(i) 4-Nitroaniline

(ii) 3-Iodosulphonic acid

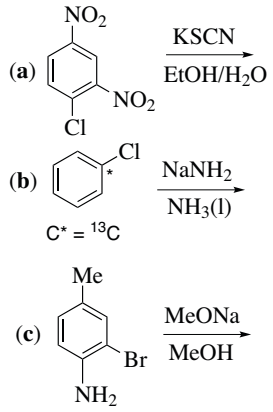
(iii) 4-Nitrocarboxylic acid

(iv) 3-Chloroaniline

4. Compare the proton chemical shifts of $[(C_6H_6)FeCp]^+$ with that of benzene.

5. Predict the number of peaks and their δ_H values for aza[18]annulene ($C_{17}H_{17}N$).

6. Determine the product(s) of the following substitution reactions.



Student Corner

Monsanto and Cativa processes of acetic acid synthesis

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In 1960, chemists at BASF developed the carbonylation of methanol into acetic acid.

$$CH_3OH + CO \xrightarrow{\text{catalyst}} CH_3COOH$$

Monsanto process

Monsanto Company introduced a new catalytic system in 1966. It is now known as the Monsanto acetic acid process, which operates at about 180 °C, under CO pressure of about 40 atm, using **rhodium catalyst**. Over six million tonnes of acetic acid are produced annually.

Catalyst

The catalyst system contains a **rhodium source** (*e.g.* $RhCl_3$, or $[RhCl(CO)(PPh_3)_2]$) and **iodide ions** (HI). The **active catalyst** is *cis*-$[Rh(CO)_2I_2]^-$.

Monsanto process consists of three coupled reactions/cycles. The cycles (i) and (iii) are **non-metallic** and (ii) is **organometallic**.

(i) Conversion of MeOH to MeI by HI.

$$MeOH + HI \longrightarrow MeI + H_2O \text{ -- (1)}$$

(ii) Catalytic carbonylation of MeI to MeCOI by the catalyst $[Rh(CO)_2I_2]^-$.

$$MeI + CO \longrightarrow MeCOI \text{ ------ (2)}$$

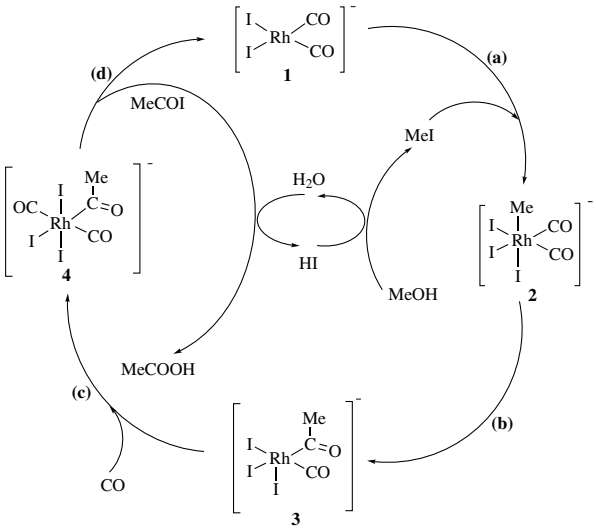
(iii) Hydrolysis of MeCOI to produce $MeCO_2H$ and HI.

$$MeCOI + H_2O \longrightarrow MeCO_2H + HI \text{ -- (3)}$$

The **overall reaction** is obtained by adding equations (1), (2) and (3), which gives

$$MeOH + CO \longrightarrow MeCO_2H$$

Let us look at the complete catalytic carbonylation process involving the active catalyst *cis*-$[Rh(CO)_2I_2]^-$. The proposed full catalytic cycle is given in scheme 1.



Scheme 1 Combined catalytic cycle for the Monsanto Process

(a) Oxidative addition of MeI to $[Rh(CO)_2I_2]^-$ **1** to give the octahedral methyl-complex ion *fac* -$[MeRh(CO)_2I_3]^-$ **2**; this is the rate determining step.

(b) Migration of Me on to a CO ligand gives the five-coordinate acetyl-complex ion $[(MeCO)Rh(CO)I_3]^-$ **3**.

(c) Coordination of another CO ligand to the complex ion **3** gives the octahedral complex ion $[(MeCO)Rh(CO)_2I_3]^-$ **4**; **4** can have either *fac*- or *mer*, *trans*-arrangement.

(d) Reductive elimination of MeCOI generates the active catalyst **1**. Finally, the hydrolysis of MeCOI produces $MeCO_2H$ and HI.

Higher alcohols can be carbonylated, but reactivity decreases in the following order.

MeOH > EtOH > PrOH

Cativa process

Cativa process was developed by BP Chemicals in 1996, and this process is based on a catalyst system containing **iridium** and **ruthenium**. The active catalyst is the anion *cis*-$[Ir(CO)_2I_2]^-$. Both Monsanto and Cativa processes are very similar, that they can use the same chemical plant. Initial studies by Monsanto had shown iridium to be less active than rhodium for the carbonylation of methanol to produce acetic acid. However, subsequent research showed that the iridium catalyst could be promoted by ruthenium, and this combination leads to a catalyst system that is superior to the rhodium-based systems. The proposed catalytic cycle is quite similar to the one shown in Scheme 1. Cativa process uses less water in the reaction mixture and decreases the formation of by-products, thus, it reduces the cost of production.

Synthesis of acetic anhydride

Industrially, acetic anhydride is produced by carbonylation of **methyl acetate** in a process that is very similar to Monsanto acetic acid synthesis.

$MeCO_2Me$ is used in place of methanol as a source of methyl iodide. **Rh(III) iodide** is the catalyst precursor. **LiI** is used instead of HI to generate MeI.

As acetic anhydride gets easily hydrolyzed, the whole process is conducted under anhydrous conditions in contrast to the Monsanto acetic acid synthesis.

Problems

1. EtBr oxidatively adds to $[RhBr_2(CO)_2]^-$ to give (**A**). (**A**) in the presence of CO, gives the acetyl complex (**B**). (**B**) reductively eliminates (**C**) to regenerate $[RhBr_2(CO)_2]^-$. Identify (**A**), (**B**) and (**C**).
2. Write the organometallic cycle for the conversion of ethanol into propionic acid using rhodium catalyst.
3. Comment on the rates of oxidative addition of MeI to the active catalyst with respect to Monsanto and Cativa processes.
4. Write balanced equations for the conversion of methyl acetate to acetic anhydride.