Hello. Hi, I am Miss varsha K. Sail

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Title of the unit: Reaction

Kinetics and mechanism.

Module name: Trans effect with respect

to square planar platinum complexes.

Outlines of the model:

Definition of the trans

effect Trans effect series.

Theories of trans effect

mechanism of trans effect.

And application of trans effect

for synthesis of isomers

of square planar complex.

The learning outcomes at the end of

this module: student will be able

to explain the concept of trans

effect and trans effect series.

Understand different theories

explaining Trans effect.

Explain the mechanism of trans

effect in square planar substitution.

Also described the application of

trans effect for synthesis of cis or

trans isomer of square planar complex.

The important feature of substitution

reaction is square planar complex

is the non label ligand that

are trans to the leaving ligand.

The legand trans to the leaving

group in square planar complex may

influence the rate of substitution.

They may also play an important

role in the type of isomer obtained.

The ability of an attached group to

direct substitution into a position

trans to itself is called trans effect.

Consider a general square

planar substitution reaction.

$[PtTX_3] + Y \longrightarrow [PtTX_2Y] + X$

The product is again a square planar complex.

Now any of one of the three ligands X

can be replaced by the entering ligand Y

The ligand X that is replaced can be either

cis or trans to ligand T, leading to either cis or trans.

Orientation of Y with respect to

T in the product.

The proportion of cis or trans

product varies appreciably with

the nature of ligand.

ligands that strongly favor

trans substitution to give a

product in the reaction are said to be

stronge Trans directing Ligand and.

A strong Trans Director ligand

T promotes more rapid substitution of

the ligand trans to itself then

it does to ligand cis itself.

Now the Trans effect series.

The series of ligands arranged

in the order with respect to their

tendency to be strong trans director

is known as Trans Effect series.

If T is a strong Sigma donor ligand or

π acceptor ligand then it greatly

accelerates substitution of ligand

that lies trans to it.

The rough order of ligand with

increasing trans effect is as below.

The order are also roughly the

order of increasing overlap of the

ligand orbital with either Sigma

or a Pi 6P orbital of platinum.

thus greater the overlap

stronger is the trans effect.

Let's not consider the different

theories of trans effect.

The stability of ground state

and the activated complex both

affect the activation energy

required for substitution reaction.

As a result,

any factor affecting the stability of

ground state and the activated complex will

influence the trans effect.

Accordingly, there are two theories.

1st Polarization theory.

2nd is the Pi bonding theory.

The former relates to the

ground state and the letter

to the activated complex.

Now let's consider first

the polarization theory.

It was given by Greenberg who first

attempted to explain trans effect.

This theory is related to the

stability of the ground state.

It is postulated that.

The primary charge on the metal ion

polarizes the electron cloud on the ligand T

and induces a

dipole moment in it.

The dipole moment on T in tern induces

dipole moment in metal(M).

The orientation of the dipole

in the metal ion is such that it

repells the negative charge in the

ligand X trans to ligand and T.

This can be shown in a figure like

this.

As a result, the ligand X is

less attracted to the metal ion

due to the presence of ligand T.

The magnitude of trans effect of T and

it's polarizability

are monotonically related.Now.

this is largely correct for ligand

and which do not form π bond

with the metal such as H^-, I^- , Cl^-

Thus trans effect is directly related

to polarization of the ligand and

now let's consider the second theory.

The pi bonding theory.

This theory explains the trans

effect of ligand,

which are strong Pi acceptor or π acids.

For example, carbonyl or alkynes.

It relates the tendency of the

ligand T to remove the orbital
electron density

on metal by pi bonding, to the

magnitude of their trans effect.

For substitution reaction in square planar,

it suggests that a transition state

with trigonal bi pyramidal geometry.

This transition state geometry is stabilized.

if empty Pi orbitals,

that is either p, d or π antibonding

ligands of T, overlap with

nonbonding filled d π orbitals

of the metal to form a π bond.

The activated complex that is a

trigonal bi pyramidal trans – MX_3YL
is shown in the figure below.

There's a metal complex metal line here.

This is a ligand (T) which is trans director.

See incoming ligand is Y

This is a ligand which is trans to the leaving group.

Now, because of this M-T pi interaction,

the electron density from the dxz

orbital of the metal line is drawn away

from the incoming nucleophile, Y
Thus the trigonal bipyramidal

transition state is stabilized.

Hence, strong by acceptor ligand

greatly accelerated the substitution

of ligand that lies trans to it.

Now let's consider the stetric course of

ligand subscription in square planar complex.

The incoming ligand Y results

in the formation of a triangular

bipyramidal 5 coordinated intermediate.

The ligand and X1 and X2 occupy

axial position.

So X1 and X2 are the ligaments

which are not leaving.

Where as X is the ligand which is

leaving group and ligand T in the

complex is a strong trans director

The entering ligand Y and the leaving

ligand X and the trans ligand

T which is the trans director ligand

shared the equatorial position of the

trigonal bipyramidal intermediate.

The new ligand Y in the

final product occupies position

vacated by the leaving group.

The reaction sequence can

be summarized as follows.

So we have the trans director, ligand T.

This is X ligand and which is

Leaving, while X1 and X2 are not leaving.

now Y is the substituting ligand.

Forming a trigonal bi pyramidal complex.
The trans Director Ligand T and

the leaving ligand and the incoming

ligand Y occupy Equitorial position.

But as the other two ligands

occupy axial position. Finally.

X lives and the incoming ligand Y

occupies a position Trans to T ligand.

Now let's consider the application

of trans effect in synthesis of

isomers of square planar complex.

Now consider the synthesis
of cis and trans isomer of $[Pt(NH_3)_2Cl_2]^{2+}$

Diammine dichloride Platinum

The cis isomer is

obtained by treatment of.

$[Pt\ Cl_4]^{2-}$ ion with ammonia.

Because Chloro has greater trans

directing effect than ammonia,

the incoming ammonia will not substitute.

In the transformation

to the existing ammonia.

It occupy a position cis to

the existing ammonia.

The reaction can be summarized as follows.

If we start with tetrachloro platinate

then the first ammonia will just

substituting so you have one position

occupied by ammonia. The 2ndI ammonia which

comes will not occupy a position

trans to chloro since it is more

trans directing so it is going to

substitute a chloro transt to it.

Finally the product is cis

isomer of the platinum. $[Pt(NH_3)_2Cl_2]^{2+}$

complex so the system will be favored.

Now the trans isomer of platinum, diiammine
Difluoro platinium $[Pt(NH_3)_2Cl_2]^{2-}$ is prepared by treating $[Pt(NH_3)_4]^{4+}$

Tetra ammine platinium complex with chloride ion.

The chloride ion has a greater

Trans effect than ammonia,

so the first chloride ion directs the second

incoming chloride to its trans position.

This actually can be summarized as follow,

So if we start with the tetrammine

complex of platinum.

The first chloro occupies

one of the place by replacing

one of the Ammonia, 2nd chloro.

will occupy a position trans to

the first choro.Since

Chloro is stronger trans directing

then ammonia and the final product is

a trans isomer of platinum.

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