**TITLE PAGE**

**A PROJECT REPORT**

**ON**

**THE EFFECT OF TEMPERATURE, CATALYSIS, AND DIELECTRIC CONSTANT IN THE KINETICS OF THE OXIDATION-REDUCTION REACTIONS OF [N-(2-HYDROXY-ETHYL)ETHYLENEDIAMINE-N’,N’,N’,-TRIACETATO COBALT (11)] BY Cu2+ CATION.**

**BY**

**EGBUONU DAVID CHUKS**

**REG. NO: U14/NAS/ICH/012**

**A PROJECT REPORT SUBMITTED TO THE DEPARTMENT OF CHEMICAL SCIENCES**

**FACULTY OF NATURAL AND APPLIED SCIENCE**

**GODFREY OKOYE UNIVERSITY**

**UGWUOMU-NIKE ENUGU**

**IN PARTIAL FUFILMENT FOR THE AWARD OF BACHELOR OF SCIENCE (B.Sc.) HONOURS DEGREE IN INDUSTRIAL CHEMISTRY**

**JULY 2018.**

**CERTIFICATION**

This is to certify that the project work titled The effect of temperature, catalysis, dielectric constant in the kinetics of the oxidation-reduction reactions of [N-(2-hydroxy-ethyl) ethylenediamine-N’,N’,N’, triacetato- cobalt(11)] by Cu2+ cation. Carried out by **Egbuonu David Chuks (U14/NAS/ICH/012)**, has been approved by the Department of Chemical Sciences of Godfrey Okoye University in partial fulfillment for the award of Bachelor of Sciences Degree in pure and Industrial Chemistry.

………………………………………. ..……………………………………

Mr. Njokunwogbu, Ambrose. Mr. Ayuk, Eugene

Supervisor HOD of Department

Date…………………………. Date…………………

…………………………………………………

External Examiner

Date………………….

**DEDICATION**

I dedicate this work to my mother, (Mrs Evelyn Egbuonu) who has been a pillar and a bedrock of my existence, through your love and prayers has brought me thus to the end of this journey. This is also dedicated to my mentor, role model and father (Chief Peters Akudigwe), for your immeasurable support and fatherly love. To God almighty with whom all things are possible and finally to my grandfather late Chief Romanus Nwobi Akudigwe (ichie ifemelumma abagana).

**ACKNOWLEDGEMENT**

My gratitude goes to God almighty, the bringer of life, and the fountain of all existence and the reason for the very air that I breathe.

I wish to express my humble gratitude to an epitome of excellence, my able and visionary supervisor, Mr Njokunwogbu, Ambrose N. for his unrelenting guidance, resourceful ability, fatherly love, and rigid criticism during the period of my project research.

To my able Head of Department Mr. Ayuk Eugene, all lecturers of chemical sciences department who has lit up a burning candle in me.

My love also goes mostly to my beloved mother Mrs Evelyn Ifeoma Egbuonu and Chief Peters Akudigwe, whose moral and financial input has made this work a success. Also to my beloved brother and Sisters, Francis (mazi), Favour, and Shekinah Glory, who laid good footsteps for me to follow and gave me a resilient spirit during my moments of drawbacks.

I dare not forget my friend who is also my aunt Chief Mrs Nkechi Akudigwe and my uncles (Mr. Francis Akudigwe and Mr. Anthony Chukwuka Akudigwe) for your financial support towards this project research.

To my friends, most especially Chukwu Nnadozie Orie, who has always been a pillow on which I lay my worries and wake up rejuvenated, Jessica (jessy berry), Miracle, my trouble mate (Anastaesia) and to Samson, and Patrick, as we were together like SpongeBob square pants.

I pray that the almighty whom we all serve reward you all abundantly.

**ABSTRACT**

The effects of temperature, dielectric constant and catalysis in the kinetics of the oxidation –reduction reactions (involving electron transfer) of N-(2-hydroxy-ethyl) ethylenediammine- N’,N’,N’-Triacetatocobalt (II) by Cu2+ cation were determined. The dielectric constant was decreased from 63.05 to 43.18 and it was found that the rates of the reaction did not show any appreciable change. This seems to mean that the change in the dielectric constant of the medium had no effect on the rates of reaction in this [CoIIHEDTAH2O]- and Cu2+ systems. At constant concentration of all the reactants, the effect of added ions on the rates of reaction was investigated by varying the concentration of acetate ion (CH3COO-) from 30x10-3 – 130x10-3 mol dm-3 and noting the rates of the reactions. The same was repeated for magnesium ion (Mg2+). For this system, the rates of reaction were found unaffected by the presence of either Mg2+ or CH3COO-The temperature dependence of rates on this reaction was investigated at 350C, 400C, 500C, 550C and 600C respectively. It was found that increase in temperature increases the rates of reaction. The plot of logkobs versus the reciprocal of the square of temperature is linear, hence the activation parameters were evaluated.

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**CHAPTER ONE**

1. **INTRODUCTION**

**1.0 BACKGROUND OF THE STUDY**

**1.1 ELECTRON TRANSFER**

Electron transfer (ET) occurs when an electron moves from an atom or a chemical species ( e.g. a molecule) to another atom or chemical species. Electron transfer is a mechanistic description of the thermodynamic concept of redox, wherein the oxidation states of both reaction partners change.

Numerous biological processes involve electron transfer reactions. These processes include oxygen binding, photosynthesis, respiration, and detoxication. Additionally, the process of energy transfer can be formalized as two-electron exchange (two concurrent electron transfer events in opposite directions) in case of small distances between the transferring molecules.

**1.2 CLASSES OF ELECTION TRANSFER**

There are several classes of electron transfer, defined by the state of the two redox centers and their connectivity.

**1.2.1 Inner sphere electron transfer**

In inner sphere electron transfer, the two redox centers are covalently linked during the electron transfer *(Burgees, 1978).* This bridge can be permanent, in which case the electron transfer event is termed intermolecular electron transfer. More commonly, however, the covalent linkage is transitory, forming just prior to the electron transfer and then disconnecting following the electron transfer event. In such cases, the electron transfer is termed intermolecular electron transfer. A famous example of an inner sphere electron transfer that proceeds by a transitory bridged intermediate is the reduction of [CoCl(NH3)5]2+ by [Cr(H2O)6]2+ *(Taub and Meyer, 1954)*. In this case the chloride ligands is the bridging ligands that covalently connects the redox partners.

**1.2.2**

**Outer sphere electron transfer**

In outer-space reactions, the participating redox centers are not linked by any bridge during the electron transfer event. Instead, the electron “hops” through space from the reducing center to the acceptor. Outer sphere electron transfer can occur between different chemical species or between identical chemical species that differ only in their oxidation sate. The later process is termed self-exchange. As an example, self-exchange describes the degenerate reaction between permanganate and its one-electron reduced relative, manganese:

[MnO4]- + [Mn\*O4]2- [MnO4]2- + [Mn\*O4]-  *(Lavallee, et al; 1973)* (1.1)

In general, if electron transfer is faster than ligands substitution, the reaction will follow the outer-sphere electron transfer. Often occurs when one/both reactants are inert or if there is no suitable bridging ligands.

**1.3 MECHANISM OF ELECTRON TRANSFER REACTIONS**

In a redox process, the oxidizing and reducing centers can react with or without a change in their coordination spheres. In some reactions, the electron transfer can only be accomplished by the transfer of ligands from reducing agent to the oxidizing agent.

There are two stoichiometric mechanism: the inner sphere mechanism involves a ligands transfer, and transient shared ligands, while the outer sphere mechanism includes the simple electron transfers, without the presence of shared ligands.

**1.3.1 Inner sphere mechanism**

The reduction of the non-liable Co complex by the aqueous Cr complex produces a reduced Co complex and an oxidized CrCl complex. The chloride ligands has been transferred between the metal centers as proven by the fact that addiction of 36Cl- to the solution results in no incorporation of 36 Cl- into the Cr complex (*Wilkins, 1991*).

The reaction is faster than reactions which remove Cl- from Co111 or introduces Cl- to Cr3+ (aq), and hence the Cl- ion must have moved directly from the coordination sphere of one complex to the other during the reaction.

N.B The intermediate has a bridging Cl-  ligand.

The Cl- ion is a good bridging ligand as it has more than one pair of electrons, and so can form bonds to each of the metal centers simultaneously. Other good bridging ligands include SCN-, N2, N3- and CN- (*Wilkins, 1991*).

****

**Fig 1.1** Shows SCN- as a good bridging ligand *(Wilkins, 1991).*

**1.3.2 The Outer Sphere Mechanism**

When both the species in the redox reaction have non-liable coordination spheres, no ligands substitution can take place on the very short time scale of the redox reaction. The electron transfer must proceed by a mechanism involving transfer between the two complex ions in outer-sphere contact.

If the redox reaction is faster than the ligands substitution, then the reaction has an outer-sphere mechanism.

When the reaction involves ligands transfer from an initially non-liable reactant to a non-liable product, there is no difficulty in assigning the inner-sphere mechanism.

When the products and reactants are liable, it is difficult to make an unambiguous assignment of either an inner or an outer-sphere mechanism (*Richardson, 1984*).





**Fig 1.2:** Shows a situation where both the reactants and products are labile *(Richardson 1984).*

**1.4 APPLICATIONS/DEVELOPMENTS IN THE ELECTRON TRANSFER REACTIONS**

**Electron transfer experiment since the late 1940s (Marcus, 1956)**

Since the late 1940s, the field of electron transfer processes has grown enormously, both in chemistry and biology. The development of the field, experimentally and theoretically, as well as it relation to the study of other kinds of chemical reactions, represents to us an intriguing history, one in which many threads have been brought together.

ET at liquid-liquid interfaces

ET at modified electrodes

ET at semiconductor electrodes

ET at polymer-liquid interfaces

chemifluminescence

Eirrev and Eo

ET at metal electrodes

ET at colloids and micelles

Solar energy conversion

Inverted effect

Quantum chemistry calculation

**Electron transfer**

**In the**

**1950’s & 1960’s**

ET in solids and polymers

photosynthesis

Solvent dynamics and ET

Organic ET’s and SN-2’s

Methyl and other transfers

Ion pairs, recombination,escape

Cross- reactions

Coupled ET and proton transfer

Long range ET in rigid media

Magnetic effects on ET

ET in proteins

ET across rigid organic bridges

**Fig. 1.3.** Examples of the applications/developments in electron transfer reactions. *(Marcus and Siddarth, 1992).*

**1.5 CHEMISTRY OF COBALT**

Cobalt is a chemical element with the symbol Co and atomic number 27. Cobalt always occurs in nature in association with Ni and usually also with arsenic (*Seyferth et al., 1989*). The most important Co minerals are smaltite, (CoAs2), and cobaltite (CoAsS) but the chief technical source of Co are residue called “speisses” which are obtain in the smelting of arsenical ores of Ni, Cu and Pb,

Cobalt is a hard bluish-white metal (mp 14930c, bp 31000c). it dissolve slowly in dilute mineral acids, the Co2+/Co potential being -0.2227 V, but it is relatively unreactive. While it does not combine directly,with C,P and S on heating, it is attacked by atmospheric O2 and by water vapor at elevated temperatures, giving CoO. Very reactive finely divided metal particles can be made by reduction of CoCl2 with Li naphthalenide in glyme (*Beattie et al., 1996)*.

**Table 1.1: OXIDATION STATE AND STEREOCHEMISTRY OF COBALT**

**(*Lippard et al., 1992)***

|  |  |  |  |
| --- | --- | --- | --- |
| Oxidation state | Coordination number | Geometry | Example |
| Co-1, d10 | 4 | Tetrahedral | [Co(Co)4-, Co(Co)3 No |
| Co0, d9 | 4 | Tetrahedral | K4[Co(CN)4], Co(PMe3)4 |
| Co1,d8 | 3  4  5a  5  6 | Planar  Tetrahedral  Tbp  Sp  Octahedral | (tempo)Co(Co)2  CoBr(PR3)3  [Co(CO)3(PR3)2]+, HCo(PR3)4, [Co(NCMe5]+  [Co(NCPh)5]ClO4  [Co(bipy)3]+ |
| Co11,d7 | 3  4a  4 | Trigonal  tetrahedral  Square  Tbp  Sp | [Co(OCBu3)2[N(SiMe3)2]]-C02 (NPh2)4  [CoCl4]2- ,CoBr2(PR3)2,Co11 in Co3O4  [(Ph3P)2N]2[Co(CN4)],[Co(py)4](Cl)(PF6)b  [Co(Me6tren)Br]4, CoH(BH4)(PCy3)2  [Co(ClO4)(MePh2AsO)4]+, [Co(CN)5]3-  [Co(CNPh)5]2+ |
|  | 6a  8 | Octahedral  Dodecahedral | [Co(NH3)6]2+  (Ph4As)2[Co(NO3)4] |
| CoIII,d6 | 4  4  5  5  6a | Tetrahedral  Square  Sp  Tbp  Octahedral | In a 12-heterpolytungstate;in the garnets  [Co(SR)4]-  RCo(saloph)  CoCl(TC-4,4)c  [Co(en)2Cl2]+, [Cr(CN)6]3-, ZnCo2O4, CoF3,  [CoF6]3- |
| Coiv,d5 | 4  6 | Tetrahedral  Octahedral | Co(1-norbornyl)4  [CoF6]2-, [Co(dtc)3]+ |
| Cov, d4 | 4 | Tetrahedral | [Co(1-norbornyl)4]+ |

**1.5.1 USES OF COBALT**

Cobalt plays an important biological role for instance;

Coenzymes B12; A vitamin known as coenzymes B12 is a known organometallic compound in nature (*Crossnoe et al., 2002*). It incorporates cobalt into a corrin ring structure. This compound is known to prevent anemia and also has been found to have many catalytic properties (*Morales et al., 2003*). Methylcobalamin can methylate many compounds, including metals. The reactions of alkylcobalamine depends on cleverage of the

alky-cobalt bond, which can result in Co(I) and an alkyl cation, Co(II) and alkyl radical, or Co (III) and alkyl anion (*Abeles, 1977*). Cobalt also contains other enzymes and proteins like glutamate mutase, dioidehydrase, methionime synthetase, and dipeptidase (*Frieden, 1985*).

* + 1. **STRUCTURES OF CoIII HEDTA(H2O)**





**1.6 CHEMISTRY OF TRANSITION METALS**

In chemistry, the term transition metal (or transition element) has three possible meanings:

The IUPAC definition (IUPAC, 2006) defines a transition metal as “an element whose atom has a partially filled d sub-shell, or which can give rise to cations with an incomplete d sub-shell”.

Many scientists describe a “transition metal” as any element in the d-block of the periodic table, which includes groups 3 to 12 on the periodic table (*petrucci* *et al.,* *2002*), (*Housecroft and Sharpe, 2005*). In actual practice, the f-block lanthanide and actinide series are also considered transition metals and are called “inner transition metals”.

Cotton and Wilkinson (*cotton and Wilkinson, 1988*) expand the brief IUPAC definition by specifying which elements are included. As well as the elements of groups 4 to 11, they add scandium and yttrium in group 3 which have a partially filled d sub-shell in the metallic state.

These last two element are included even though they do not (so far) seem to possess the catalytic properties which are so characteristic of the transition metals in general. Lanthanum and actinium in group 3 are however classified as lanthanides and actinides respectively.

English chemist Charles Bury (1890-1968) first used the word transition in this context in 1921, when he referred to a transition series of elements during the change of an inner layer of electrons (for example n=3 in the 4th row of the periodic table) from a stable group of 8 to one of 18, or from 18 to 32. (*Jensen,2003*), (*Bury, 1921*), (*Bury, 2008*) These elements are now known as the d-block.

**1.6.1. AIM AND OBJECTIVE**

**Aim**

The study is aimed at generating kinetic data which will expand our knowledge of the actions and functions of vitamin B12, enzymes, coenzymes and proteins, mostly as it pertains to cobalt and copper in the kinetics of oxidation – reduction reactions involving electron transfer of [N-(2-hydroxy-ethyl) ethylenediamine –N’,N’,N’,- Triacetatocobalt (11)] by Cu2+ cation.

**Objective**

The objectives of this research is to determine the effects of :

1. Temperature
2. Dielectric constant
3. Catalysis, on the rate of reactions in the oxidation-reduction reactions of [CO11HEDTAH2O]- and Cu2+

**Justification**

An enormous amount of electron transfer chemistry goes on biological systems, and nearly all of them critically depend on metal-containing electron transfer agents *(cotton et al, 2004).*

Biologically iron is the most important transition element as its complexes play very important biological roles *(Lead, 1996).*

We have come to note that cobalt and copper also play important biological roles for instance, coenzymes B12; A vitamin known as coenzymes B12 is the only organometallic compound in nature *(Crossnoe et al; 2002).* It incorporates cobalt into a corrin ring structure. This compound is known to prevent anemia and also has been found to have many catalytic properties *(Morales et al; 2003).* Methylcobalamin can methylate many compounds, including metals. The reactions of alkylcobalamine depends on cleverage of the alkyl-cobalt bond, which can result in Co(I) and an alkyl cation, Co(II) and alkyl radical, or Co(III) and alkly anion *(Abeles, 1977).*

Cobalt also contains other enzymes and proteins like Glutamate mutase, dioidehydrase, methionime synthetase, and dipeptide. *(Frieden, 1985).*

Copper also contains important enzymes and proteins like Tyrosinase, amine oxidase, laccase, ascorbate oxidase, ceruloplasmin, superoxide dismutase, plastocyanim, nitric redutase, e.t.c *(Gary and Donald,2011).*

In many organisms, such as arthropods and molluses, oxygen is transported by copper protein known as haemocyamin, which unlike haemoglobin, is extracellular *(Alkins et al; 2006).*

**CHAPTER TWO**

**2.0 LITERATURE REVIEW**

**2.1 DIELECTRIC CONSTANT**

This is a quantity that is used in measuring the ability of a substance to store electric current in an electric field. It is expressed by the equation

D = C (2.1)

√ k

Where D is the dielectric constant, C is the velocity in a vacuum and K is the rate of the redox reaction. Hence it gives information on the velocity of the particles.

Dielectric constant is the capacity or ability of a material to store electric charge or electrostatic field energy in the presence of an electric field, and maybe expressed as the ratio of the electrical capacity of the same condenser containing the material to the capacity of the same conductor with the material replaced by vacuum (*Sharma, 2011*).

**2.1.1 DIELECTRIC PROPERTIES**

The following important properties of insulation are taken into consideration in electrical insulating materials. They are:

* Resistivity
* Dielectric/polarization
* Dielectric constant
* Dielectric strength.

We have been largely concerned with the properties of charge carriers in metals and semiconductors. However, there are many other materials with very few electrons to take part in normal electric conductivity. Such materials have dielectric properties and so it is possible to conceive the ideal insulators which would have no free electrons. A dielectric material has interesting electrical properties because of the ability of an electric field to polarize the material to create electric dipoles. A dipole is an entity in which equal positive and negative charges are separated by a small distance; the electric dipole moment is given by

µ = *q dl*  (2.2)

The electric dipole is a vector (*pillai, 2010*). In its simplest model, a dipole moments consists of two point charges of opposite sign, +*q* and –*q* separated by a distance *dl.*

**Table 2.1 The relative permittivity of some selected substances at 20oc (*pillai, 2010*).**

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| ***Dielectric*** | ***Ɛr*** | **Dielectric** | ***Ɛr*** | ***Dielectric*** | ***Ɛr*** |
| Vacuum | 1 (by definition) | Polyethylene | 2.25 | Cotton | 5 |
| Air | 1.0006 | Polyvinyl chloride | 6 | Hydrogen chloride | 1.003 |
| Paraffin | 2.2 | PVC | 3.6-11 | Chloroform | 5.1 |
| Benzene | 2.284 | Epoxy resin | 50 | Ethyl alcohol | 25.8 |
| Ice at -50c | 2.9 | Glycerine | 81 | Nitrobenzene | 36.5 |
| Rubber | 2.94 | Water (distilled) | 6.1 | Potassium chloride | 4.8 |
| Amber | 2.7 | Calcite | 7 | Rock salt | 6 |
| Quartz | 3.8 | Neoprene | 2.7 | Calcite | 6.1 |
| Bakelite | 5 | Bee wax | 1200 | Hydrogen | 1.00027 |
| Glass | 5-10 | Barium titanate | 25 | Oxygen | 1.00055 |
| Mica | 3-6 | Liquid ammonia(-780c) | 25.62 | Nitrogen | 1.0006 |
| Germanium | 16 | Sodium chloride | 2.2 | Ehtylene | 1.00138 |
| Marble | 10-15 | Transformer oil | 2.2 | Carbon tetrachloride | 2.24 |

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Diamond | 5.5 | Transformer oil | 2.6 | Benzene | 2.28 |
| Porcellian | 5.5 | Viscous Vaseline  Polystyrene  Ammonia | 1.00072 | Toluene | 2.39 |

As pointed out earlier, insulators or dielectrics are materials whose electrons are bound to the nucleus by strong forces and hence they are not free under the influence of an external field. Dielectrics may be broadly divided into *non-polar* and *polar* *materials.* In polar materials the molecules, which are usually diatomic and composed of two atoms of the same type, may be represented as positive nuclei of charge *q* surrounded by a symmetrically distributed negative electron cloud of charge –*q*. In the absence of an applied field the centre’s of gravity of the positive and negative charge distributions coincide. When the molecules are placed in an external electric field the positive and negative charges experience electric forces ending to move them apart in the direction of the external field. The distance moved is very small (10-10 m) since the displacement is limited by restoring forces which increases with increasing displacement. The centres of positive and negative charges no longer coincide and the molecules are said to be polarized. Each molecules now forms a dipole whose movement is defined as

µ=q**dx** (2.3)

Where, **dx** is the distance between the two centres of the charges and is a vector pointing from the negative o he positive charge. Dipoles so formed are known as *induced dipoles* since when the field is removed the charges resume their normal distribution and the dipoles disappear. For molecules *e* will be of the order of the electronic charge (10-19C) and **dx** of the order of molecular dimensions (10-10m). So µ will be of the order of 10-29C-m=3 Debye unit (*pillai, 2010).*

In polar dielectrics the molecules, which are normally composed of two or more different atoms, have dipole moments even in the absence of an electric field, that is, the centres of their positive and negative charges do not coincide. Normally these molecular dipoles are randomly oriented throughout the material owing to thermal agitation, so that the average moment over any macroscopic volume element is zero. In the presence of an externally applied field the molecules tend to orient themselves in the direction of the field in such a manner that the elementary volume has a net dipole moment.

In some polar materials a spontaneous dielectric polarization can exist even in the absence of an applied electric field. Such materials are known as *ferroelectrics.*

**2.2 THE MICROSCOPIC CONCEPT OF POLARIZATION**

Dielectric polarization is nothing but the displacement of charged particles under the action of the electric field to which they are subjected. Devices based on this manifestation are numerous. They range from condensers and switch-gear equipment in power and distribution installations to rectifiers, resonators, amplifiers and transducers-convertors of electrical energy to other forms of energy-in communication technology. They include memory devices used for storage of information in modern computers.

The above said displacement of electric charges results in the formation of electric dipole moment in atoms, ions or molecules of the material. The three important types of polarizations are:

* Electronic polarization
* Ionic polarization
* Orientational polarization.

**2.3 EFFECT OF VARIATION OF DIELECTRIC CONSTANT OF THE MEDIUM**

An increase in the rate constant is noticed on decreasing the dielectric constant of the medium. Plot of lg*k*obs, versus I/D(r=0.9901). gives straight line with positive slope (*Amis; 1976*).

**Table 2.2**  **Effect of the variation of dielectric constant of the medium on reaction rates *(pushpalatha and Vekanadam; 2013).***

[Met]= 0.04mol dm-3,[NBN]=0.004mol dm-3, [HCL] = 0.8 mol dm-3. Hg (CH3COO)2 = 0.005 mol dm-3 [NaClO4] = 0.1 mol dm-3. Temperature 308K

|  |
| --- |
| CH3COOH (%) H2O(%) *D* Kobs x 105(s-1) |

50 50 37.50 4.45

55 45 34.75 5.25

60 40 31.50 6.23

65 35 28.50 7.35

(*Pushpalatha and Vekanadam; 2013*), noted that in the kinetics of oxidation of methionine, an important sulphur-containing essential amino acid, by N-bromonicotinamide (NBN) in the presence of 0.8 mol dm-3 HCl in aqueous acetic acid medium at constant ionic strength, an increase in the rate constant is noticed on decreasing the dielectric constant of the medium. Atiga(*1915*), also noted that in the electron transfer reaction of trioxosulphate (IV) ion with dinuclear iron (11) - salen complex in perchloric acid medium, while varying the dielectric constant between 55.32 to 72.63 using propan-2-one/H2O mixture, an increase in the rate with decreasing dielectric was observed. The table below points this out very clearly.

**TABLE 2.3 EFFECTS OF THE DIELECTRIC CONSTANT (D) AT:**

**I=0.05 mol dm-3, [Fe (salen)2adi]= 1x 10-4 mol dm-3, [SO32-] = 7x10-3 mol dm-3, [H+] = 5 x 10 -3, T = 28 ± 1 0C and λmax = 455 nm *(Atiga et al; 1915).***

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Dielectric | 72.63 | 66.86 | 61.09 | 55.32 |
| 10-3 Kobs | 2.76 | 3.12 | 4.80 | 5.60 |

**2.4 CATALYSIS**

**Catalysis and its characteristics**

In 1836, J.J Berzelius studied three different reactions. These were the conversion of starch into sugar in the presence of acids, the decomposition of H2O2 in alkaline solutions, and the combination of hydrogen and oxygen on the surface of spongy platinum. In these three cases, the acids, the alkaline ions and the spongy platinum were the materials which increased the rate and yet were unchanged as a result of reaction. Berzelius came to the conclusion that catalytic force was in operation in such cases.

Although the concept of a catalytic force has now been discarded, the term **catalysis** is retained to describe all processes in which the rate of a reaction is influenced by a substance that remains chemically unaffected. Although the catalyst remains unchanged at the end of the process, there is no requirement that the materials do not take part in the reaction. Now it has been established that catalyst does actively take part in the reaction.

The mechanism of catalysis has shown that free energy of activation is lowered by the presence of a catalyst. Thus a catalyst is effective in increasing the rate of a reaction because it makes possible an alternative mechanism, each step of which has a lower free energy of activation than that for the uncatalysed process. For example, for the reaction between hydrogen and oxygen in presence of spongy platinum, this concept would suggest that hydrogen combines with spongy platinum to form an intermediate substance, which reacts with oxygen to provide the final product and reproduce the catalyst. This mechanism, involving the platinum surface occur at a faster rate than the reaction between hydrogen and oxygen alone. Thus, the energies of activation for forming the intermediate compounds and for their decomposition into products are lower than that for the homogenous combination of hydrogen and oxygen. A relatively small amount of catalyst can cause conversion of a large amount of the reactants. For example, the cupric ions in the concentration of 10-9 N appreciably increase the rate of oxidation of sodium sulphide by oxygen.

When the reaction does not involve a chain mechanism, it is generally true that the rate of the reaction is proportional to the concentration of the catalyst. For hydrogen and oxygen reaction in presence of spongy platinum catalyst, the extent of the surface of the platinum influences the rate of reaction. The rate has been found to be directly proportional to the platinum surface. Similarly, the hydrolysis of esters in an acid solution will depend on the concentration of **H+** ions acting as a catalyst.

The position of equilibrium in a reversible reaction is not influenced by the presence of the catalyst. For example, the oxidation of SO2 by O2 has been studied using three catalysts-platinum, ferric oxide, and vanadium pentaoxide. In all the cases the equilibrium compositions of SO2, O2 and SO3 were the same.

The equilibrium constant of a chemical reaction is equal to the ratio of the reaction-velocity constants for the forward and backward reaction. That is, K=k1/*k2*. If the equilibrium constant does not change by the presence of the catalyst, it is well evident that the ratio of the reaction velocity constants for the forward and reverse reactions must be the same, Therefore the catalyst for promoting the forward reaction must also be a catalyst for the reverse reaction. For example, platinum, which is an effective catalyst for the oxidation of SO2 to SO3, has also been found to speed up the decomposition of SO3 into SO2 and O2. The definition of catalysis in its general form suggests only that the material has an influence on the rate of reaction. Examples are known of so called negative catalysis where the rate of reaction decreases by the presence of catalyst. The most reasonable theory of negative catalysis has been developed for chain reactions. In these cases it has been postulated that the catalyst breaks the reaction chains or sequence of steps in the mechanism of the process. For example, nitric oxide reduces the rate of decomposition of acetaldehyde and ethyl ether. Nitric oxide is capable of combining with the free radicals involved in the reaction mechanism. Iodine also acts as negative catalyst in certain homogeneous gaseous reactions. In the combination of H2 and O2, involving a chain mechanism, iodine probably acts by destroying the free radicals necessary for the propagation of the chains.

Catalytic reactions are conveniently divided into two main groups, depending upon whether the catalyst and the reaction mixture form a homogenous phase. The hydrolysis of an ester in an aqueous solution containing H+ ions is an example of homogenous catalysis. The combination of H2 and O2 to form water vapor in the presence of spongy platinum is heterogeneous catalysis, since the platinum catalyst forms a separate phase from the reaction mixture. Heterogeneous catalysis need not involve only gas and solid phases. For example in emulsion polymerization, the reactants maybe in the liquid phase and the catalyst in the solid phase or separate liquid phase. One of the most important and common industrial examples of homogenous catalysis is the gas phase oxidation of SO2 in the chamber process for the manufacture of H2SO4 in the presence of NO gas catalyst *(Sharma, 2004).*

**2.4.1. GENERAL CHARACTERISTICS OF CATALYSED REACTIONS**

Although there are various types of catalyzed reactions, but in spite of their many differences, they show the following characteristic properties:

* **The catalyst remains unchanged in chemical composition at the end of the reaction.** The amount of the catalyst recovered at the end of the reaction is found to be the same as the amount taken at the start of the reaction. Hence, a catalyst does not undergo any chemical change although; its physical form may change completely. Thus manganese dioxide, used as a catalyst in the decomposition of potassium chlorate, changes from coarsely powdered form to fine powder at the end of the reaction. Similarly, smooth platinum gauze, used as a catalyst in the oxidation of ammonia, becomes rough after some time.
* **Only a small amount of the catalyst is required to bring about the reaction.** There are many cases known where a very small amount of the catalyst is sufficient to convert large quantities of the reactants into the products, e.g., one gram of platinum is sufficient to cause decomposition of 108 liter of hydrogen peroxide.

This is not invariably true. There are some homogeneous catalyzed reactions where the rate of the reaction increases with the increase in the concentration of the catalyst as, for example, the inversion of cane sugar in the presence of hydrochloric acid which acts as a catalyst. There are also some heterogeneous reactions where the rate proportionally increases with the increase in the area of the surface of the catalyst.

Attempts have been made to determine the exact quantity of the catalyst required for a reaction, but it has not been very successful.

* **A catalyst does not alter the final position of equilibrium in a reversible reaction and hence does not modify the value of the equilibrium constant.** It has been found from thermodynamics that whether a reversible reaction takes place in the presence of a catalyst or not, the free energy of the process is the same. A catalyst accelerates equally the rates of both forward and reversible reactions and helps to establish equilibrium quickly.

This has been found to be true where the amount of the catalyst used is small. If the catalyst is present in large quantity, the magnitude of the equilibrium constant changes. For example, in the hydrolysis of ethyl acetate in presence of large quantity of the catalyst, HCl, the equilibrium constant is affected.

* **A catalyst does not start or initiate a reaction, but merely increases or decreases its speed.** A catalyst simply changes the speed of a reaction which is already proceeding, though very slowly. The function of the catalyst is to help a reaction to attain an alternative path which requires minimum energy of activation.
* **A catalyst is specific in action.** This implies that a given catalyst can catalyze only particular reaction and cannot be used to bring about every reaction. For example, manganese dioxide will catalyze only decomposition of potassium chlorate and will fail to catalyze other reactions. Similarly, enzymes are also specific in action.

Thus proper catalyst for a particular reaction is chosen after numerous experiments.

* **A catalyst has an optimum temperature.** The temperature at which the catalyst is most active.
* **A catalyst is poisoned by the presence of small quantities of certain substances called catalytic poisons.** Some of the most powerful catalytic poisons are arsenious oxide, hydrogen cyanide and carbon monoxide. The presence of these substances makes the catalyst inactive.
* **The activity of a catalyst is enhanced by the presence of a substance called promoter.** For example, in Haber’s process for the manufacture of ammonia, molybdenum is used as a promoter to the catalyst iron *(Sharma and Sharma; 1999).*

**2.4.2. TYPES OF CATALYSIS**

There are generally two types of catalyst: (i) Homogeneous catalysis, and (ii) Heterogeneous catalysis.

*Homogeneous catalysis*: In this type, the catalyst is present in the same phase as the reactants. There can be gaseous or liquid phase.

Examples of homogenous catalysis in gas phase. Catalyzed homogenous gas reactions are very rare. A common example of this is the oxidation of sulphur dioxide to sulphur trioxide in the presence of nitric oxide in the lead-chamber process of sulphuric acid.

NO

2SO2 + O2 2SO3 (2.4)

Nitric oxide can also catalyze the combination of carbon monoxide and oxygen and the decomposition of nitrous oxide to nitrogen and oxygen.

NO

2CO + O2 2CO2 (2.5)

NO

2N2O 2N2 + O2 (2.6)

Another example is the decomposition of methyl-ethyl, diethyl and di-isopropyl ethers in the presence of iodine vapours which acts as a catalyst. Iodine vapours also act as a catalyst in the decomposition of acetaldehyde.

**I2 vapors**

CH3CHO CH4 + CO (2.7)

It is found to be of second order and the rate is given by

dx/dt = k CCH3CHO.C12 (2.8)

*Heterogeneous catalysis:* In this type, catalyst constitute a separate phase from the reactions. The catalyst is generally solid and reactant are mostly gases and sometimes liquids. The catalysts which are frequently used here are the metals such as platinum, nickel, copper and iron and sometimes oxides of metals such as ferric oxide, zinc oxide, molybdenum oxide e.t.c. These catalysts are used in a state of fine powder so as to give a large surface area.

In heterogenoues catalysis, we have number of reactions which are of commercial importance. Some important example are given below: (i) Haber’s Process for the manufacture of ammonia: Combination of nitrogen and hydrogen (ratio 1:3) is catalyzed by iron in the presence of a promoter (molybdenum).

 (2.9)

(ii) Contact process for the manufacture of sulphuric acid. Combination of sulphur dioxide and oxygen in the presence of platinum.

 (2.10)

(iii) Formation of water is brought about by combining hydrogen and oxygen in the presence of platinum.

 (2.11)

(iv) In the manufacture of nitric acid, oxidation of ammonia is done in the presence of a mixture of ferric oxide and bismuth oxide.

 (2.12)

Bi2

(v) Hydrogenation of unsaturated hydrocarbons in the presence of nickel.

 (2.13)

(vi) In the preparation of hydrogen, combination of carbon monoxide and water gas is done in the presence of ferric oxide.

 (2.14)

(vii) Hydrochloric acid can be manufactured by passing a mixture of hydrogen and chlorine over activated charcoal prepared from wood.

 (2.15)

**2.4.3. CATALYTIC POISONING**

There are certain substances which, if present even in small quantities, are sufficient to diminish the rate of the reactions. These substances make the catalyst useless and are termed *catalytic poisons*. For example, in the manufacture of sulphuric acid by contact process, activity of the platinum catalyst is very much reduced if some arsenous oxide is present as impurity in sulphur dioxde and oxygen. The decomposition of hydrogen peroxide by colloidal platinum is paralysed by hydrocyanic acid. The activity of iron catalyst in the manufacture of ammonia by Habery’s process is reduced if nitrogen and hydrogen gases are contaminated with carbon monoxide.

The reason for the poisoning of catalyst is probably due to the preferential adsorption of the poison on the active centres of the catalyst. This renders the catalyst useless. The poisoning of the catalyst may be temporary or permanent. If the poison is held on the surface of the catalyst by strong chemical forces, the poisoning is permanent, In such cases, activity of the catalyst can be restored only by chemical rejuvenation.

The poisoning of the catalyst has proved very useful in many cases. For example, addition of lead tetra ethyl to petrol in an internal combustion engine minimizes the knocking effect. Similarly, the oxidation of sodium sulphite to sodium sulphate by o xygen gas can be prevented by adding a small quantity of alcohol, aniline or benzaldehyde. Decomposition of hydrogen peroxide can be slowed down by adding a small amount of acetanilide or glycerine. The slowing down of the speeds of the reaction by the addition of some foreign substance is referred to *inhibition or negative catalysis (Sharma and Sharma, 1999).*

**2.4.4. AUTOCATALYSIS.**

There are certain reactions in which one of the products formed during the course of the reaction catalyze the reaction. For example, in titration of oxalic acid by potassium permanganate, it has been observed that when first portion of permanganate is added to hot oxalic acid, the reaction is slow and it takes some time for the decolorisation of permanganate. However, the second portion and succeeding portions of permanganate, are decolorized quickly . This is due to the presence of manganous ions formed during the course of the reaction .

2KMnO4 + 3H2 SO2 ­- K2­SO4  + 2MnSO4 + 3H2O + 5[O] (2.16)

COOH

5[O] + 5 10CO2 + 5H2O (2.17)

COOH

Similarly , in the action of nitric acid on copper , the reaction is slow in the beginning but becomes fast as soon as nitrous acid is formed during the course of the reaction .

This phenomenon in which one of the products of the reaction itself acts as a catalyst is known as *auto-catalysis* *(Sharma and Sharma; 1999).*

**2.4.5 EXAMPLES OF CATALYTIC PROCESSES**

Almost the whole of modern chemical industry depends on the development selection and application of catalysts, and all we can attempt to do here is to give an indication of the breadth of application rather than going into the details of technological applications

**Table 2.4: Applications of catalytic processes**

|  |  |  |
| --- | --- | --- |
| Catalyst | Function | Example |
| Metals | Hydrogenation  Dehydrogenation | Fe, Ni, Pt, Ag |
| Semiconducting oxides and sulphides | Oxidation  Dehydrogenation  Desulphurization | NiO, ZnO, MgO,  Bi2O3/MoO3 |
| Insulating oxides  Acids | Dehydration  Polymerization  Isomerization  Cracking  Alkylation | Al2O3, SiO2, MgO,  H3PO4.H2SO4  SiO2/Al2O3 |

**2.5. EFFECT OF TEMPERATURE ON REACTION VELOCITY**

The temperature e has got a significant effect on the rate of the reaction. It has been observed experimentally that increase in temperature leads to a remarkable increase in the rate of a chemical reaction and hence in rate constants. Variation of rate or rate constant of a reaction with temperature belongs to any one of the five forms shown in Fig. 2.1.

Type 1 curve is obtained for most of the reactions. Type II curve is obtained for explosions. In this curve, a sudden rise in the rate of the reaction is shown. This happens at the ignition temperature. Type III of the curve is obtained in catalytic hydrogenations and in enzyme reactions. Curve IV is obtained when carbon is oxidized. Curve V is obtained only for the reaction which exhibits a negative temperature coefficient.



**Fig 2.1**: Effect of temperature on reaction velocity *(Sharma and Sharma;1999).*

Type I correspond to the curves as given by Arrhenius when he studied the variation of rate constant with temperature. Hence this is known as Arrhenuis temperature dependence while types II to V are referred to as anti-Arrhenuis curves.

For homogenous reactions, an important generalization is that rate that is doubled or trebled for every 10oC rise of temperature (Type I is in agreement with this statement). The first empirical equation to show the variation of rate constant *(k* *)* of a reaction with temperature *(T)* was suggested by Hood. His equation is

Log*k* = *A’- B****/****T* (2.18)

Where *A’* and *B* are positive empirical constants and *T* is absolute temperature.

The verification of this equation lies in the fact that a plot of log *k* versus 1/T is nearly a straight line with negative slope for most of the reactions. This equation was theoretically justified by Van’t Hoff in 1884. His arguments were based on the variation of equilibrium constants with temperature. Arrhenius extended his ideas and suggested a similar equation to show the variation of rate constant with temperature in the year 1889. The Arrhenius equation is,

*d* ln k/*d*T = Ea/RT2 (2.19)

In this equation, *k* is the rate constant, T the absolute temperature, R the gas constant in calories and Ea is known as Energy of activation for the reaction. If Ea is a constant with respect to temperature, integration of equation (2) above gives the result.

*ln k = -*Ea/RT + constant (2.20)

The constant in equation (3) is found to be log A. Therefore, the exponential form of equation (3) above is *k = ke-Ea/RT.* The constant a and Ea are related to A and B in equation (1). The factor A is known as the frequency factor. A plot of *k* versus Ea according to this exponentials similar to type I curve.

Rewriting equation (3) as

Log *k* = -Ea/2.303*RT +* log A (2.21)

This equation is identical with the empirical equation (1). According to this equation , a plot of log *k* versus 1/T should be a straight line with a slope –*Ea /*2.303R and intercept logA knowing the slope, the value of constant Ea which is characteristic of the reaction can be calculated e.g., for the decomposition of N2O5, the slope is -5400. Hence Ea is given by:

Ea = -(-5400) (2.303) (1.987) = 24,700 cals/mol. (2.22)

Ea can also be determined if the specific rate constants are known at two different temperatures: if *k*1 is the specific rate constant at temperature T1 and *k*2 at another temperature T2 then from equation (4)

Log k2/k1= Ea/2.303R (T2-T1/T2T1) (2.23)

**Log *k***

**1/T X 10**3

**Fig 2.2: variation of log *k* with 1/T for the decomposition of N2O5**

It is evident from the equation that if the specific rate constants at two different temperatures are known, Ea can be readily evaluated or when Ea and specific rate constant at one temperature are known, then specific rate constant at any other temperature can be calculated.

**2.6 The Bioinorganic Chemistry of Copper**

Copper is one of the transition elements frequently found at the active site of proteins. The copper containing enzymes and proteins constitute an important class of biologically active compounds. The biological functions of copper proteins/enzymes include electron transfer, dioxygentransport, oxygenation, oxidation, reduction and disproportionation *(Mukherjee,2003).*

In nature, a variety of copper proteins are essential consyituents of aerobic organisms, including hemocyanins (arthropods and molluskan O2 carriers) and enzymes that activate O2, promting oxygen atom incorporation into biological substrates. The latter include tyrosinase (a monooxygenase, incorporating one oxygen atom to the substrate and reducing the other to water) and dopamine β-hydroxylase (a mono oxygenase). “Blue’’ multicopper oxidases [ e.g, laccase (phenol and diamine oxidation), ascorbate oxidase (oxidation of *l-*ascorbate) and ceruloplasmin] prmote substrate one-electron oxidation while reducing O2 to water *(Mukherjee,2003).*

Ceruloplasmin may be involved in copper metabolism. Cytochrome *c* oxidase transducer energy from the same 4e-/4H+ reduction of O2 ocurring at a heme-Cu binuclear cemtre and couple this to membrane proton translocation utilized in ATP synthesis. Amin oxidases and galactose oxidase effect amine aldehyde oxidative deaminations and alcohol aldehyde oxidative dehydrogenations, respectively. Copper ion reactions with reduced dioxygen derivatives ( e.g. superoxide (O2), hydrogen peroxide) are essential in Cu-Zn superoxide dismutase, and may be involved in copper-mediated oxidative damage in biological media, including possibly in Alzheimer’s disease.

Correlated with the enzymatic activity, the copper proteins exhibit unique spectroscopic properties and accordingly, the proteins are divided in mainly three types: Type 1 copper proteins (also called “blue” copper proteins) are known to have copper ion in the active site. This copper ion shows some remarkable spectroscopic features: an intense absorption around 600 nm, with an extinction coefficient of about 3000M-1cm-1. Another characteristic feature of the type 1 copper proteins is the extremely small hyperfine splitting in the EPR spectra (Aµ≈ 40-90 x 10-4 cm-1). Type 11 copper proteins have no distinct unique properties. The spectroscopic data of these proteins are comparable to those of normal copper compounds. Type 111 copper proteins contain antiferromagnetically coupled copper dimmers. These proteins are diamagnetic and therefore are EPR silent.

In some proteins, all three types of copper sites are present. Such proteins were proposed to classify as Type IV. In ascorbate oxidase one of the copper ions is found in a distorted tetrahedral (trigonal pyramidal) coordination with two histidines, a methionine and a cysteine. This resembles the active site of the blue copper protein plastocyanin. Also, a trinuclear copper site was found consisting of a type 111 copper pair and a normal Type 11 copper ion.

Reactions that copper proteins carry out have long interested inorganic chemists. Copper is an important element in oxidation catalysts for laboratory and industrial use. Interest in the copper-dioxygen complexes stems from the diverse occurrence of copper proteins which function as highly efficient biooxidation catalysts. Copper-dioxygen adducts are suggested as key reactions intermediates in these enzymatic reactions. The differentiation in the function of these proteins is attributed primarily to the coordination structure of the copper-dioxygen intermediate formed in the protein matrices, depending on the ligand donors, the geometry, and the coordination mode of the dioxygen. However, the correlation between these structural factors and the function/catalysis of the enzymes remains to be elucidated *(Holm et al; 1996).*

**Table 2.5**

**Pseudo-first order rate constant for the reaction of [Co11HEDTA(H2O)] and [Cu11] at [Co11 HEDTA(H2O)]=1X10-4 (mol dm-3), T=29±10C and λmax=510nm *(Njoku and Eni, 2015).***

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **103  [Cu2+] (mol dm-3)** | **103 [H+ ] (mol dm-3)** | **I, NaClO4 (mol dm-3)** | **103 kobs** | **K2** |
| 2.0 | 5.0 | 0.05 | 4.2989 | 21.4945 |
| 5.0 | 5.0 | 0.05 | 4.606 | 9.212 |
| 2.0 | 5.0 | 0.05 | 5.066 | 7.237 |
| 10.0 | 5.0 | 0.05 | 6.333 | 63.33 |
| 12.0 | 5.0 | 0.05 | 8.0605 | 67.171 |
| 7.0 | 3.0 | 0.05 | 5.389 | 7.699 |
| 7.0 | 5.0 | 0.05 | 6.275 | 8.964 |
| 7.0 | 7.0 | 0.05 | 6.37 | 9.1 |
| 7.0 | 9.0 | 0.05 | 7.860 | 11.229 |
| 7.0 | 11.0 | 0.05 | 9.81 | 14.014 |
| 6.0 | 5.0 | 0.02 | 10.608 | 17.68 |
| 6.0 | 5.0 | 0.03 | 7.64696 | 12.743 |
| 6.0 | 5.0 | 0.04 | 5.47485 | 9.125 |
| 6.0 | 5.0 | 0.05 | 3.915 | 6.525 |
| 6.0 | 5.0 | 0.06 | 3.247 | 5.412 |

**CHAPTER THREE**

**3.0 MATERIALS AND METHODS**

**3.1 MATERIALS**

**3.1.1 Chemicals**

All the chemicals used for this work were of analytical grade. A list of the chemical used during the entire work is shown below:

1. Sodium perchlorate
2. Cobalt (II) chloride
3. Perchloric acid
4. N-(2-hydrox-ethyl) ethylenediamine-N’,N’,N’-triacetic acid
5. Acetic acid
6. Copper (II) tetraoxosulphate (iv) salt
7. Magnesium chloride hexahydrate
8. Sodium acetate

**3.1.2 Apparatus/Equipments**

* Beakers
* Measuring cylinders
* Weighing balance
* Micro pipettes
* Stop clock
* Thistle funnel
* Filter paper
* Conical paper
* Curvet
* Reagent bottle
* Glass rod
* Test tubes
* Test tube rack
* Spatula
* Spectrophotometer
* Aluminium foil

**3.2 METHODS**

**3.2.1 Preparations of the complex [CoIIHEDTAH2O]**

All the chemicals used were of analar grade. The stock solution of the complex [Co11HEDTAH2O] was prepared according to the method of *(Mansour, 2013),* 0.500g of (HEDTA) was weighed and transferred into a beaker. This was dissolved in a minimum amount of 0.01MHCL. The CoCl2 solution was prepared by weighing 0.360g of salt into a beaker and dissolving with a little quantity of distilled water.

A solution of [Co11HEDTAH2O] was then prepared by mixing the solution of the CoCl2 with a slight excess of HEDTA solution. This was made up to 500 cm3 with distilled water and allowed to stand for a minimum of 24h to ensure complete formation.

**3.2.2. Preparation of 0.1M of perchloric acid**

About 4.0 ml of concentrated perchloric acid solution was diluted in a 500ml standard volumetric flask to prepare 0.1mol/dm3 stock solution.

**3.2.3. Preparation of the standard solution of sodium perchlorate**

0.5moldm-3 stock solution of sodium perchlorate was prepared by dissolving about 30.61g of the salt in distilled water and making up the solution to 500ml in a standard volumetric flask.

**3.2.4. Preparation of the standard solution of copper (11) tetraoxosulphate (VI) salt**

To prepare 0.03moldm-3 stock solution, about 3.75g of CuSO4 was dissolved in distilled water. The solution was then made up to 500ml in a standard volumetric flask.

**3.3 DETERMINATION OF THE λmax (510nm)**

The λmax (510nm) was determined by running the electronic spectrum of the solution of [Co11HEDTAH2O] in the wavelength range of 340-700nm and plotting a graph of the absorbance against wavelength.

**CHAPTER FOUR**

**4.0. RESULTS AND DISCUSSION**

**4.1. Determination of the rate constant of the reactions (kobs).**

kobss is the pseudo-first order rate constant. It is derived from the equation: (A ͚- At) = A ͚- Ao e-kobs.t  where A ͚ and Ao are the final and initial absorbances respectively, At is the absorbance at time t and kobss is the pseudo-first order rate constant. In the case of determining the dielectric constant, a plot of log (At - A ͚) versus time is made and the slope is the kobss. Typical plot is represented as figure 4.1 below :

**X=TIME IN SECONDS**

|  |
| --- |
| 0.80 10 20 30 40 50 60 70 80 90 100 110 120  -1.00  -1.10  -1.20  -1.30  -1.40  -1.50  -1.60  -1.70  -1.80 |

**Y=Log of (At-A ͚ )**

|  |  |
| --- | --- |
| **Time** | **Log(At - A ͚ )** |
| 10secs | * 1.108 |
| 20secs | * 1.18 |
| 30secs | * 1.38 |
| 60secs | * 1.55 |
| 90secs | * 1.75 |
| 120secs | - |

**Fig 4.1 : Graph of Log(At - A ͚ ) versus Time**

**4.2 THE EFFECT OF DIELECTRIC CONSTANT**

The effect of dielectric constant (D) on rate of reactions between the (Co11HEDTAH2O) and Cu11 ions was investigated at constant concentration of oxidant and reductant.

While the temperature, acidity and ionic strength of the medium was kept constant, the dielectric constant of the medium was varied using acetone and water mixture.

The oxidation of (Co11HEDTAH2O)- by Cu11 at [H+] = 5.0 x 10 -3 moldm-3, I = 0.05 moldm-3, (NaClO4) and T = 29.0 ± 1 oC showed independence of rates on the dielectric constant D.

Decreasing the dielectric constant from 63.25, 61.09, 58.93, 56.76, 54.60, 52.44, and 43.78 (CH3COCH3/H2O) as shown in Table 4.1 below, did not change kobss.

**Table 4.1: CALCULATIONS OF THE DIELECTRIC CONSTANT FOR Cu2+ IN THE OXIDATION OF [Co11HEDTAH2O]- BY Cu 2+**

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Volume of water | Volume of acetone | % weight of water | % weight of acetone | Dielectric constant |
| 2.95 | 1.05 | 73.75 | 26.25 | D1=63.25 |
| 2.80 | 1.20 | 70.00 | 30.00 | D2= 61.09 |
| 2.67 | 1.35 | 66.25 | 33.75 | D3= 58.93 |
| 2.50 | 1.50 | 62.50 | 37.50 | D4= 56.76 |
| 2.35 | 1.65 | 58.75 | 41.25 | D5 = 54.60 |
| 2.20 | 1.80 | 55.0 | 45.0 | D6= 52.44 |
| 1.60 | 2.40 | 40.00 | 60.0 | D7= 43.78 |

Density of Acetone = 0.97g/ml

Density of water = 1.0 g/ml

Dielectric constant for Acetone = 20.7

Dielectric constant for water = 78.4

Total volume of Acetone and Water = 4.0 ml

**TABLE 4.2 : Dependence of rate on dielectric constant (D) for oxidation of [Co11HEDTAH2O]- by Cu2+ at [Cu2+] = 2.0 x 10-3 mol dm-3, [Co11HEDTAH2O] = 1.0 X 10-4 mol dm-3, [H+] = 5.0 x 10-3 mol dm-3, I = 0.05 mol dm-3 (NaClO4), λ = 510nm, T= 29 ± 10C**

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| **D** | 63.25 | 61.09 | 58.93 | 56.76 | 54.60 | 52.44 | 43.78 |
| **10 3 kobs (S-1)** | 2.44 | 2.63 | 2.63 | 2.07 | 1.92 | 1.91 | 2.99 |

**Stock solution:** HClO4 = 0.1 mol dm-3, NaClO4 = 0.5 mol dm-3 , Cu 2+ = 3x10-2 mol dm-3, [Co11HEDTAH2O]- = 0.003mol dm-3.

From table 4.2 above, it is seen that the rates of reaction in this experiment is independent of the dielectric constant,because as we decrease the dielectric constant, the rates of the reaction do not either increase or decrease markedly. In other words, as we increase the volume of acetone in the solvent, the rates of reaction do not give any noticeable change.

**4.3. THE EFFECT OF ADDED IONS:**

At constant concentration of all other reactants, the effect of added ions on the rates of the reactions was investigated by varying the concentration of X where X is either acetate ion (CH3COO-) or magnesium ion (Mg2+).

For the oxidation of [CoIIHEDTAH2O]- by Cu2+, X was varied from 30 x 10-3 – 130 x 10-3 mol dm-3. For this system, the rates of reactions were found to be unaffected by the presence of either Mg2+ or CH3COO- as shown in Table 4. 3 below:

**Table 4.3: Dependence of rate constant on added ions for the oxidation – reduction reactions of [CoIIHEDTAH2O]- = 1.0 x 10-4 mol dm-3, [Cu 2+] = 2.0 x 10-3 mol dm-3, [H+] = 5.0 x 10-3 mol dm-3, I = 0.05 mol dm-3 (NaClO4), λ max = 510nm, T= 29 ± 10c**

|  |  |  |
| --- | --- | --- |
| **X** | **103 [X] mol dm-3** | **103 kobs (S-1)** |
| **Mg 2+** |  |  |
|  | 30.0 | 1.50 |
|  | 50.0 | 1.50 |
|  | 70.0 | 1.75 |
|  | 90.0 | 1.50 |
|  | 110.0 | 1.61 |
|  | 130.0 | 1.76 |
| **CH3COO-** | 30.0 | 1.38 |
|  | 50.0 | 1.70 |
|  | 70.0 | 1.72 |
|  | 90.0 | 2.21 |
|  | 110.0 | 1.70 |
|  | 130.0 | 1.34 |

**4.4. TEMPERATURE DEPENDENCE OF RATES OF REACTIONS**

The dependence of temperature on the rates of the reactions for the oxidation of [CoIIHEDTAH2O]- by Cu2+ was investigated at 350C, 400C, 500C, 550C and 600C respectively. The rate constants determined are reported in table 4.4.

From Eyring equation and thermodynamics,

Log kobs/T = log k/h + S#/2.303R - H#/2.303RT2 (2.24)

Where kobs = Temperature dependent rate constant.

k= Boltzmann’s constant

h= Planks constant

S# = Entropy of activation

H# = Enthalpy of activation

R = universal gas constant

T = Temperature

From the plots of log kobs/T versus 1/T2, the activation parameters were determined from the slopes and intercepts as in table 4.4

**Table 4.4 : Temperature dependence of rate constants for the oxidation- reduction reaction of [CoIIHEDTAH2O]- and Cu2+, at [CoIIHEDTAH2O]- = 1.0 x 10-4 mol dm-3, [Cu2+] = 2.0 x 10-3 mol dm -3, [H+] = 5.0 x 10-3 mol dm-3, I= 0.05 mol dm-3, (NaClO4), λmax = 510nm.**

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **Temp. (K)** | **102 kobs(S-1)** | | **Logkobs/T** | **105 1/T2** |
| **308** | **1.7** | | **­-4.26** | **1.05** |
| **313** | **1.9** | | **-4.22** | **1.02** |
| **323** | **2.1** | | **-4.19** | **0.96** |
| **328** | **3.2** | | **-4.01** | **0.93** |
| **333** | | **3.5** | **-3.98** | **0.90** |

logkobs

-3.70 9.1 .92 .93 .94 .95 .96 .97 .98 .91 1.0 1.1 0.2

-3.80

-3.90

-4.00

-4.10

-4.20

-4.30

**Fig 4.2 A graph of logkobs / T versus 1051/T2**

**Table 4.5 : Activation parameter for the reaction of [CoIIHEDTAH2O]-1 and Cu2+**

|  |  |  |
| --- | --- | --- |
| **Oxidant** | **H#** | **S#** |
| Cu2+ | -24.184kJmol-1 | **-**185.374JK-1 mol-1 |

For the determination of Ea (activation energy) the equation K = Ae-Ea/RT is used.

The constant A is called the frequency factor or pre-exponential factor; Ea is the activation energy. Converting the above equation to logarithmic form, gives

Log10K = Log10A – Ea#/2.303RT (2.25)

It is apparent that by determining the values of K at several temperatures, the plot of log10k versus 1/T will yield the activation energy from the slope of the curve and the frequency factor from the intercept. Although the frequency factor may depend slightly on temperature, unless the temperature range is very great. The determination of the activation energy is an important objective of any kinetic investigation.

**Table 4.6: Table for graph of temperature 1/T(k-1) versus Logkobs**

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **Temp** | **kobs** | **Log kobs** | | **103 1/T(k-1)** |
| 308 | 0.0170 | -1.77 | | 3.25 |
| 313 | 0.017 | -1.72 | | 3.19 |
| 323 | 0.021 | -1.68 | | 3.10 |
| 328 | 0.032 | -1.49 | | 3.04 |
| 333 | 0.035 | -1.46 | 3.00 | |

From the table 4.6, it is seen that the rate of reaction increases as the temperature of the reaction increases.

10 1/T(K-1)

logkobs 2.05 3.00 3.05 3.10 3.15 3.20 3.25 3.30

-1.20

-1.30

-1.40

-1.50

-1.60

-1.70

-1.80

**fig 4.3**. A graph of kobs versus 1**/**T

from the graph, the intercept is -1.38 = 0.0417 = A.

G# = H#  - T S#

Hence -24.184JK-1 mol-1 – 333 x -185.374Jk-1mol-1

= -24.184JK-1mol-1 + 61729.542

= 61705.358JK-1mol-1

= 61.705kJmol-1

Therefore the activation parameters are increased including the activation energy, the frequency factor and free energy of activation in the table below:

**Table 4.7 : The activation parameters for the reactions of [COIIHEDTAH2O]- and Cu2+**

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| **Oxidant** | **H#** | **S#** | **G#** | **Ea#** | **A** |
| Cu2+ | -24.184 J mol-1 | **-**185.374JK-1mol-1 | 61.705kJmol-1 | 26.19J mol-1 | 0.042 |

**CHAPTER FIVE**

**5.1 CONCLUSION**

This work on the kinetics and mechanisms of oxidation-reduction reaction (Electron Transfer Reactions) of [COIIHEDTAH2O]-  and Cu2+ was started by Enih Rita Bamidele in 2015. She and her group synthesized the [COIIHEDTAH2O]complex, determined the λ max for the complex, the stoichiometry for the reaction, determined the pseudo-first order rate constants for the reaction, worked on the effect of acidity and ionic strength.

Hence this present work is a continuation of the above work which specifically bordered on the effect of dielectric constant on the rates of this reaction, the effect of added ions on the rate of this reaction, the effect of temperature and hence the determination of the activation parameters on this reaction.

Hence from table 4.2 above, it is seen that the rates of reaction in this experiment is independent of the dielectric constant, because as we decrease the dielectric constant, the rates of the reaction do not either increase or decrease markedly. In other words, as we increase the volume of acetone in the solvent, the rates of reaction do not give any noticeable change.

For the oxidation of [CoIIHEDTAH2O]- by Cu2+, X was varied from 30 x 10-3 – 130 x 10-3 mol dm-3. For this system, the rates of reactions were found to be unaffected by the presence of either Mg2+ or CH3COO- as shown in Table 4. 3

From the table 4.6, it is seen that the rate of reaction increases as the temperature of the reaction increases.

Hence the activation parameters so determined in this work is as shown in table 5.1

**The activation parameters for the reactions of [COIIHEDTAH2O]- and Cu2+**

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| **Oxidant** | **H#** | **S#** | **G#** | **Ea#** | **A** |
| Cu2+ | -24.184 J mol-1 | **-**185.374JK-1mol-1 | 61.705kJmol-1 | 26.19J mol-1 | 0.042 |

**5.2 RECOMMENDATION**

This complex requires to be studied in both liquid and solid forms to enhance the chance of the reductants and the design of the reactions. Hence spectroscopic characterization of this complex is highly desired.

There is the need to establish the test for intermediate complexes formed in the course of this reaction, and to analyze the various products formed at the various stage of this reaction and finally to elucidate the mechanisms of the reaction.

These are some of the areas which we hope that subsequent researchers can be of use.