Acetic acid had a world demand of about 4.68 billion pounds per year in 1995. By 2002, this figure had grown to 5.63 billion pounds. This growing demand for Acetic acid is a major driving force to find a better catalyst to produce acetic acid more efficiently. About 60 percent of the acetic acid produced worldwide is made by the carbonylation of methanol. In 1960, the Monsanto Process for carbonylizing methanol was invented, which uses a rhodium catalyst. This was the leading technology until 1996 when BP introduced the Cativa™ Process, which involves an iridium catalyst. This paper will focus on the differences of the two catalysts and their respective mechanisms.

The first step is to take an in depth look at the Monsanto Process. This process requires a feed of methanol and carbon monoxide and produces ethanoic acid (acetic acid). The overall stoichiometry is as follows:

based on what? MeOH?

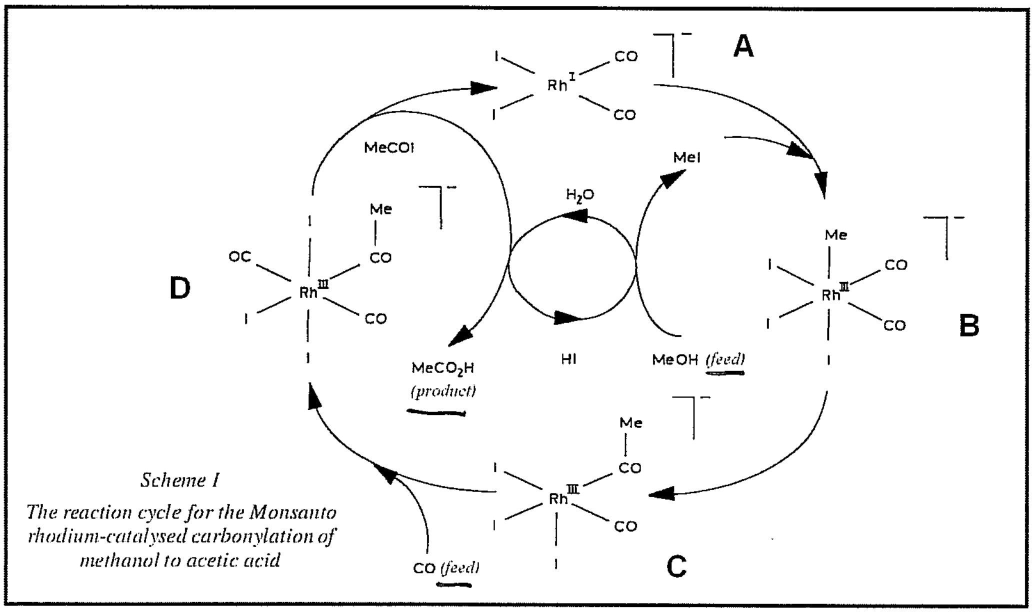
$$CH_3OH + CO \rightarrow CH_3COOH \tag{1}$$

tough to beat. What is the goal of a new catalyst.

This process runs at pressures of 30 to 60 atmospheres and temperatures of 150 to 200°C. The selectivity for this process is over 99 percent. The carbonylation reaction is done in a continuous stirred tank reactor (CSTR). Since the reactor is a CSTR, it can be estimated that the bulk of the reactor is product, acetic acid. The acetic acid is the solvent and the water, hydrogen iodide and catalyst are solutes. This liquid methanol is fed to the top and gaseous carbon monoxide is bubbled in from the bottom. The liquid products are taken off the bottom, and the gaseous byproducts such as CO_2 and H_2 are taken off the top. The byproducts are then scrubbed and discarded. The liquid from the bottom goes to a flash tank, where the acetic acid and byproducts are taken off as vapors. These are fed to a series of distillation columns to attain the final product. The liquid that remains in the flash tank contains dissolved catalyst and is recycled to the reactor.

The catalyst is a rhodium dicarbonyl diiodide anion, $[Rh(CO)_2I_2]^-$. *Scheme I*, shown below, is the accepted reaction mechanism for the rhodium catalyzed reaction. There are four main steps the rhodium complex cycles through, labeled **A**-**D**. Two more reactions occur independent from the rhodium complex, which make up the six distinct reactions found in this process.

The first reaction involves the methanol feed and the hydrogen iodide in the reactor, which react to form methyl iodide and water. The next step occurs at step **B** found in *Scheme I* below. The methyl iodide adds oxidatively to the rhodium catalyst, which creates a rhodium methyl complex. Next, at step **C**, the methyl group rapidly moves from the rhodium center to a neighboring carbonyl group. The movement of the methyl group leaves an open bond site on the rhodium complex. This site is filled by a CO molecule which is supplied in the feed, shown at step **D**. Reductive elimination of the $-COCH_3$ and -I gives CH_3COI, and the original rhodium dicarbonyl diiodide complex, seen at **A**. Attack by water on the CH_3COI species yields CH_3COOH, acetic acid, and hydrogen iodide, HI.



Scheme I
The reaction cycle for the Monsanto rhodium-catalysed carbonylation of methanol to acetic acid

In this system, the amount of water present is very important. If the water in the system is above 8% by weight, the rate determining step (RDS) is the addition of the CH_3I to the rhodium complex. Under these conditions, the reaction rate is observed to be first order in catalyst and methyl iodide concentrations. All other parameters are basically independent. The rate expression resembles:

$$\text{Rate} \propto [\text{Rh catalyst}] \times [CH_3I] \qquad (2)$$

The rate changes if the amount of water in the system is less than 8% by weight. The RDS becomes the reductive elimination of the CH_3COI from the catalyst complex shown at **D**. which only occurs if there is H_2O

Earlier it was mentioned that this reaction has a selectivity of over 99 percent. There are still, however, some side reactions that can prove to be very costly. good The first side reaction is the production of unwanted gases. The rhodium complex will catalyze ✓ the water gas shift reaction. This happens when the HI in the system adds oxidatively to the $[Rh(CO)_2I_2]^-$ complex, as seen at **A**. The reaction stoichiometry is as follows:

$$[Rh(CO)_2I_2]^- + 2HI \rightarrow [Rh(CO)_2I_4]^- + H_2 \qquad (3)$$

$$[Rh(CO)_2I_4]^- + H_2O + CO \rightarrow [Rh(CO)_2I_2]^- + CO_2 + 2HI \qquad (4)$$

Overall $$H_2O + CO \rightarrow H_2 + CO_2 \qquad (5)$$

The first concern from this reaction is the loss of water from system. Water is inexpensive to replace, but if not controlled, can become costly. As mentioned above, there must be 8% by weight of water in the system to keep the reaction running at an acceptable rate. ✓

A bigger concern is for the CO from the feed that is lost. This reaction produces two gasses (CO_2 and H_2) that will dilute the CO feed, therefore lowering it's partial pressure. For this reason, there are large amounts of gas vented off from the system. Overall, 85% of the CO from the feed reacts to form product. This is good, but improvements can be made to become more efficient.

The biggest concern in this system is the loss of catalyst. From ~~form~~ **D**, a side reaction of the rhodium catalyst with the HI in the system reacts unfavorably:

$$[RhI_3(CO)(COCH_3)]^- + HI \rightarrow [RhI_4(CO)]^- + CH_3CHO \qquad (6)$$

$$[RhI_4(CO)]^- \rightarrow RhI_3 + I^- + CO \qquad (7)$$

The complex $[RhI_4(CO)]^-$ is inactive, and RhI_3 is insoluble. This is the foremost cause of catalyst loss from this system. In 1990, the cost of rhodium was about $5,200 per troy ounce, or $75,833 per pound! This reaction occurs most frequently in CO deficient areas of the reactor system. Side products for this reaction include propionic acid (from ethanol impurities in the methanol feed), acetaldehydes and iodide derivatives. These side products only appear as trace amounts, and don't affect product yield or purity.

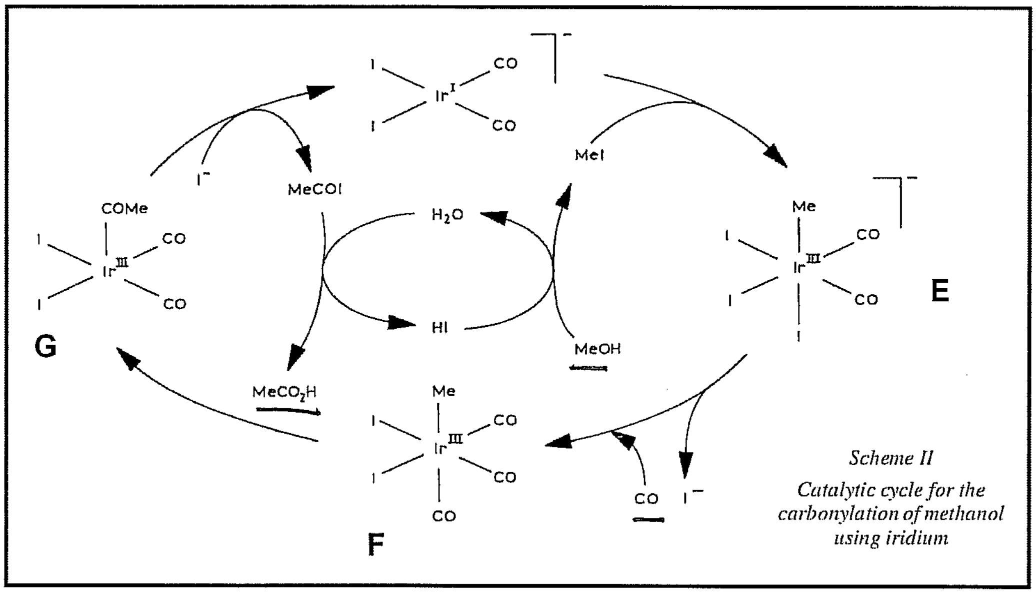
-sure this prevents re generating the carbonyl

As a result of the above limitations, as well as the high price of rhodium, research into an iridium catalyst was resumed. In 1990, iridium came in at around $300 per troy ounce, or $4,375 per pound. Monsanto had researched iridium, but found it to be less effective than a rhodium catalyst. Although it was less effective by itself, it has proven to be much better when used with the help of a promoter.

The iridium complex cycle is almost the same as that of the rhodium complex. However, the process has many advantages over the rhodium catalyst. The iridium catalyst has proven to be much more stable in conditions where the rhodium complex would decompose to inactive and insoluble species. The iridium complex is much more

Good if same rate expression as before.

soluble in the reaction mixture, therefore enabling higher catalyst concentrations and higher reaction rates to be obtained. Shown below is *Scheme II*, the reaction cycle for the iridium catalyst.



Scheme II
Catalytic cycle for the carbonylation of methanol using iridium

The oxidative addition of methyl iodide to the iridium complex is about 150 times faster than the same step in the rhodium mechanism, as seen at **E**. At **F**, we lose an I^- from the iridium center as we add a third –CO from the feed. The improvement of step **E** changes the reaction rate completely. The rate is no longer largely dependant on the methyl iodide species at step **E** and is no longer the RDS. The "slow step" becomes the movement of the CH_3 ligand from the iridium center to the CO ligand, **G**. The rate law then becomes:

good.

$$\text{Rate} \propto \frac{[\text{Ir catalyst}] \times [\text{CO}]}{[\text{I}^-]} \qquad (8)$$

✓

This reaction rate indicates that lower concentrations of $[I^-]$ help raise the reaction rate. It can be inferred that a species that can help remove the iodide from the complex will promote this new reaction mechanism. Promoters that can do this are simple iodide salts, such as ZnI, HgI, GaI and InI. Other promoters include carbonyl-iodide complexes, such as ruthenium and osmium ($[Ru(CO)_2I_2]$, $[Os(CO)_2I_2]$). Below is *Table I*, showing a study of promoter additives present and the subsequent rate of carbonylation.

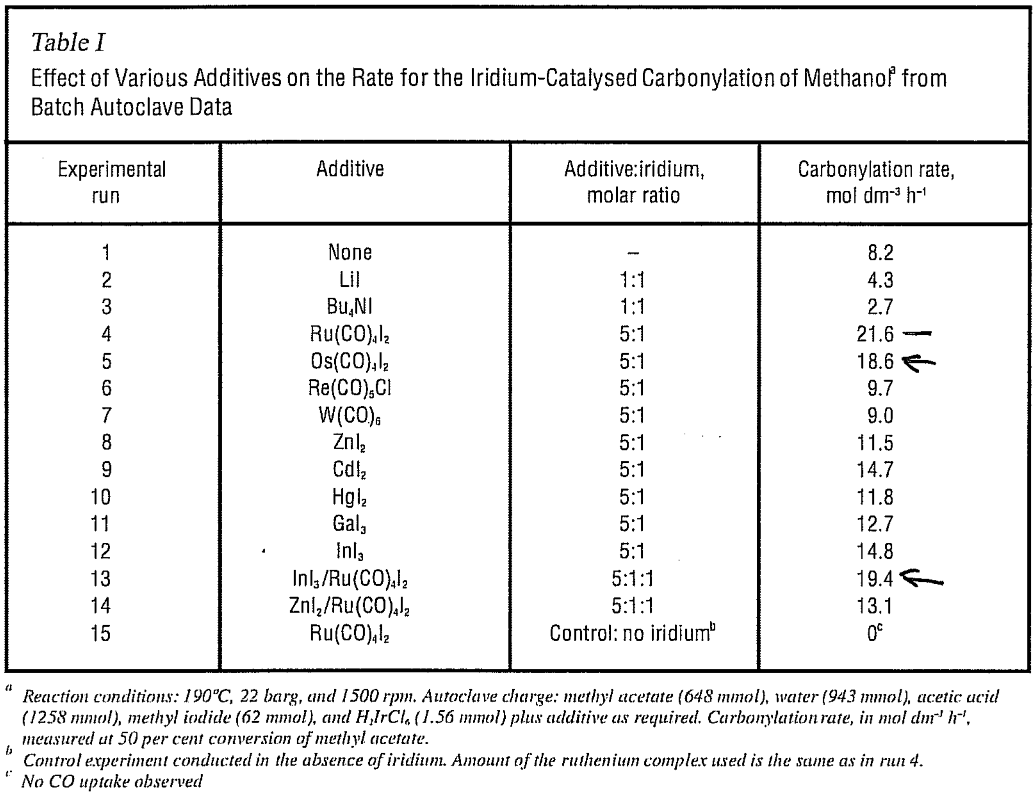


Table I

Effect of Various Additives on the Rate for the Iridium-Catalysed Carbonylation of Methanol[a] from Batch Autoclave Data

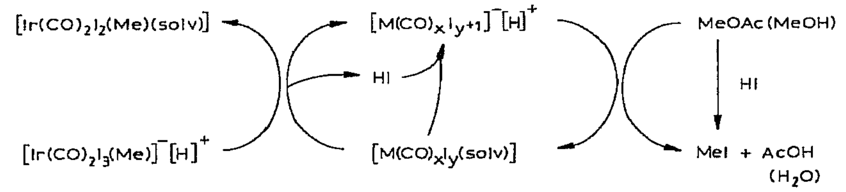
Experimental run	Additive	Additive:iridium, molar ratio	Carbonylation rate, mol dm^{-3} h^{-1}
1	None	–	8.2
2	LiI	1:1	4.3
3	Bu_4NI	1:1	2.7
4	$Ru(CO)_4I_2$	5:1	21.6
5	$Os(CO)_4I_2$	5:1	18.6
6	$Re(CO)_5Cl$	5:1	9.7
7	$W(CO)_6$	5:1	9.0
8	ZnI_2	5:1	11.5
9	CdI_2	5:1	14.7
10	HgI_2	5:1	11.8
11	GaI_3	5:1	12.7
12	InI_3	5:1	14.8
13	$InI_3/Ru(CO)_4I_2$	5:1:1	19.4
14	$ZnI_2/Ru(CO)_4I_2$	5:1:1	13.1
15	$Ru(CO)_4I_2$	Control: no iridium[b]	0[c]

[a] *Reaction conditions: 190°C, 22 barg, and 1500 rpm. Autoclave charge: methyl acetate (648 mmol), water (943 mmol), acetic acid (1258 mmol), methyl iodide (62 mmol), and H_2IrCl_6 (1.56 mmol) plus additive as required. Carbonylation rate, in mol dm^{-3} h^{-1}, measured at 50 per cent conversion of methyl acetate.*

[b] *Control experiment conducted in the absence of iridium. Amount of the ruthenium complex used is the same as in run 4.*

[c] *No CO uptake observed*

The promoter plays another vary important role. It helps prevent the creation of inactive species of the catalyst ($[Ir(CO)_2I_4]^-$ and $[Ir(CO)_3I_3]$) which resemble the inactive rhodium complexes. These two inactive species are intermediates of the water gas shift reaction. Because the water gas shift reaction is reduced with promoters present, CO efficiency is raised to 94% from 85%. From equation (2), we see that the rate for the rhodium system is only dependant on the concentrations of catalyst and methyl iodide. The promoted iridium catalyst system is slightly more complex. *Scheme III* below shows how the metal promoter works with the iridium catalyst.

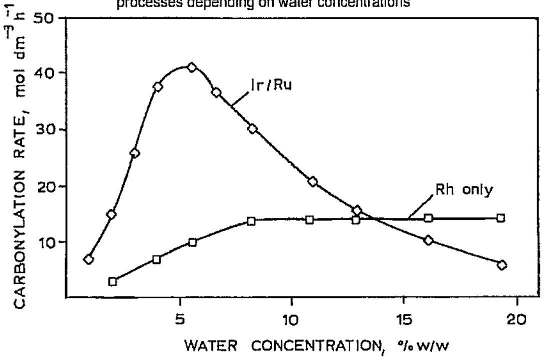


Scheme III

A proposed mechanism for the promotion of iridium catalysis by a metal promoter, $[M(CO)_xI_y(solv)]$*. The solvent could be water or methanol*

The iridium process does not require as much water present in the system to achieve high reaction rates. The water in the system can be reduced about 38 percent, down to about 5% water by weight. If the water content drops below this, the inactive species and water gas shift reaction are observed. To the right, *Figure 1* shows the relationship of the water concentration to the rate of carbonylation for both processes. The rate of carbonylation is much higher for the iridium process at concentrations around 5% by weight water, and drop significantly with increases of water in the system. — but still higher than Rh only.

Figure I Comparison of carbonylation rates for iridium/ruthenium and rhodium processes depending on water concentrations



There are several other factors that dictate the reaction rates of the two processes. *Table II* below maps out the rate dependence for each system due to the different compounds present in each system.

The concentration of methyl acetate does not affect the rate of the rhodium process. However, the methyl acetate concentration does positively affect the rate of the iridium process. Although higher concentrations are achievable in both processes, only the iridium process shows an increase in reaction rate.

Table II

The Rate Dependence Differences between the Rhodium and Iridium Systems

	Rhodium	Iridium/promoter
Water	1st order below 8 wt.% Independent above 8 wt.%	Increases with increasing water up to ~ 5 wt.%, then decreases with increasing water
Methyl acetate	Independent above ~ 1 wt.%	Increases with increasing methyl acetate
Methyl iodide	1st order	Increases with increasing methyl iodide up to ~ 6 wt.%, then independent
CO partial pressure	A minimum CO partial pressure is required; above this, independent	Increases with increasing CO partial pressure. As the CO partial pressure falls below ~ 8 bara the rate decreases more rapidly
Corrosion metals	Independent	As the corrosion metals increase in concentration, the rate decreases
Rhodium	1st order	Non applicable
Iridium	Non applicable	1st order, effect tails off at high catalyst concentrations
Promoter	Non applicable	Increases with increasing promoter, effect tails off at higher concentrations

Also from *Table II*, the iridium process ~~has~~ is less dependant on the methyl iodide concentration than the rhodium process. This is due to the fast rate of addition seen at **E** on *Scheme II.* The CO concentration in the iridium process has a much greater effect on the overall reaction rate, from equation (8). Corrosive metals such as iron and nickel present in the iridium process are destructive to the reaction rate. The metals attack the iridium complex, preventing the loss of iodide, seen at step **F** in *Scheme II.* The effect of promoters is particularly important in the iridium process. Promoters such as the ruthenium and osmium complexes can accelerate the carbonylation rate to more than double when added at a 5:1 molar ratio with the iridium complex, from *Table I.*

The two processes are very similar in operation. The same feed stocks are used, as well as the same reactor and plant controls. The two processes are so similar that it is a relatively easy transition from rhodium to iridium. Economics, like thermodynamics, weigh heavily in decision making. Other than the fact that iridium costs 5.8% of what rhodium costs, the iridium process uses significantly less water. At the end of both processes, the products from the reaction are fed to a distillation column for separation. With a smaller water concentration running through the system, 30% less steam is used in the distillation section of the iridium process compared to rhodium. Utilization of CO is 9% better in the iridium process, saving money in the feed stocks.

The Monsanto process and the Cativa™ process mechanisms have many similarities. However, a key difference in the RDS affects running conditions and subsequently byproduct production. Due to catalyst price and lower byproduct production, it is clear that acetic acid producers will continue to make the switch from rhodium complexes to iridium.

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