Oxidative Addition

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Contents

• Introduction to oxidative addition reactions;
• Mechanism of oxidative addition reactions;
• Some examples in mechanism research;
• Summary and outlook.
• Acknowledgement
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General information about oxidative addition

The origin of modern organo transition metal chemistry can be traced to the discovery of ferrocene in 1951

Vaska’s complex


General Information

Most common cases

\[ \text{oxidative addition} \quad \text{reductive elimination} \]

\[ \text{LnM} + A \quad \text{B} \]

16e \quad \Delta \text{O.S.} = +2

18e \quad \Delta \text{C.N.} = +2

These reactions are not limited to transition metals; perhaps the most familiar oxidative addition is the formation of Grignard reagents, but it can also occur whenever an element has two accessible oxidative oxidation states two unit apart:

\[ \text{MeBr} + \text{Mg} \quad \text{MeMgBr} \]

\[ \text{ClCl} + \text{PCl}_3 \quad \text{PCl}_5 \]

Other types of oxidative addition reactions

1. Electrophilic attack of metals

\[ \text{LnM} + E^+ \quad \text{LnM}^+ \quad E \]

\[ \Delta \text{O.S.} = +2 \]

\[ \Delta \text{C.N.} = +1 \]

Examples:

\[ \text{Fe(CO)}_5 + \text{H}^+ \quad [\text{HFe(CO)}_5]^+ \]

\[ [\text{Mn(CO)}_5]^- + \text{CH}_3\text{I} \quad \text{CH}_3\text{Mn(CO)}_5 + \Gamma \]
2. Binuclear oxidation reactions

![Diagram of binuclear oxidation reactions]

\[ \text{LnM} \quad \text{Ln} \quad \text{A} \quad \text{B} \quad \text{LnM} \quad \text{Ln} \quad \text{A} \quad \text{B} \]

\[ \Delta \text{O.S.} = +1 \]
\[ \Delta \text{C.N.} = +1 \]


3. Oxidative Coupling

![Diagram of oxidative coupling]

The Cr on the right now has two new anionic alkyl ligands forming a metalloccyclopentane ring system.

While this is an oxidative addition, there is a special term for this type of reaction called **oxidative coupling**.

The driving force for this reaction is

1. formation of a new C-C s-bond (stronger than a p-bond)
2. creation of two new strongly donating anionic ligands that can better donate to the metal even though one has technically lowered the electron count.
Definition of Oxidative addition

• An oxidative addition reaction is one in which (usually) a neutral ligand adds to a metal center and in doing so oxidizes the metal, typically by \(2e^-\) and new anionic ligands end up bonded to the metal center.

• The transferring of the two electrons from the metal to the incoming ligand breaks a bond in that ligand forming two new anionic ligands.

• At least one of these new anionic ligands ends up bonded to the metal center.

Oxidizes the metal and coordinative number increases !!!

General Features of Oxidative Additions

the more electron-rich the metal is the easier the oxidative addition to the metal center:

• strongest donor ligands
• fewest \(\pi\)-acceptor ligands
• most negative charge
Electronic effect               Steric effect             Metal center

The formal oxidative state change is always +2

What about the real charge on the metal changes???

The real charge on the metal changes much less than that because A and B do not end up with pure -1 charges in LnM(A)(B).

The change in real charge depends on the electronegativity of A and B.

Carbonyl Stretching Frequencies of the Oxidative Addition Products from Vaska's Complexs

<table>
<thead>
<tr>
<th>Reagent</th>
<th>ν(CO)(cm⁻¹)</th>
<th>Δν(CO)(cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td>1967</td>
<td>0</td>
</tr>
<tr>
<td>O₂</td>
<td>2015</td>
<td>48</td>
</tr>
<tr>
<td>D₂</td>
<td>2034</td>
<td>67</td>
</tr>
<tr>
<td>HCl</td>
<td>2046</td>
<td>79</td>
</tr>
<tr>
<td>MeI</td>
<td>2047</td>
<td>80</td>
</tr>
<tr>
<td>C₂F₄</td>
<td>2052</td>
<td>85</td>
</tr>
<tr>
<td>I₂</td>
<td>2067</td>
<td>100</td>
</tr>
<tr>
<td>Cl₂</td>
<td>2075</td>
<td>108</td>
</tr>
</tbody>
</table>

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Mechanism of oxidative addition reactions

Oxidative addition

Two-electron Mechanism

$S_N2$  Ironic  Three center Cis-addition

Single-electron Mechanism

Radical mechanism

Chain  non-chain
Two-Electron Mechanisms Oxidative Addition

Three-Center Cis-Addition (Concerted pathway)

The characteristics of this reaction mode would be
(a) Retention of configuration
(b) rate = k[LnM][AB]
(c) Metal center must be coordinatively unsaturated with a dn configuration where n > 2.
(d) A and B must be cis

these molecules do NOT contain electro-negative atoms and/or are not good oxidizing agents. Aside from H₂, they are often considered to be "non-reactive" substrates:

H₂, C-H bonds, Si-H bonds, S-H bonds, B-H bonds, S-S bonds, C-C bonds, etc.
The Characteristics of this mechanism are:
(a) Inversion of configuration of carbon
(b) A cationic intermediate
(c) \( \text{rate} = k[LnM][R-X] \)
(d) Classical RX structure/reactivity patterns
Me>primary>secondary>tertiary and R-OTs > I>Br>Cl>F
(e) R and X might be cis or trans after the recombination step

If the starting metal complex is 16e (as shown above) both ligands will usually end up coordinated to the metal to make an 18e complex.

What about the starting metal complex is 18e??
In the case of a starting $^{18}\text{e}$ complex (shown below) only one of the two anionic ligands (usually the strongest binding) generated from the oxidative addition will end up coordinated to the metal unless a separate substitution reaction occurs.

Another example:

$$\text{Na}_2[\text{Fe(CO)}_4] + \text{RX} \rightarrow \text{Na}[\text{Fe(CO)}_4] + \text{NaX}$$

**Rate Law**

$$\text{rate} = k[\text{Na}_2\text{Fe(CO)}_4][\text{RX}]$$

**Steric factor:**

<table>
<thead>
<tr>
<th>RI</th>
<th>RBr</th>
<th>ROTs</th>
<th>RCl</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.13</td>
<td>4*10^{-3}</td>
<td>1.4*10^{-5}</td>
<td>&lt; 1*10^{-5}</td>
</tr>
</tbody>
</table>

**Leaving group effect**

<table>
<thead>
<tr>
<th>RI</th>
<th>RBr</th>
<th>ROTs</th>
<th>RCl</th>
</tr>
</thead>
<tbody>
<tr>
<td>51</td>
<td>1</td>
<td>0.58</td>
<td>2.3*10^{-3}</td>
</tr>
</tbody>
</table>
How to determine stereochemistry at carbon?

The processes involving CO and MeOH are known not to change configuration at carbon.


Anion Assisted S_N2 oxidative addition

General:

M^{n+} + Y \rightarrow [Y-M^{n+}]^{-}

[Y-M^{n+}]^{-} + X \rightarrow [Y-M-CO]^{-} \rightarrow X'

K_1 > K_2

Ionic Mechanism

Some molecules (e.g. HCl, HBr, HI) dissociate into ions in polar solvents:

\[
\text{HCl} \rightarrow \text{H}^+ + \text{Cl}^-
\]

Therefore oxidative addition of these molecules in polar solvents must involve ionic species.

\[
\text{LnM} + \text{H} - \text{X} \rightarrow \text{LnM}_{n-x}^+ + \text{H}^+ + \text{Cl}^-
\]

Pt(PPh3)4

18e d19 tetrahedral

[Pt(PPh3)3]+ + H+ + CT \rightarrow [Pt(PPh3)2]+ + Cl−

16e d8 square planar

[Ir(cod)L2]+ + H+ + CT \rightarrow [IrCl(cod)L2]+ + H2

16e d8 square planar

RCO2H, HgCl2 also react by the same mechanism

One-electron Mechanisms for Oxidative Addition

1. Atom Abstraction and combination of the Resulting Radical with a Second Metal

\[ \text{rate determining step} \]

\[ M^{n\text{th}} + RX \rightarrow X^{n\text{th}} + \bullet R \]

\[ \bullet R + M^{(n+1)} \rightarrow R^{(n+1)} \]

Net: \[ 2M^{(n)} + RX \rightarrow R^{(n+1)} + X^{(n+1)} \]

This is not a chain-mechanism!

Characteristics:
(a) 2:1 stoichiometry
(b) Racemization of carbon
(c) \( \text{rate} = k[M][RX] \)
(d) Reaction sequence reverse of SN2
\[ 3^+ > 2^+ > 1^+ > \text{Me} \]
(e) Reaction sequence with respect to X
\[ \text{R-I} > \text{R-Br} > \text{R-Cl} >> \text{R-OTs} \]

Thus R-OTs reacts fast in SN2, slow in Radical mechanism.

Other examples: Mn(CO)5; M(Cp)(CO)3 (M=Cr,Mo,W) 17-electron complexes!
2. Inner-sphere Electron transfer/Caged Radical-Pair Mechanism General:

\[ M^{(n)} + RX \rightarrow M^{(n+1)} + \cdot X + R \]

Characteristics:
(a) The products are very similar to those of a S_n2 reaction
(b) The reactivity order is
   \[ R-I > R-Br > R-Cl > R-OTs \]
   (this order is determined by thermodynamics)
   Note: in S_n2 R-OTs most reactive
   \[ 3' > 2' > 1' > Me \]
   (this order is determined by the relative order of the radicals)
   This order is opposite to S_n2 mechanism
(c) This pathway requires a coordinatively unsaturated metal capable of undergoing a formal two-electron oxidation
(d) ArOH does not work as an inhibitor
If Ar = (2,4,6-tri-tert-butyl) bromobenzene, the aryl radical can be detected directly by ESR in the reaction mixture.


Follows the order $3^\circ > 2^\circ > 1^\circ$

The radical $R$ is not trapped by $ArOH$ as $R$ does not leave the cage

$\bullet R + ArOH \rightarrow RH + ArO\bullet$

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**3. Outer-sphere Electron-Transfer Mechanism**

$RX + M^{n} \underset{\text{fast}}{\longrightarrow} RX^{\bullet} + [M^{n+1}]^{\bullet}$

$[RM^{n+2}]^{\bullet} + X^{-} \rightarrow R^{0} + X^{-} + [M^{n+1}]^{\bullet}$

Net $M^{n} + RX \rightarrow [RM^{n+2}]^{\bullet} + X^{-}$

This reaction is associated with coordinatively saturated metal centers
The rearrangement is indicative of radical formation

cyclopropyl carbinyl radical butenyl radical

4. Radical Chain pathway

Initiators = impurities, O₂, hv
(b) racemization of R
(c) The reactivity order is R-I > R-Br > R-Cl > R-OTs
   Note: in SN₂ R-OTs most reactive
(d) R-° > R-1° > R-2° > Me
   This order is opposite to SN₂ mechanism
(e) ArOH does work as an inhibitor
The reaction can be stopped by ArOH

The oxidative addition of $\text{C(sp}^3\text{-})X$ to $\text{Pd}^0$

The oxidative addition of $\text{C(sp}^3\text{-})X$ to $\text{Pd}^0$ complexes [PdL$_2$] (L=phosphane) is usually an associative bimolecular process ($S_N2$ reaction)

Inversion at stereogenic center

The oxidative addition of C(sp²)-X to Pd⁰

1. The palladium species in the catalytic cycle

Classical Mechanism for Cross-Coupling Reactions
Jutand and Amatore demonstrated that the three-coordinated anionic Pd(0) species $[\text{Pd(PR}_3)_2\text{OAc}]^-$ or $[\text{Pd(PR}_3)_2\text{Cl}]^-$ were formed, instead of the classical two coordinated complex, by the reaction of Pd(II) salts with phosphine and are involved in the oxidative addition step.

\[
\begin{align*}
\text{PhR}_3\text{P} & \quad \text{OAc} \\
\text{AcO} & \quad \text{C} \\
\text{PPH}_3 & \quad \text{P}
\end{align*}
\]

$[\text{Pd(OAc)ClCl}]^-$ $\quad \text{+} \quad [\text{AcO-PPH}_3]$ $\quad \text{H}_2\text{O} \quad \text{H}^+$

$[\text{Pd(OAc)ClCl}]^-$ $\quad \text{HCl} \quad \text{OPPH}_3$

$[\text{Pd(OAc)ClCl}]^-$

\[
\begin{align*}
\text{PhR}_3\text{P} & \quad \text{PhR}_3\text{P} \\
\text{Cl} & \quad \text{Cl} \\
\text{PhR}_3\text{P} & \quad \text{Cl}
\end{align*}
\]

The oxidative addition of C(sp²)-X to Pd⁰

2. cis complexes in the oxidative addition

A concerted interaction of a reactive [PdL₂] or [Pd(L-L)] (L-L=diphosphane) species with RX in a **three-center transition state**

\[
\begin{align*}
\text{Pd} + R + X & \rightarrow [\text{PdL}_2RX] & \rightarrow \text{PdL}_2RX \\
\text{Pd} + R + X & \rightarrow [\text{Pd(L-L)RX}] & \rightarrow \text{Pd(L-L)RX}
\end{align*}
\]

The intermediates observed in the catalytic cycle are trans-[PdRXL₂]

In fact cis complexes are observed to result from the oxidative reaction in a few cases with C(sp²) electrophiles

Model reaction for the cis–trans isomerization:

One of the two main pathways:

mono-iodo-bridged intermediate


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\[ S_n^2 \quad \text{Ironic} \quad \text{Three center} \quad \text{Cis-addition} \]

Single-electron Mechanism

\[ \text{Radical mechanism} \]

\[ \text{Chain} \quad \text{non-chain} \]

Acknowledgement

- Prof. Zhangjie Shi
- All members in our group
Thank you for your attention!