Student Corner

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Hydroformylation of olefins

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Hydroformylation or introduction of an "oxo" group to an olefin is referred to as the '**oxo process**' which is catalyzed by homogeneous catalysts based on cobalt or rhodium. This is a prominent method of producing tons of aldehydes and their alcohol derivatives.

Formation of **aldehydes** through the reaction between a mixture of CO and H_2 (**synthesis gas**) and olefin in the presence of a cobalt catalyst, *e.g.*, $[Co_2(CO)_8]$ was discovered by Otto Roelen in 1938.

$$RCH{=}CH_2 + CO + H_2 \xrightarrow{\text{catalyst}} \underset{\text{normal-product (linear)}}{RCH_2CH_2CHO} + \underset{\text{iso-product (branched)}}{RCH(CH_3)CHO}$$

This reaction can be viewed as an addition of a **H** and a formyl group **CHO** across a double bond. A terminal olefin ($RCH{=}CH_2$) can generate two products (i) **terminal** aldehyde RCH_2CH_2CHO known as the '**normal**' product and (ii) **branched** isomer, $RCH(CH_3)CHO$, known as the '**iso**' product. In most cases, the normal isomer is obtained as the major product.

It is an important reaction because (i) it increases the number of carbon atoms in the olefin, and (ii) the resulting aldehyde group can be further converted into other functional groups such as alcohol, carboxylic acids, acid chlorides, halide, *etc.*

Catalysts

Some of the simple catalysts/precatalysts that can be used for this reaction are $[Rh_2(CO)_4Cl_2]$, $[Co_2(CO)_8]$, $[Rh_4(CO)_{12}]$ $[RhCl(CO)(PPh_3)_2]$, $[Rh(acac)(CO)_2]$, and $[RhH(CO)(PPh_3)_3]$. Rh/$[P(OR)_3]$-systems are also known to be very effective for this reaction.

Applications

One of the main applications of this process is to manufacture *n*-butyraldehyde (**1**) and isobutyraldehye (**2**) from propene.

$$CH_3CH{=}CH_2 + CO + H_2 \xrightarrow{\text{catalyst}} \underset{n\text{-butyraldehyde}}{CH_3CH_2CH_2CHO} + \underset{iso\text{-butyraldehyde}}{CH_3CH(CH_3)CHO}$$

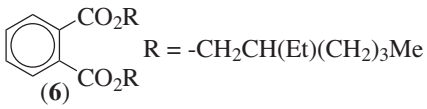
Butyraldehyde (**1**) is used to manufacture *n*-butanol (**3**), 2-ethylhexanol (**4**) and 2-ethylhexanoic acid (**5**) as shown below.

(i) $CH_3CH_2CH_2CHO + H_2 \longrightarrow \underset{(3)}{CH_3CH_2CH_2CH_2OH}$
(1)

(ii) $2\ CH_3CH_2CH_2CHO \xrightarrow{-H_2O} CH_3CH_2CH_2CH{=}C(Et)CHO \xrightarrow{H_2} CH_3CH_2CH_2CH(Et)CH_2OH$ (4)

$CH_3(CH_2)_3CH(Et)COOH$ (5) $\xleftarrow{[O]}$

2-Ethylhexyl phthalate (**6**) is a plasticizer used for poly(vinyl chloride).



(6)

Another important application is the conversion of 1-octene to 1-nonanol. 1 Nonanol is used to produce detergents. Main industrial processes of hydroformylation of olefins are given below.

a) Original Roelen Process
b) Shell Process
c) Union Carbide Process

Original Otto Rolene process

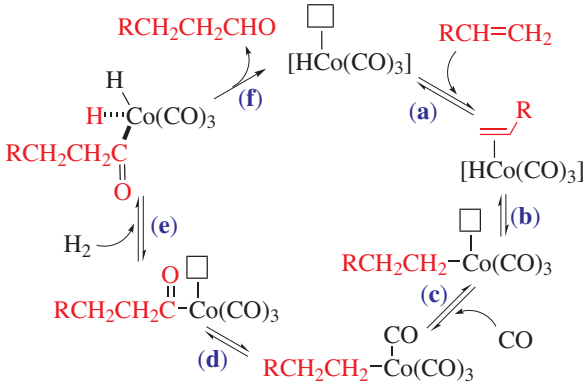
The original Roelen process, set up in 1938 by BASF Company to produce aldehydes. It operates at elevated temperatures around 150 °C and high CO/H_2 pressure (200-350 atm). Thus, the cost of running is high. Under these conditions, the catalyst precursor is converted into the active catalyst **$[HCo(CO)_3]$** as shown below.

$[Co_2(CO)_8] + H_2 \rightleftharpoons 2\,[HCo(CO)_4]$
(18e) **(18e)**

$+ CO \rightleftharpoons - CO$

$2\,[HCo(CO)_3]$
(16e)

The proposed catalytic cycle is shown in scheme 1. The square depicts a vacant site.



Scheme 1. The proposed catalytic cycle for the hydroformylation of $RCH=CH_2$ to the linear isomer RCH_2CH_2CHO.

(a) Coordination of olefin
(b) H-migration/insertion of olefin
(c) Coordination of CO
(d) Alkyl migration / insertion of CO
(e) Oxidative addition of H_2
(f) Reductive elimination of RCH_2CH_2CHO.

Note that the branched product is also formed under the same conditions.

The Roelen process gives a linear to branched product ratio of 3-4:1.

Shell process

The Shell process was developed by Slaugh and Mullineaux in 1966 for the Shell Company. It improved the original Roelen process by adding tri(n-butyl) phosphine (PBu^n_3) to the cobalt catalyst. The two major advantages of this process over the existing Roelen process are (i) it can be performed at a lower pressure (5-10 atm) of CO/H_2 (ii) It improves the linear/branched ratio to around 10:1. The active catalyst is believed to be $[HCo(CO)_2(PBu^n_3)]$. Coordination of the bulky phosphine ligand increases the formation of the linear product. The major drawback of this process is that it further reduces the desired aldehyde to the corresponding alcohol.

Union carbide process

This process was introduced by Union Carbide in 1976. It uses a mixture of rhodium carbonyl and PPh_3 as the catalytic system. The active catalyst is believed to be $[HRh(CO)(PPh_3)_2]$. The advantage of this process is (i) it works under normal temperature and pressure, and (ii) it is very selective for the linear product (linear: branch ratio = 30 : 1). The catalytic cycle is similar to that discussed under original Roelen process.