechanism can explain the formation of N-oxide-TRA. The proposed radical intermediate mechanism is favoured for Fe (VI) leading predominantly to N-desmethyl-TRA (ca. 40%), whereas the proposed oxygen transfer prevails for O (3) attack resulting in N-oxide-TRA as the main OP (ca. 90%).

Dr. Kirti Biyadgi et al were described the oxidation of clopidogrel hydrogen sulfate, by permanganate ion in aqueous perchloric acid medium at a constant ionic strength spectrophotometrically. The reaction between clopidogrel hydrogen sulfate and permanganate in acid medium exhibits a 5:4 stoichiometry. The identified oxidation products, 4,5,6,7-tetrahydrothieno[3,2-c] pyridine, (2-chlorophenyl) oxoacetic acid, and formaldehyde as a byproduct, are different from those obtained by biological metabolism. The reaction is first-order in MnO4– and less than first-order in both the clopidogrel hydrogen sulfate and H+ ion concentrations. The oxidation reaction in acid medium was found to proceed through a permanganate–clopidogrel complex that decomposes slowly in a rate-determining step. The main products were identified by spot test and IR and GC-MS spectral studies. The reaction constants involved in different steps of the mechanism were calculated at different temperatures. The activation parameters with respect to the slow step of the mechanism were computed, and thermodynamic quantities were also determined.

Antonio Zanocco Loyola Artículo de publicación ISI Detection of O,('A,) phosphorescence emission, A = 1270 nm, following laser excitation and steady-state competitive methods was employed to measure total rate constants, k,, for the reactions of the diuretic furosemide, 2- methylfurane and furfurylamine with singlet oxygen in several solvents. Correlation of k, values with solvent parameters and product identification shows that the reaction mechanism is strongly solvent dependent. In non protic solvents, the dependence of kT on solvent parameters resembles the behavior found for 2-methylfurane and furfurylamine, implying that mostly a 2 + 4 cycloaddition mechanism of singlet oxygen to furane ring of furosemide occurs in these solvents. These mechanistic differences are explained in terms of hydrogen-bonding interactions between the carboxylic group in the aromatic ring and the amino group of furosemides. Furthermore, direct generation of O2('Ag) by furosemide was detected. This last result may be related, at least partially, to the photodynamic effects of this diuretic drug.

Gajala Tazwar et al were described The Cu (II)-catalyzed oxidation of ciprofloxacin (CIP) by hexacyanoferrate (III) (HCF) spectrophotometrically in an aqueous alkaline medium at 40°C. The stoichiometry for the reaction indicates that the oxidation of 1 mol of CIP requires 2 mol of HCF. The reaction exhibited first-order kinetics with respect to [HCF] and less than unit order with respect to [CIP] and [OH^-]. The products were also identified on the basis of stoichiometric results and confirmed by the characterization results of LC-MS and FT-IR analysis. All the possible reactive species of the reactants have been discussed, and a most probable kinetic model has been envisaged. The activation parameters with respect to the slow step of the mechanism were computed, and thermodynamic quantities were also determined.

Leo GU et al were studied the thermal reactivity of ketorolac tromethamine (1) in aqueous buffer solutions was studied at 60 °–100 ° C from pH 1.1 to 12.4. Four products (2–5) were formed and their distribution was pH dependent. The apparent degradation was both acid — and base-catalyzed and the rate depended on the oxygen concentration in a linear fashion at pH > 4.8. At low pH (2.15). Mechanisms involving either base-catalysed deprotonation or uncatalyzed hydrogen abstraction at the tertiary carbon (α to the carboxylic group of ketorolac) followed by reaction with O_2 are proposed to account for the observed kinetics and product distribution at pH > 4.8.

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Suzuko Yamazaki-Nishida et al. studied the oxidation reaction of arsenious acid (H_3AsO_3) by the peroxodisulfate ion ($S_2O_8^{2-}$) is greatly accelerated by irradiation with visible light of aqueous acid solutions containing the tris(2,2′-bipyridine) ruthenium (II) ion ($(Ru(bpy)_3]^{2+}$). The mechanism of the reaction consists of a chain reaction being initiated by the quenching reaction of the photoexcited ruthenium (II) complex ion ($[Ru(bpy)_3]^{2+*}$) with $S_2O_8^{2-}$ ion, followed by the oxidation reaction of arsenious acid by the SO_4^- radical and $Rub(bpy_3)^{3+}$. The rate law is expressed and the bimolecular quenching rate constants k_q are determined. The rate constants of the reaction between $[Ru(bpy)_3]^{3+}$ and arsenious acid are evaluated at 25 °C and ionic strength of 0.05 mol dm^{-3} with stopped-flow method.

Franscisco J Real et al were reported Oxidation of three pharmaceuticals (primidone, ketoprofen, and diatrizoate sodium) by means of several advanced oxidation processes including such as ozonation, UV radiation, and Fenton's reagent. first-order rate constants were determined in most of the oxidation systems. Specifically, for the reactions with ozone, the following rate constants were obtained for primidone, ketoprofen, and diatrizoate, respectively. the quantum yields were also determined for every compound at different pH and temperatures. Additionally, the competition kinetic model, which was also used in Fenton's reagent experiments, Furthermore, the simultaneous oxidation of these selected pharmaceuticals in some natural water systems (a commercial mineral water, a groundwater, and surface water from a reservoir) was studied. The influence of the operating conditions on the removal efficiency was established. Finally, a kinetic model was proposed.

Pragya Rani Sahoo et al Cetyltrimethylammonium dichromate has been used as a lipid compatible oxidant to study the oxidation kinetics of SV in organic media. The reaction undergoes via an ionic mechanism without any side product. The reaction is found to be acid catalyzed and sensitive to solvent polarity. The increase in the rate constant due to an increase in hydrophobicity (apolarity) of the solvent indicates the existence of a less polar transition state. Furthermore, the decrease in the rate constant due to an increase in [CTAB] suggests partitioning of the substrates and the oxidants into two different domains with different polar characteristics akin to a reversed micellar aggregate. Considering the above results and the thermodynamic parameters, a reaction mechanism has been proposed.

G Vijayalakshmi et al were studied the rates of oxidation of adenosine and chlorogenic acid by tert-butoxyl radicals (t-BuO) by spectrophotometrically. t-BuO radicals were generated by the photolysis of tert-butyl hydroperoxide (t-BuOOH) in presence of tert-butyl alcohol to scavenge OH radicals. The rates and the quantum yields (phi) of oxidation of chlorogenic acid by t-BuO radicals were determined. An increase in the concentration of adenosine was found to decrease the rate of oxidation of chlorogenic acid. From competition kinetics, the rate constant of chlorogenic acid reaction. The quantum yields (phi expt) were calculated. phi expt and phi cal values suggested that chlorogenic acid not only protected adenosine from t-BuO radicals, but also repaired adenosine radicals, formed by the reaction of adenosine with t-BuO radicals

Lanhua Hu et al were investigated conducted to examine the oxidation of carbamazepine, by potassium salts of permanganate (Mn (VII); KMnO4) and ferrate (Fe (VI); K2FeO4). Results show that both Mn (VII) and Fe (VI) rapidly oxidize carbamazepine. Reaction kinetics follow a generalized second-order rate law, with apparent rate constants at pH 7.0 and 25 degrees C reaction rates exhibit no pH dependence, whereas Fe (VI) reaction rates increase dramatically with decreasing pH. Further studies with Mn (VII) show that most common nontarget water constituents, including natural organic matter, have no significant effect on rates of carbamazepine oxidation.

Liping Li et al. reported Cefazolin was demonstrated to exert high reactivity toward permanganate (Mn (VII)). In this study, five transformation products were found to be classified into three categories three (di-)sulfoxide products, one sulfone product and one di-ketone product. Products analyses showed that two kinds of reactions including oxidation of thioether and the cleavage of unsaturated C═C double bond occurred during transformation of cefazolin by Mn (VII). Subsequently, the plausible transformation pathways under different pH conditions were proposed based on the identified products and chemical reaction principles.

Ewa Borowska et al were studied the efficiency of wastewater ozonation for the abatement of three nitrogen-containing pharmaceuticals, two antihistamine drugs, cetirizine (CTR) and fexofenadine (FXF), and the diuretic drug, hydrochlorothiazide (HCTZ). Species-specific second-order rate constants for the reactions of the molecular, protonated (CTR, FXF) or deprotonated (HCTZ) forms of these compounds with ozone were determined. All three compounds are very reactive with ozone (apparent second order rate constants. Transformation product (TP) structures were elucidated using liquid chromatography and mass spectrometry, including isotope-labeled standards. The main TPs of cetirizine and fexofenadine are their respective N-oxides, whereas chlorothiazide forms to almost 100% from hydrochlorothiazide. In the bacteria bioluminescence assay the toxicity was slightly increased only during the ozonation of cetirizine at very high cetirizine concentrations.

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Yingling yung et al investigated the reaction kinetics and toxicity of diclofenac (DCF) oxidation by ferrate (VI) under simulated water disinfection conditions. reaction between DCF and Fe (VI) followed first-order kinetics with respect to each reactant. Furthermore, the effects of pH and temperature on DCF oxidation by Fe (VI) were elucidated using a systematic examination. The apparent second-order rate constants (k(app)) increased, as the pH of the solution decreased, and the acid-base equilibriums of Fe (VI) and DCF were proposed to explain the pH dependence of kapp. The acute toxicity of DCF solution during Fe (VI) oxidation was evaluated using a Microtox bioassay. Overall, the DCF degradation process resulted in a rapid increase of the inhibition rate of luminescent bacteria.

Ana Ison et al were studied Chlorine dioxide oxidation of cysteine (CSH) is investigated under pseudo-first-order conditions (with excess CSH) in buffered aqueous solutions, p[H+] 2.7−9.5 at 25.0 °C. The rates of chlorine dioxide decay are first order in both ClO_2 and CSH concentrations and increase rapidly as the pH increases. In acidic solutions, it hydrolyzes to give CSO_2H (sulfinic acid) and HOCl, which in turn rapidly react to form CSO_3H (cysteic acid) and Cl-. As the pH increases, the (CSOClO) adduct reacts with CS- by a second pathway to form cystine (CSSC) and chlorite ion (ClO_2-). The reaction stoichiometry changes from 6 ClO2:5 CSH at low pH to 2 ClO2:10 CSH at high pH. The ClO_2 oxidation of glutathione anion (GS-) is also rapid with a second-order rate constant of 1.40 × 108 M-1 s-1. The reaction of ClO2 with CSSC is 7 orders of magnitude slower than the corresponding reaction with cysteinyl anion (CS-) at pH 6.7.

Chlorite ion reacts with CSH; however, at p[H+] 6.7, the observed rate of this reaction is slower than the ClO_2/CSH reaction by 6 orders of magnitude. Chlorite ion oxidizes CSH while being reduced to HOCl. The reaction products are CSSC and CSO_3H with a pH-dependent distribution similar to the ClO_2/CSH system.

Nootan Bhattarai and David stanbarywers described The aqueous oxidations of glutathione (GSH) by [IrCl(6)](2-), [Fe(bpy)(2)(CN)(2)](+), and [Fe(bpy)(CN)(4)](-).

All three reactions are highly susceptible to catalysis by traces of copper ions, but this catalysis can be fully suppressed with suitable chelating agents. The direct oxidation by [IrCl(6)](2-) yields [IrCl(6)](3-) and GSO(3)(-); some GSSG is also obtained in the presence of O(2).

The kinetics of these reactions have been studied at 25 °C and μ = 0.1 M between pH 1 and 11. All three reactions have rate laws that are first order in [M(ox)] and [GSH](t) and show a general increase in rate with increasing pH. Detailed studies of the pH dependence enable the rate law to be elaborated. These pH-resolved rate constants are interpreted with a mechanism having rate-limiting outer-sphere electron-transfer from the various thiolate forms of GSH

Luo X et al. investigated kinetics, stoichiometry, and products of the oxidation of trimethoprim (TMP), by ferrate (VI) (Fe (VI)). The pH dependent second-order rate constants of the reactions of Fe (VI) with TMP were examined using acid–base properties of Fe (VI) and TMP. The kinetics of reactions of diaminopyrimidine (DAP) and trimethoxy toluene (TMT) with Fe (VI) were also determined to understand the reactivity of Fe (VI) with TMP. Oxidation products of the reactions were identified by liquid chromatography-tandem mass spectrometry (LC–MS/MS). Reaction pathways of oxidation of TMP by Fe (VI) are proposed to demonstrate the cleavage of the TMP molecule to ultimately result in 3,4,5, -trimethoxy benzaldehyde and 2,4-dinitropyrimidine as among the final identified products. The oxidized products mixture exhibited no antibacterial activity against E. coli after complete consumption of TMP. Removal of TMP in the secondary effluent by Fe (VI) was achieved.

II. CONCLUSION

The Main aim of Pharmaceutical Drug to serve the human to make them free from potential illness or prevention of the Disease. For the medicines to serve the purpose they should be free from impurity or other interferences which might harm Humans. kinetic methods are powerful tools for drug analysis as they use modern instrumentation and computers, which are essential for shortening analysis times and enhancing the quality of routine analyses.

This paper reviews novel kinetic and thermal approaches to the determination of various types of drugs in pharmaceutical materials. The review also highlights oxidation and degradation kinetics by using various analytical methods which are developed since decades.

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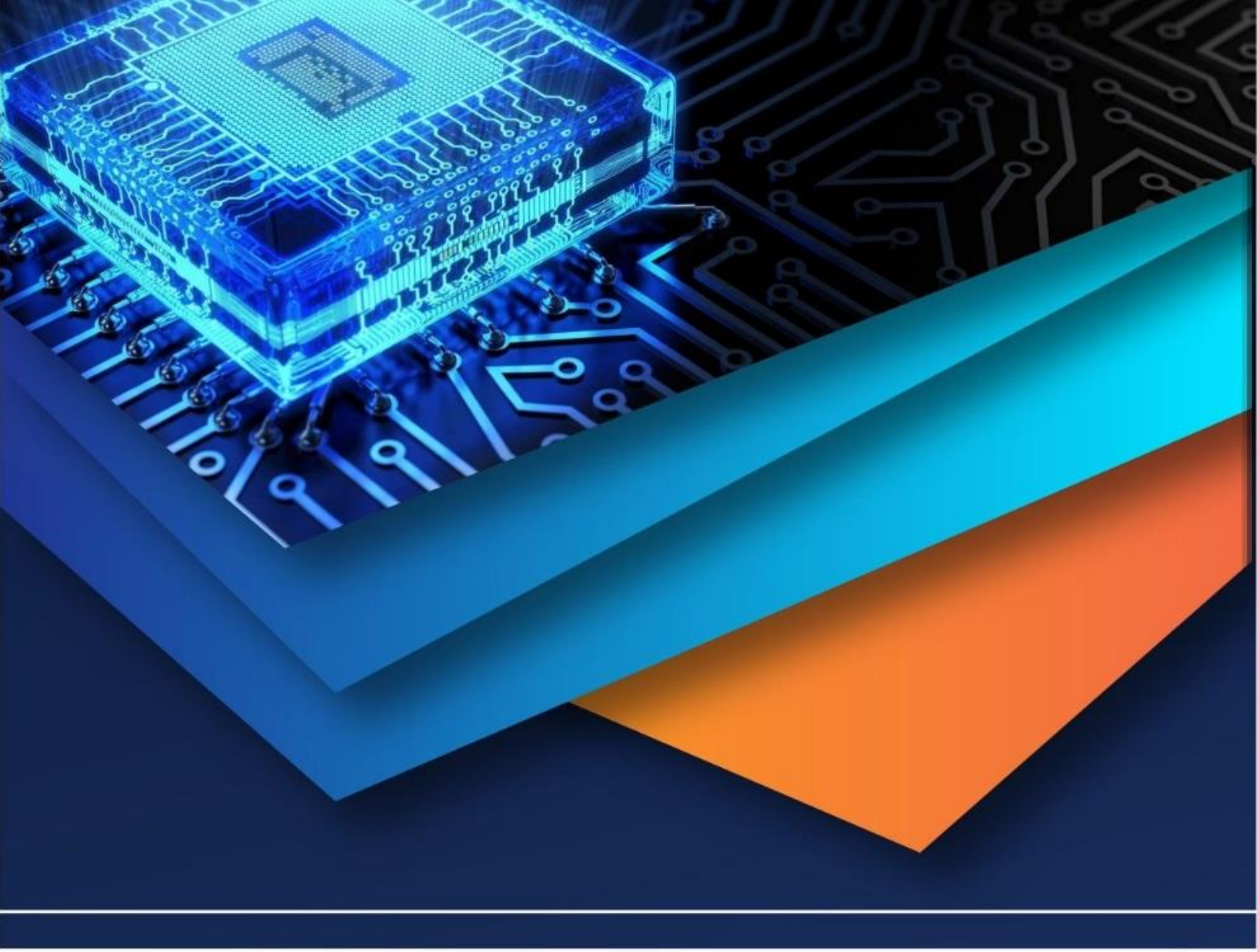

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