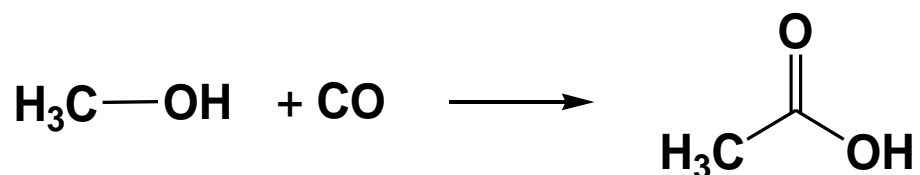


## Monsanto (BP) Acetic Acid & Related Processes

The carbonylation of methanol produces acetic acid:

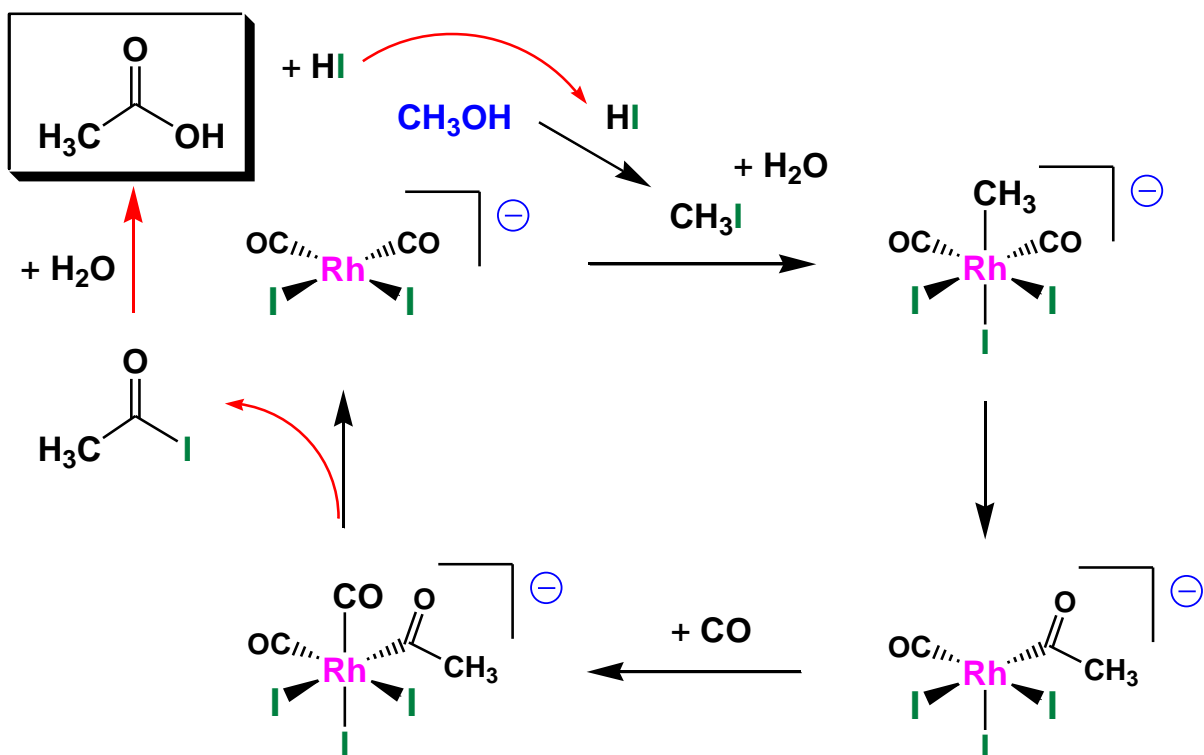


This is the second largest industrial homogeneous carbonylation process with over 7 billion pounds of acetic acid produced each year using this technology. Prior to 1970, acetic acid was made using cobalt catalysts (BASF process) requiring rather severe conditions. In 1970 Monsanto commercialized a rhodium carbonyl iodide catalyst that is commonly called the **Monsanto Acetic Acid Process** (developed in the late 60's by James Roth and his research team at the corporate research center in St. Louis). In 1986 Monsanto sold the acetic acid plant and technology to British Petroleum (BP), but it is still commonly referred to as the Monsanto Acetic Acid process.

As with hydroformylation catalysis, rhodium is  $10^3$  to  $10^4$  times more active than the corresponding cobalt catalyst, which means that much lower CO pressures and moderately lower temperatures are required. Most importantly, the rhodium catalyst gives extremely high selectivities to acetic acid:

	<b>Cobalt</b>	<b>Rhodium</b>
Concentration	$\sim 10^{-1}$ M	$\sim 10^{-3}$ M
Temperature	$\sim 230^\circ$ C	$\sim 180^\circ$ C
Pressure	500-700 atm	30-40 atm
Selectivity	90%	> 99%
H <sub>2</sub> effect	CH <sub>4</sub> , CH <sub>3</sub> CHO, EtOH byproducts	no adverse effect

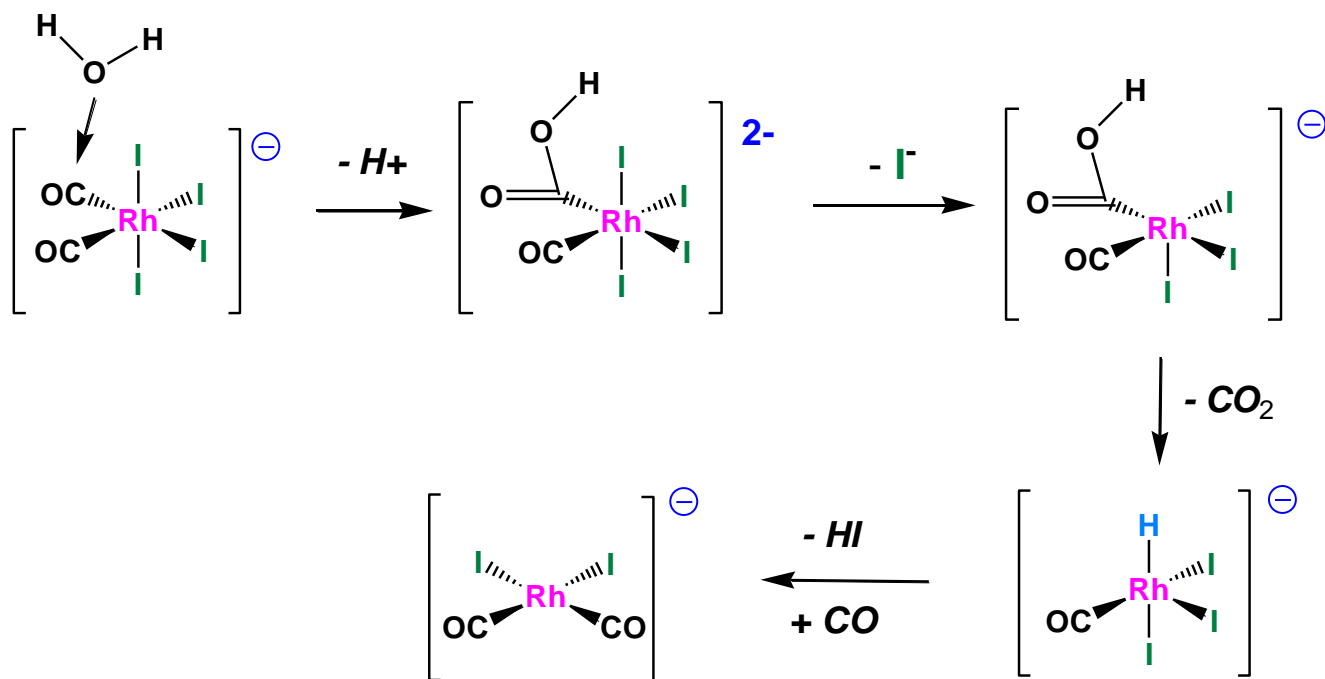
The mechanism has been extensively studied by Forster and coworkers at Monsanto and is shown below. This catalytic reaction is an unusual dual cycle system involving HI as one catalyst and  $[\text{RhI}_2(\text{CO})_2]^-$  as the transition metal component. HI catalyzes the conversion of MeOH to MeI and  $\text{H}_2\text{O}$  at the beginning of the Rh-catalyzed carbonylation reaction, followed by regeneration of HI at the end of the Rh-cycle by hydrolysis of the acyl-iodide. The Rh catalyst carbonylates the MeI to produce the acyl-iodide.



The reaction is independent of CO pressure, and first order in both rhodium and MeI. The rate determining step is the oxidative addition of MeI to the  $[\text{Rh}(\text{CO})_2\text{I}_2]^-$  catalyst. Thus, the production of MeI from methanol, catalyzed by HI, is critically important. Iodide ligands are considered to be quite important in this reaction due to the HI catalyzed conversion of MeOH to MeI and their relatively good donor abilities on the Rh center. The negative charge on the  $[\text{Rh}(\text{CO})_2\text{I}_2]^-$  catalyst is believed to be critical in assisting the oxidative addition of MeI to the rhodium center. The alkyl species,  $[\text{Rh}(\text{CO})_2(\text{Me})\text{I}_3]^-$ , is extremely reactive towards CO insertion to form the acyl complex.

## Celanese LiI Modified “Low Water” Catalyst System

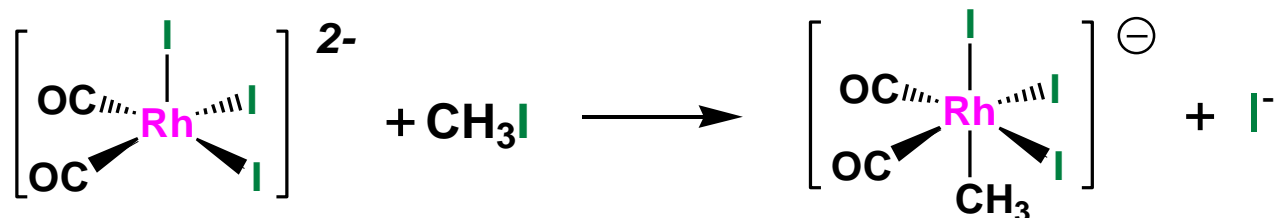
One problem with the original Monsanto process is that moderately high amounts of  $\text{H}_2\text{O}$  are needed to produce  $\text{H}_2$  in the reactor via the **water-gas shift rxn** ( $\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2$ ). The water and  $\text{H}_2$  were needed to react with precipitated  $\text{RhI}_3$  and “inactive”  $[\text{RhI}_4(\text{CO})_2]^-$ , which formed from side reactions, to regenerate the active Rh(I) catalyst. The reaction of water with inactive  $[\text{RhI}_4(\text{CO})_2]^-$  to generate active Rh(I) catalyst,  $[\text{RhI}_2(\text{CO})_2]^-$ , is shown below.



The relatively high amounts of  $\text{H}_2\text{O}$  needed also increases the amount of the highly corrosive  $\text{HI}$  present leading to engineering problems. The water reactivation process is also not especially efficient leading to more inactive Rh present in the reactor.

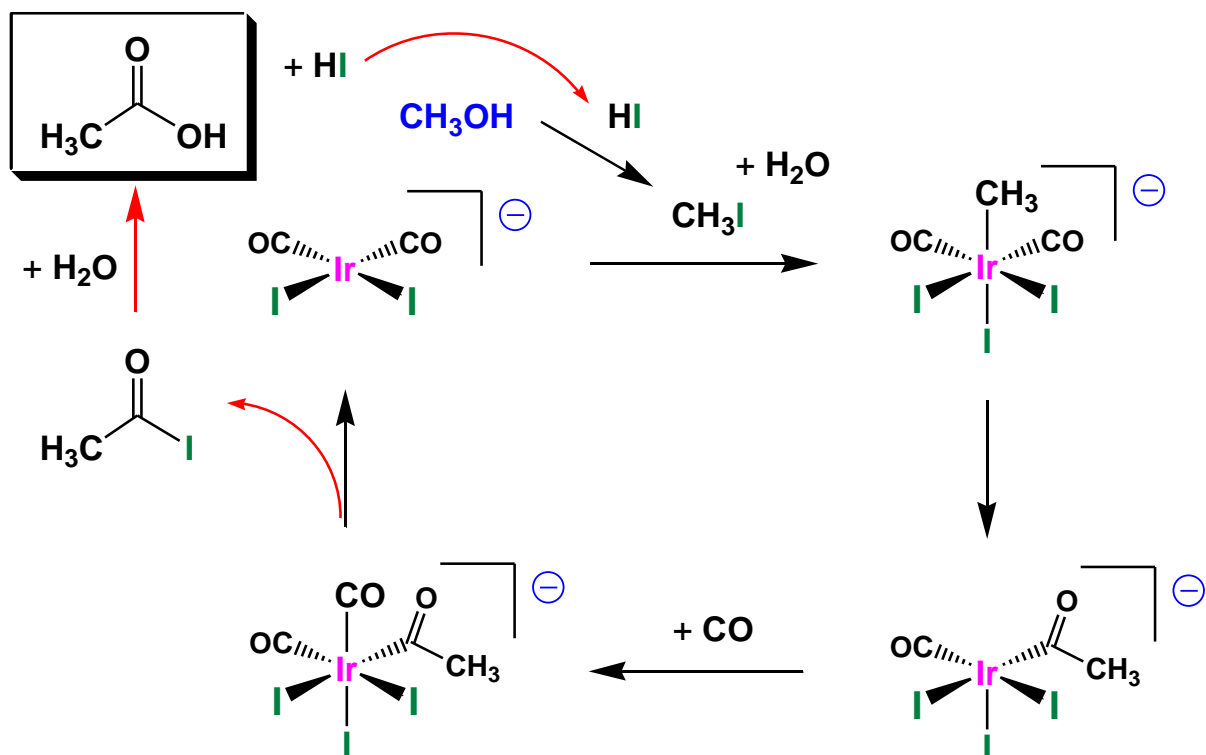
In the late 70's Celanese developed a major improvement on the Monsanto technology not covered by their narrow patent that involved the simple addition of  $\text{LiI}$  (and other proprietary modifiers) to reduce the amount of  $\text{H}_2\text{O}$  (and  $\text{HI}$ ) used in the catalysis. Added  $\text{LiI}$  increased the catalyst stability by minimizing the side reactions that produced inactive Rh(III) species. It also increased the amount of the more reactive dianionic  $[\text{RhI}_3(\text{CO})_2]^{2-}$  catalyst species. This considerably increased the catalyst activity, throughput, and efficiency.

**Problem:** Increasing the iodide concentration increases the amount of the following 18e- complex. Why is this more reactive and why doesn't this saturated 18e- complex slow down the subsequent oxidative addition reaction with MeI?



### BP Ir-Based Cativa System

The Cativa Ir-based acetic acid catalyst system was announced with much fanfare in 1999. However, much of this catalytic chemistry was part of the original Monsanto Acetic Acid patent. The Ir cycle was originally studied in considerable detail by Forster (along with the Rh system) in 1979 (*JCS Dalton*, 1979, 1639). The fundamental mechanism is essentially the same as the Rh cycle:



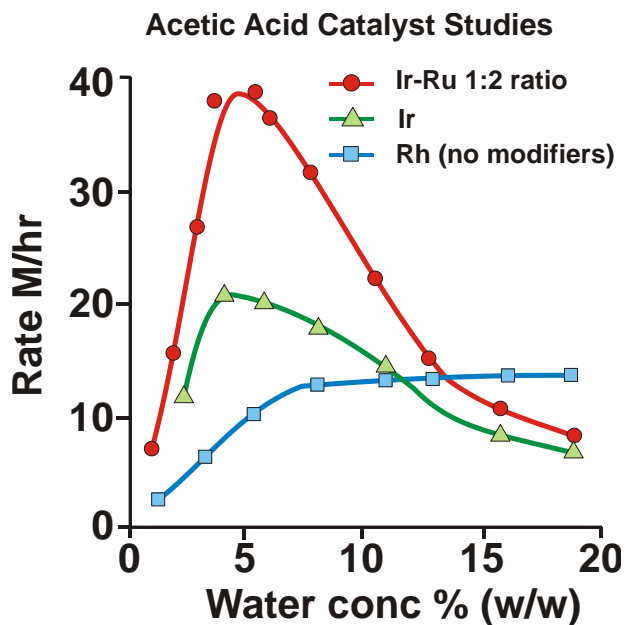
The main differences between the Ir and Rh catalyst systems:

- 1) The rate determining step for Ir is the migratory insertion of the Ir-CH<sub>3</sub> and Ir-CO ligands. The MeI oxidative addition step is faster for Ir due to its lower electronegativity.
- 2) The stronger Ir-ligand bonds slow down the migratory insertion step and reductive elimination steps (Foster noted this in 1979 paper).
- 3) There are considerably fewer side reactions in the Ir system to make inactive M(III) complexes (soluble or insoluble). This is also tied into point #2.

This enables the use of low water conditions that makes the BP Ir system competitive with the Celanese LiI modified low water high-activity Rh catalyst. Due to patents issued by Celanese and Eastman (see next section), BP could not make use of “normal” additives to convert the Rh catalyst to a low water system.

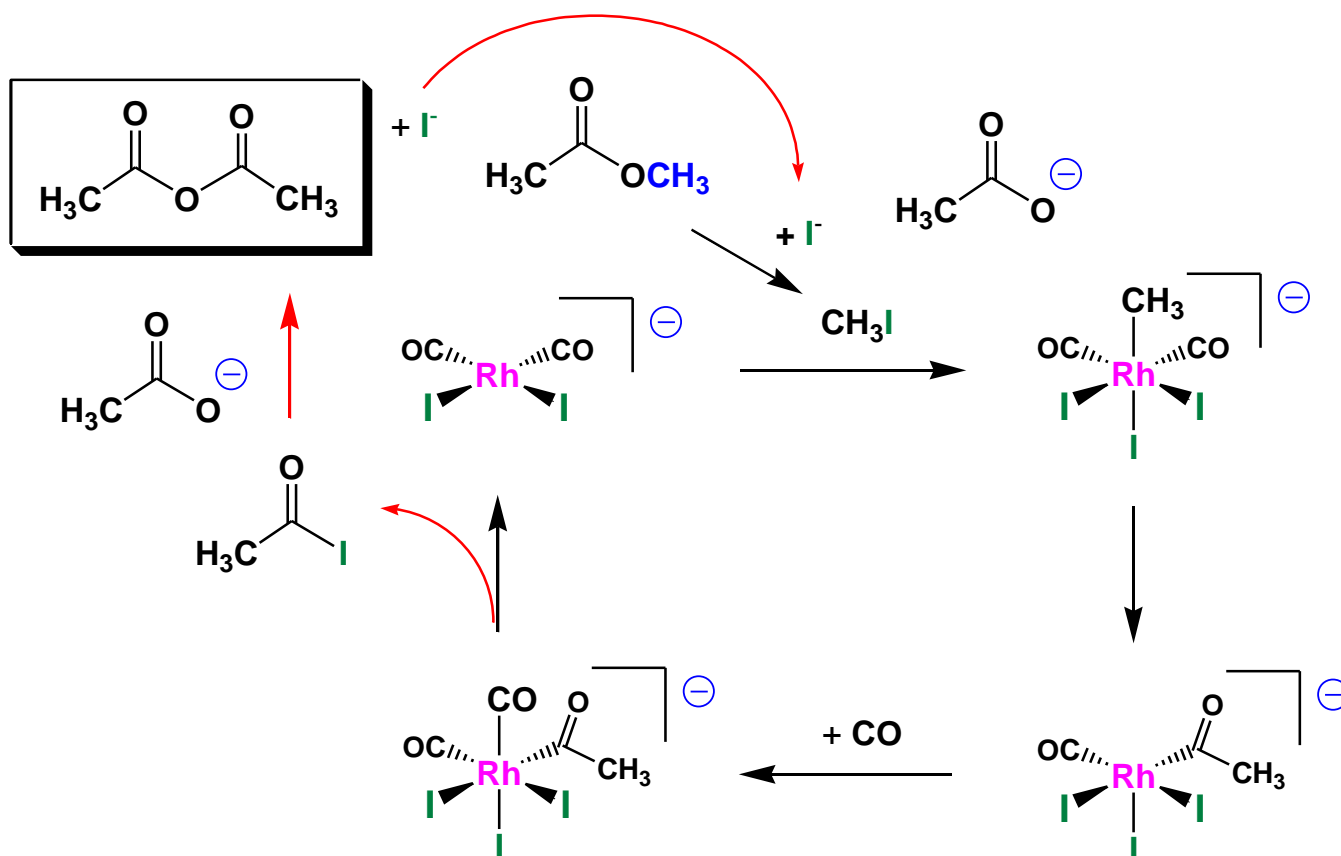
BP found, however, that a modifier was needed to remove an iodide ligand to generate less electron-rich (more unsaturated) complexes that would favor the CO-methyl migratory insertion and the final reductive elimination of acyl-iodide. They found that added RuI<sub>2</sub>(CO)<sub>3</sub> would reversibly abstract an iodide ligand from the [IrI<sub>3</sub>(CH<sub>3</sub>)(CO)<sub>2</sub>]<sup>-</sup> complex to enhance the rate of the CO-methyl migratory insertion. The enhancing effect is shown in the graph to the right.

(Haynes, *JACS*, 2004, 126, 2847)



## Eastman Chemical Acetic Anhydride Process

A very closely related process is the Eastman Chemical carbonylation of **methyl acetate** to produce acetic anhydride. This was commercialized in 1983 and produces over 800 million pounds of acetic anhydride a year at their Kingston, TN plant.



Note that this is essentially the same as the Monsanto/Celanese processes, only the initial reactant has changed. Eastman also worked out that adding excess Li(acetate), much like Celanese adds LiI, eliminates the need for water completely, which is important if one wants to make water sensitive acetic anhydride.

Since this wasn't covered by the Monsanto (or Celanese) patents, Eastman Chemical didn't have to pay any royalty or licensing fee, saving them a bunch of \$\$.