

Hello students,

today we will be doing CHC 109 in

organic chemistry for semester 6.

And the unit title is organometallic

chemistry, where we will be doing the

Ean rule and the 18 electron rule.

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Miramar . So the outlines for

today's topic is we will be doing.

Mainly it is coming under the

topic of organometallic chemistry

and what applications Ean rule and

the 18 electron rule have towards

organometallic chemistry and

specifically towards metal carbonyls.

So learning outcomes after

completing this module,

students will be able to define the Ean

rule as well as the 18 electron rule.

They will be also able to apply this

rules for prediction of molecular
formula of metal carbonyls.

So specifically we're going to use
these rules only for prediction
of molecular formula of different
types of metal carbonyls.

Then,
after finding out the EAN rule
or whether it is applicable and
18 electron rule.

We will be able to predict the stability
of complexes by applying this rules.

So now let us go to the introduction
first of what is the EAN rule?

In carbonyls,
the carbon monoxide molecule or
the CO molecule is bonded to the
metal through the carbon atom.

There are three types of metal
carbonyl linkages.

The carbonyl molecule behaves

as it can behave in three ways,

so as a) monodentate ligand b)a

bridge between 2 metal atoms and

c) which is less frequently a

bridge between 3 metal atoms.

So as I have said,

the first one which is the carbonyl

behaving with mono dentate

ligand and it is more common.

Second is the bridge between 2 metal atoms.

It is little less common and very less.

Less frequently is the bridge

between 3 metal atoms..

Now let us see which are those

examples and how do you nominate

the CO groups ,so the mono Dented

terminal CO groups are most common

in examples of nickel Tetra,

carbonyl and iron Penta carbonyl.

So these are the two common ones.

Besides that there are more.

I featured 2 examples.

Later on I will show you more

examples in a tabular form.

The KETONIC or the doubly bonded CO

groups occur in polynuclear carbonyls.

Example is Co_2C_8 and Fe_2CO_9 .

Now here there are two metal atoms.

As you can see in the first one in the

mono dented there is only one metal atom.

Then the third one is the triple bridging

type has been found on very few compounds

and I've given only two examples.

So the first one is cobalt 4 carbonyl

twelve and Rh₆ CO 16.

So one is of cobalt with carbonyl

and one is of rhodium with carbonyl.

So now let us see how these are different

and how the electron contribution

is present in all the three types.

So in a terminal MCO group.

The carbonyl donates 2 electrons

to an empty metal orbital.

There is only one in this in the
bridging metal carbonyl metal group,
it is assumed that each metal carbon
bond is formed by 1 metal electron,
and one carbon electron.

Because it is a double feature.

Maximum number of electron bonds a
metal might form with carbon monoxide
molecules is limited by the number
of vacant orbitals available on
the metal atom or by the geometric
considerations in the space around it.

The number of available orbitals is
obtained from the EAN or the 18 electron rule,
which is only a modified form of the EAN rule.

So now let us come to the main rule,
which is the effective atomic number rule.

So how do you define it?

In complexes,
the metal atom or ion every time
it may not be an atom,

so sometimes it can also be an ion
it accepts electron pairs from
the ligands till the total number
of electrons associated with the
metal becomes equal to the atomic
number of the next inert gas element
in the periodic table.

So as you know,
there are many elements in the
periodic table, so you have to see.

Which one coincides?

That shows the stability
of the metal carbonyl.

Now one example,
which I have given over here is.

Nickel Tetra carbonyl.

So let us see first is the atomic
number which is represented
by Z for nickel it is 28.

Now there are four carbonyls.

So electrons donated by 4 carbonyl ligands.

Each ligand will donate 2 electrons,

so 4 into 2 is 8.

So total will be $28 + 8$ that is equal to 36.

So 36 corresponds to atomic

number of inert gas.

Krypton

so most of the metals in the complexes obey

the rule and are diamagnetic in nature.

Examples are a metal carbonyls

like nickel Tetra carbonyl ,iron

penta carbonyl or chromium hexa Carbonyl.

In order to attain the EAN next

inert gas configurations,

metals with even atomic number

combined with integral number of

CO ligands and obey the rules,

that means equal numbers.

So when there is an equal number,

the diamagnetic property will be satisfied.

On the other hand,

metals with odd atomic number

dimerize forming polynuclear

carbonyls and obey the rules.

So if you have an odd number then it

won't match up to any of the inert gases.

Which is having an even number,

so they haven't even atomic number.

So how do you match it so then what

they will do if there is an odd

atomic number then it will dimerize,

forming polynuclear carbonyls

and obey the rule.

Now let me give you an example

of a polynuclear carbonyl.

So for example,

we have di manganese DECA

carbonyl where you are meant to see CO ten.

Here the atomic number of manganese is 25

and each manganese is coordinated to five.

Ligands again which donate

10 electrons to manganese.

Now in addition there is an

electron from the Mn-Mn Bond.

Electrons donated by the five

carbonyl ligands.

So let us sum it up is equal to 5 into 2

that is equal to 10 for each manganese atom.

So, total it will correspond to see now

here we have an example of manganese

which is an odd atomic number.

So as I told you,

it will dimerize.

Mostly time arises or atomic number,

metal atoms and so the total

year will be $25 + 10 + 1$.

That is equal to 36 which is

corresponding to the atomic

number of the inert gas Krypton.

So the next one,

now this is to show you that

sometimes there is an exception to

the rule and the exception to the

rule here is shown by vanadium hexa.

Carbonyl vanadium has an odd atomic number of 23 and electrons which are donated by 6 carbonyl ligands will be equal to 6×2 that is equal to 12.

So then you take the addition $23 + 12$ is equal to 35. So in the case of.

Vanadium hexa carbonyl.

It does not obey the rule and is paramagnetic in nature.

OK,

so now quickly let us have a look at the table and just to show you see we have some mononuclear and some polynuclear

I have taken only two metal atoms.

OK so dinuclear.

So let us see the first example.

So chromium is 24 and electrons from the terminal carbonyl as 6×2 is 12.

There are no electrons from bridged, no electrons from M-M bond.

So total is 36 and that will coincide to

Inert gas Krypton now another

example is a manganese carbonyl

so this is polynuclear that

is dinuclear so atomic number

is 25 then by the terminal carbonyl atoms of

each $1/5$ into two is 10, $10 + 25$ will be 35.

So how does it follow the rule?

There is one electron from the M-M bond

so that coincides with script on the

same is seen for iron carbonyl which

is a similar example like chromium.

But your atomic number is 26.

Five into 10. Do is 10 and 36 so Krypton?

Another example is nickel Tetra

carbonyl which is atomic number

28 four into two equal to 36 Krypton.

Then we have another one which

is polynuclear carbonyl of

Cobalt. Cobalt is an odd atomic number

so it dimerizes it gives you $27 + 6$

and 2 electrons from bridge carbonyl
plus one electron from the M-M bond.
So total this comes up to 36 then we
have one with tungsten and one with
rhenium so with tungsten it is a
mononuclear by a high atomic number of
74 and four rhenium high atomic number of 75.

The only difference between the two.

Is 1 electron short,

so that will be utilized from the

M-M bond so that both becomes 86 and

it is radium OK and last one is

vanadium hexa carbonyl which is 23

and 6 into 2 equal 12 so that becomes 35.

So you can see in this whole table

there is only one metal carbonyl

which does not follow the EN rule.

Now the last part of this is

the 18 electron rule.

This is an alternative statement

to the Ean rule to explain

stability in transition metals.

The ns np and $n - 1$ d orbitals and
the total number of valence electrons
that can be accommodated is 18.

Therefore, according to this rule,
stable electronic configuration of 18 will
result when you add up all the orbitals.

OK,

all the electrons in the orbitals,
so ns will be 2.

And p will be 6 and $n - 1$ d should have 10,
so they're completely filled by
utilizing lone pair of electrons
from the carbonyl ligands.

So again, we have another table.

This is for the 18 electron rule,
so we can see that there are
fewer metal carbonyls over here.

So the more successful one is the Ean rule.

This is the modified one,
but this also is applicable.

This also can be used to see

the stability of complexes.

So the first example is chromium hexa.

Carbonyl atomic number is 24.

So what we have to do is we have to

look at the valence electronic shell

SO $3d_54s_1$ that makes 6 electrons.

Plus 12 electrons from the terminal

carbonyl and then no electrons from

bridged and no electrons from the M-M bond.

So that becomes total number

of valence electrons 18.

Now here we are not looking at

any inert gas configuration.

Yeah, we're looking at the 18 electron rule.

That is all the orbitals in ns,

np and n-1d should

be completely filled.

The next one is Mn_2CO_{10} .atomic number is 25.

Outer electronic configuration is

$3d_54s_2$ so 10 electron contribution,

one electron from the M-M bond and

total number of electrons will be 18.

Then we have Iron Penta carbonyl

where the atomic number is 26 and 3d

6s² outer electronic configuration.

Total number of electrons from terminal CO 10.

So 6 + 2 and 10 so that is 18.

Then we have a dicarbonyl.

OK then we have Co₂C₈ that is Octa,

carbonyl of cobalt and atomic

number is 27 and three d⁷4s² is the

outermost electronic configuration.

So 3 into 2 is equal to 6 and 7+8=9.

So then add up 15 sixteen 17 and 18.

So total comes to 18 and the last one

is nickel Tetra carbonyl where we

have atomic number 28 and electronic

configuration of the outermost

shell is 3d⁸4s².

So terminal electrons contribution is

4 into 2 eight and no electrons from

bridged and no electrons from M-M

bond because it's a mononuclear carbonyl.

So that brings it up to 18

So the references for this part of the

module is JD Lee Concise inorganic chemistry.

Puri Sharma ,Lakshmi Devi Tuls,

Basu,

and Shriver Atkins.

Thank you students.