KINETICS AND MECHANISMS OF SOME OXIDATION REACTIONS

BY

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DEPARTMENT OF CHEMISTRY

SUBMITTED

IN FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE OF

DOCTOR OF PHILOSOPHY

TO THE

INDIAN INSTITUTE OF TECHNOLOGY, DELHI

1986

Dedicated

to

My Parents

C E R T I F I C A T E

This is to certify that the thesis entitled, "Kinetics and Mechanisms of Some Oxidation Reactions" being submitted by Mr. Raj Kumar Dhar to the Indian Institute of Technology, Delhi for the award of Degree of Doctor of Philosophy in Chemistry, is a record of bonafide research work carried out by him. Mr. R.K. Dhar has worked under my guidance and supervision and has fulfilled the requirements for the submission of this thesis, which to my knowledge, has reached the requisite standard.

The results contained in this thesis have not been submitted, in part or full, to any other university or institute for the award of any degree or diploma.

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A C K N O W L E D G E M E N T S

It is indeed a great pleasure to express my deep sense of gratitude and heart-felt thanks to my guide Dr. Rajagopala Varadarajan for suggesting and supervising this research work. His keen interest, thought provoking discussions and continuous encouragement were invaluable.

I wish to express my sincere thanks to Professor B.L. Khandelwal, Professor N.K. Jha and Professor R.P. Gandhi for their moral encouragement, and providing me necessary facilities in this department.

I have no words to paint my feelings of indebtness for my uncle, Sh. S.K. Dhar, who had been my moral support during the days of my research work.

I express my deep regards to my close friend Mr. Sanjiv Mazumdar, who stood by me for all bright and dark days during my stay in IIT Delhi. His sincere cooperation, timely help and constructive criticism much needed at times were invaluable.

Professor G.N. Rao, Dr. A.S.N. Murthy, Dr. A.S. Brar and Dr. G. Basu helped me in many ways with unreserved interests during the entire period of my research work. I am thankful to them from the core of my heart.

I am grateful to the members of the supporting staff especially Mr. L.C. Sharma, Mr. Durga Singh and

Mr. Baladutt Phuloria of the Instrumentation Laboratory who helped to record the spectral data. I am also thankful to Mr. Shimpi and Mr. Nagpal for procuring the chemicals at the earliest possible time for my research work.

I am indebted to several of my friends and colleagues especially Drs. Kamal Pandita, K.S. Reddy, Rajeev Bhat and Messers V. Ramesh, N. Homendra, Nand Kishore, Rakesh Rawley, Jayanta Ghosh, Anil Wali, Akhilesh Gupta and Jagdish K. Lohia for sharing problems and pleasures with me.

My grand parents and aunt, Mrs. Kanta Tikoo, have always been a constant source of inspiration to me. My younger brothers, Rakesh and Vivek, who always thought high of me and wished the best for my success, deserve a special word of admiration.

Care has been taken to give proper credit for the work of other authors in the literature. The author would like to apologize for any unintentional omissions which might have occured by oversight.

Finally, I thank the authorities of the Indian Institute of Technology, Delhi, for financial assistance.

Date 15.8.1986

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ABSTRACT

The work described in this thesis entitled, "Kinetics and Mechanisms of Some Oxidation Reactions" comprise of kinetics of oxidation studies on carbohydrates (monosaccharides), substituted piperidones, aminopolycarboxylic acids, monoterpenes, and an alkaloid (pyrroloquinazoline alkaloid). For all these substrates pyridinium fluorochromate (PFC) has been taken as the model oxidant. For few substrates however, pyridinium chlorochromate (PCC) and Co^{3+}_{aq} ion have also been undertaken.

For monosaccharides study, D(+)-glucose oxidation has been carried out under wide range of acidity, ionic strength and temperature by PCC and PFC. The effect of substituents of C-1 and C-2 positions of D(+)-glucose has been studied by comparing the rates of oxidation of D(+)-glucose with 1-O-methyl-α-D-glucopyranoside, 2-deoxy-D-glucose and α-D-glucosamine-hydrochloride. Further, the bimolecular rate constants of D-glucose oxidation have been compared with other monosaccharides viz., aldohexoses (D-galactose, D-mannose), ketohexoses (L-sorbose, D-fructose) pentoses (D-ribose, D-xylose), a tetrose (D-erythrose) and a triose (DL-glyceraldehyde). A probable mechanism for the oxidation of D-glucose has been proposed consistent with product analysis and kinetic

data. Anomeric effects on rate of oxidation at a higher acidity and ionic strength have also been carried out by comparing the rates of oxidation of α and β epimers of D(+)-glucose and 1-O-methyl-D-glucose by PFC, which further substantiates the mechanism of oxidation of D(+)-glucose.

A brief study on oxidation of D(+)-glucose and 2-Deoxy-D-glucose by aquo cobaltic ion has also been carried out to understand the mechanism of oxidation.

In substituted piperidones, kinetics of oxidation of a series of substituted piperidin-4-ones have been carried out in aqueous acetic acid medium. Substituted piperidones studies are : 3-R_1 and 3,5-R_2-substituted-2,6-diphenyl piperidin-4-one, where R = hydrogen, methyl, ethyl and isopropyl. Further, the effect on rate of oxidation of 2,6-diphenyl piperidin-4-one has also been studied by comparing its oxidation rates with $-NO_2$, $-OCH_3$ substituted piperidones (introduced at para position in phenyl rings of these piperidones). A probable mechanism consistent with kinetic results and product analysis (GCMS) has been presented. A primary isotopic effect and solvent effect has also been examined to substantiate the mechanism.

The kinetics and mechanisms of oxidation of aminopolycarboxylic acids viz., glycine, iminodiacetic

acid (IDA) nitrilotriacetic acid (NTA) and ethylene-diaminetetraacetic acid (EDTA) has been studied, and a probable free radical mechanism presented in favour of kinetic evidence and product analysis.

The kinetic measurements for the oxidation of all these substrates have been carried out by spectrophotometric method, under pseudo-first order conditions, where [substrate] >> [oxidant]. Activation energies (E_a) and connected thermodynamic parameters like $\triangle H^*$, $\triangle S^*$ and free energy of activation ($\triangle G^*$) have been computed and discussed.

The work has been further extended to the studies on monoterpenes (α-pinene and $\triangle^3$-carene) and an pyrroloquinazoline alkaloid (vasicine). Some novel oxidation product by PFC have been isolated by column chromatography/preparative TLC. Identification of the products have been carried out by PMR, IR, UV-visible, GC, GCMS and C and H analysis. New oxidation products of vasicine have been identified.

A cyclic voltammetric study on PCC and PFC has been attempted to visualize the reduction steps of Cr(VI) to Cr(III) of these complexes in acidic medium.

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