

## An investigation on the effects of iodide salts in iridium catalyst in methanol carbonylation process

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**Abstract:** In this study, iodide salts and carbonyl complexes of specific metals used as promoters in carbonylation of methanol in iridium/iodide based catalyst. The iridium catalyzed carbonylation of methanol to acetic acid is promoted by two distinct classes of promoters; simple iodide salts of zinc, cadmium, mercury, indium and gallium and carbonyl or halocarbonyl complexes of tungsten, rhenium, osmium and ruthenium. All of these promoters are led to increase the rate of methanol carbonylation. In this experimental research, it has been observed that the effect of ruthenium promoter in rate of methanol carbonylation and high reaction rate is achieved by increasing the ruthenium concentration. The experimental tests are carried out to identify the effect of different promoters. In the presence of ruthenium and iridium, it has been observed that the maximum activity is achieved between 5 to 6 weight percent of water concentration.

**Keywords:** Methanol carbonylation, Iridium, Promoter, Iodide salt.

### Introduction

The global annual production capacity of acetic acid in 2004 was about 9.3 million tones. The main uses for acetic acid are in production of vinyl acetate (VAM), solvents in the manufacturing of the terephthalic anhydride, acetic anhydride which mainly used to make cellulose acetate and acetate esters, such as ethyl and butyl acetates (Figure 1). About 61% of annual manufacturing of acetic acid is based on methanol carbonylation technology [1]. The first process of the carbonylation of methanol, commercialized by BASF in 1960, used a cobalt catalyst and iodide co-catalyst. Operating conditions were

at 250°C and 680 bar pressure [2-3]. Monsanto discovered rhodium based catalyst for carbonylation of methanol under relatively mild conditions rather than previous method, 250°C operating temperature and 680 bar pressure, and commercialized its process at Texas City in 1970 [4-5]. In 1996, BP Chemicals announced a new method carbonylation process, named Cativa™, based upon a promoter and iridium/iodide catalyst [6-9]. In Monsanto process, the conditions in the reactor have to be maintained within certain limits to prevent precipitation of the expensive rhodium catalyst in downstream areas where the catalyst is separated from product in a CO deficient zone of the plant. To prevent rhodium loss, the

reactor composition is maintained within limits on water, methyl acetate, methyl iodide and rhodium concentrations. To prevent catalyst precipitation and achieve high reaction rate, high water concentration is required. These restrictions place a limit on plant productivity and increase operating costs since the distillation section of the plant has to remove a considerable amount of water from the acetic acid product for recycling to the reactor [10]. The greater stability of iridium catalyst in low water concentration can be avoided of the precipitation of iridium occurring [11]. By removing one of the distillation column completely and decreasing the size of the remaining drying column in purification section, the operating costs of the process decreased and consequently the energy saving increased [12].

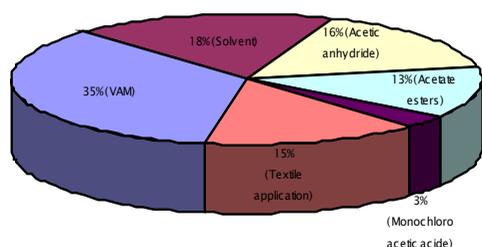


Figure 1 The major users of acetic acid.

### Mechanism of iridium-catalyzed in carbonylation of methanol

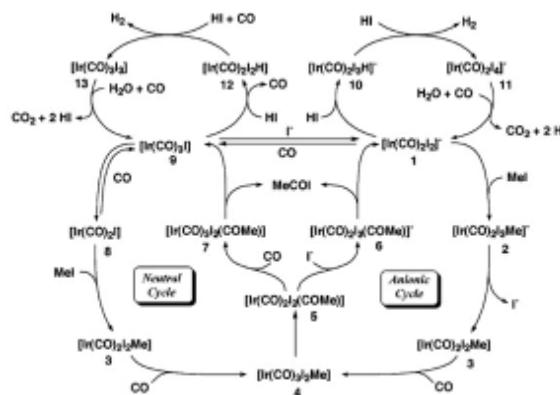
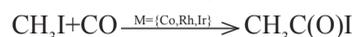
The iridium cycle is thought to involve similar to those in rhodium system. Forster proposed [13] that two different cycles exist, one involving the natural iridium complexes and the other anionic species, Foster's mechanism for iridium catalyzed is shown in Figure 3. Similar regular anionic cycles, named natural cycle, were also proposed for the comparing water gas shift reaction.

At very low concentration of water and iodide ( $[H_2O] < 4\%$  w/w), the natural cycle operated with  $[Ir(CO)_3I]$ , (9), as the resting state and rate determining oxidative addition of MeI to  $[Ir(CO)_2I]$ , (8).

At higher water and iodide concentrations ( $[H_2O] > 5\%$  w/w), the anionic cycle predominated, and the catalyst resting state was  $[Ir(CO)_2I_2Me]^-$ , (2). Under these conditions, the rate of catalysis increased

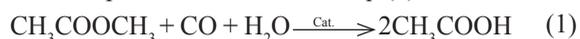
with CO pressure but was inhibited by ionic iodide. The rate determining step involves dissociative substitution of  $I^-$  by CO in (2), followed by migratory CO insertion in species is  $[Ir(CO)_3I_2Me]$ , (4) [13]. This contrasts with the rhodium system, in which oxidative addition of MeI to  $[Rh(CO)_2I_2]^-$  is rate determining. Studies have shown that addition of MeI to  $[Ir(CO)_2I_2]^-$  is 100 times faster than to rhodium analogue [14]. In contrast, the rate of subsequent migratory insertion reaction was estimated to be 105 times faster for rhodium than for iridium [12].

A key feature of the promoters in Cativa™ process is the ability of iodide absorbing from (2) and producing (4). Kinetic studies show that these species (4) to be more liable towards migratory insertion than its anionic precursor (2) [15]. The organo-metallic catalyst is the promotion of oxidative addition and/or migratory insertion of CO, with the net effect of increasing the carbon number of the reacting substrate,  $CH_3I$  [16].

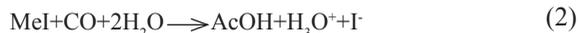


### Role of promoters in iridium-catalyzed in carbonylation of methanol

The overall reaction occurring in these batch studies can be represented therefore as eq. (1)



Each turnover of the iridium cycle generates 1 molar of HI that be expected to be largely dissociated as  $H_3O^+$  and  $I^-$  according to the shown in eq. (2) [15].



The HI produced using the Ir cycle must be recycled by the reaction with methyl acetate or methanol to generate MeI. This recycling is accelerated by promoters such as  $[\text{Ru}(\text{CO})_4\text{I}_2]$ , thereby moderating the steady state concentration of HI. In this mechanism the natural promoter species such as  $[\text{Ru}(\text{CO})_4\text{I}_2]$  and  $\text{InI}_3$  scavenges HI to give  $[\text{Ru}(\text{CO})_3\text{I}_3]^-$  and  $\text{H}_3\text{O}^+$  or  $\text{InI}_4^-$  and  $\text{H}_3\text{O}^+$ . These species act as a catalyst for reaction of HI and MeOAc and enhancing the turnover in Ir cycle eq. (3) [15].



By two equilibrium eqs. 4 and 5, the role of promotion of ruthenium in eq. 3 and the proposed mechanism is shown finally in Figure 4. The principle role of Ru appears to be related to the promotion of an iodide abstraction process via the eq. (4) [16].

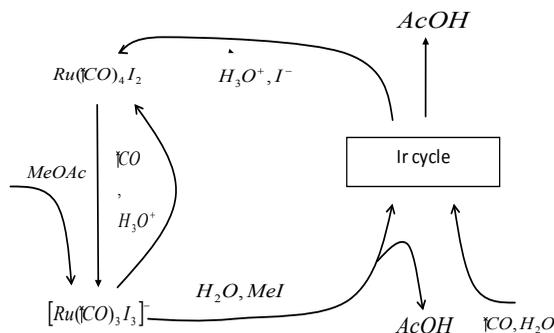
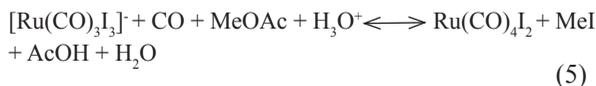
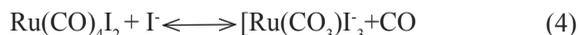


Figure 4 Role of natural promoters like  $[\text{Ru}(\text{CO})_4\text{I}_2]$  besides in Iridium cycle in methanol carbonylation [15].

The catalyst is distributed between an active form,  $[\text{Ir}(\text{CO})_2\text{I}_3\text{Me}]^-$ , (2) and an inactive form  $[\text{Ir}(\text{CO})_2\text{I}_4]^-$ , (11), formed as an intermediate in the water-gas shift reaction (Figure 3).

It has been observed that HI competes more effectively than MeI for  $[\text{Ir}(\text{CO})_2\text{I}_2]^-$ , (1), with respect to the formation of undesired oxidative addition products  $[\text{HIr}(\text{CO})_2\text{I}_3]$ , (10), and  $[\text{Ir}(\text{CO})_2\text{I}_4]^-$ , (11) eqs. (6-7).

Ruthenium competes more effectively than iridium for HI via eq. (4) with an inhibition of the oxidative addition of HI to (1), and subsequent conversion into the undesired like species (11), [16].



Also, another role of Ru is abstraction of iodide from the anionic resting state of the iridium catalyst to facilitate formation of the neutral  $[\text{MeIr}(\text{CO})_3\text{I}_2]$ , (4), which is considerably more susceptible than its anionic analogue  $[\text{Ir}(\text{CO})_2\text{I}_3\text{Me}]^-$ , (2) towards migratory CO insertion and methyl iodine formation [15-16].

### Experimental

For each batch of carbonylation experiments the one liter autoclave batch reactor was charged with water, methyl acetate, methyl iodide, water and acetic acid as the component of liquid reaction, iridium solution as a catalyst reaction (Hexachloroiridic acid  $[\text{H}_2\text{IrCl}_6]$ ) and with additive if required. Gas supply to the autoclave was provided from a ballast vessel, after weighting the component, in about 250 grams, they have been charged in 450 mL Parr Hastelloy B2™ autoclave. The reactor was pressure tested with nitrogen, vented via a gas sampling system, and flushed with carbon monoxide several times (3-5 barg) and heated with stirring (about 1000 rpm) to reaction temperature (190°C). The reactor pressure was maintained constant by a pressure reduce regulator. The autoclave was pressurized at approximately 28 barg. The range of component is shown in Table 1. The rate of carbon monoxide consumption was used to calculate the carbonylation

rate, at a particular point for each run, the consumption of 1 mol of carbon monoxide together with 1 mol of methyl acetate and 1 mol of water being equivalent to the carbonylation of 1 mol of methanol. While the entrance's valve of CO was opened, the consumption of it was started. Samples of the liquid reaction composition and gases in the headspace of the autoclave were analyzed by Gas Chromatography. A schematic of the acetic acid bench scale set-up and also the part of this is shown in Figure 5 and 6, respectively [17].

Table 1 Range of different component in acetic acid batch experiments

components	Range
Water	(w/w %) 1-8
Methyl Acetate	(w/w %) 23
Methyl Iodide	(w/w %) 7
Acetic Acid	(w/w %) 62-69
Catalyst	300 ppm
Promoter	0-2250 ppm

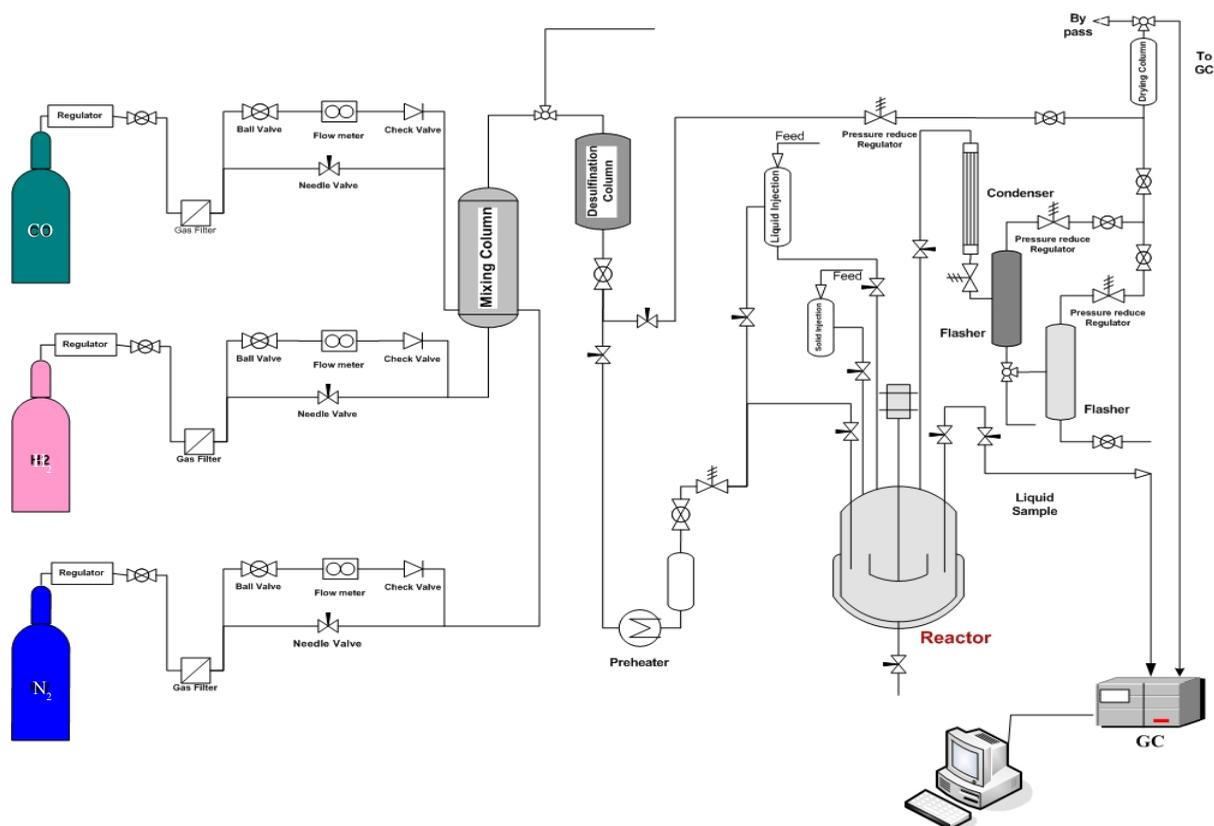


Figure 5 A schematic of flow diagram of acetic acid set-up



Figure 6 Acetic acid experimental set-up

## Results and Discussion

### 1-Effect of promoters in carbonylation rate

One of the key features of the Cativa process is the use of promoters to enhance the performance of the iridium catalyst. The promoters fall into two categories: simple iodide complexes of zinc, cadmium, mercury, gallium and indium, and carbonyl or halocarbonyl complexes of tungsten, rhenium, osmium and ruthenium. None of the promoters show any detectable activity in the absence of iridium

catalyst; although ruthenium has been reported to catalyze methanol carbonylation under harsh conditions and with the relatively low concentration (at 250°C operating temperature and 680 bar pressure) [18].

For each batch carbonylation experiment the catalyst,  $\text{H}_2\text{IrCl}_6$ , dissolved in a portion of the acetic acid liquid reactor charge and then added to the reactor and during of each experiment the operation conditions were kept constant.

The experiment No. 1 was performed with iridium catalyst and the other experiments, 2 to 9, in presence of different iodide salts (Table 2).

For a promoter: iridium mass ratio 5:1 the carbonylation rate enhanced by factors of 1.4 for  $\text{ZnI}_2$ ,  $\text{HgI}_2$  and  $\text{GaI}_3$ ; 1.04 for  $\text{CdI}_2$  and  $\text{InI}_3$ ; 2.3 for  $\text{Ru}(\text{CO})_4\text{I}_2$ ; 1.6 for  $\text{Ru}(\text{CO})_4\text{I}_2/\text{ZnI}_2$ ; and 2.6 for  $\text{Ru}(\text{CO})_4\text{I}_2/\text{InI}_3$  (Table 2).

In addition, according to Table 3 some carbonyl complexes such as ruthenium, tungsten and osmium at the same conditions but with a promoter: iridium mass ratio 2:1 were tested and it was observed that the carbonylation rate enhanced by factors of 2.1 for  $\text{Ru}(\text{CO})_4\text{I}_2$ ; 1.2 for  $\text{Os}_3(\text{CO})_{12}$ ; and 1.07 for  $\text{W}(\text{CO})_{12}$ . Ru is the most effective in carbonylation rate (Table 3).

Table 2 Effect of iodide salts and combination of them in carbonylation rate; Reaction condition: 190°C, 28 barg and 1000 rpm; carbonylation rate measured at 20% conversion of methyl acetate.

Experiment	[Ir] (ppm)	Additive	Additive: Ir (ppm / ppm)	[MeI] (% W/W)	[MeOAc] (%W/W)	[H <sub>2</sub> O] (%W/W)	Carbonylation Rate*1000 (mol/min)
1	306	None	0	7.09	23.04	5.73	7.09
2	302	$\text{ZnI}_2$	5:1	7.00	23.00	5.72	10.08
3	300	$\text{HgI}_2$	5:1	7.30	23.05	5.75	9.37
4	300	$\text{GaI}_3$	5:1	7.05	23.04	5.71	9.91
5	300	$\text{CdI}_2$	5:1	7.00	23.00	5.70	7.28
6	300	$\text{InI}_3$	5:1	7.00	23.00	5.72	7.32
7	300	$\text{Ru}(\text{CO})_4\text{I}_2$	5:1	7.07	23.03	5.75	16.15
8	300	$\text{InI}_3/\text{Ru}(\text{CO})_4\text{I}_2$	5:1:1	7.00	23.00	5.70	18.4
9	300	$\text{ZnI}_2/\text{Ru}(\text{CO})_4\text{I}_2$	5:1:1	7.00	23.00	5.70	11.3

Table 3 Effect of carbonyl complexes in carbonylation rate; reaction condition: 190°C, 28 barg and 1000 rpm; carbonylation rate measured at 20 % conversion of methyl acetate.

Experiment	[Ir] (ppm)	Additive	Additive: Ir (ppm / ppm)	[MeI] (% W/W)	[MeOAc] (%W/W)	[H <sub>2</sub> O] (%W/W)	Carbonylation Rate*1000 (mol/min)
1	306	None	0	7.09	23.04	5.73	7.09
10	301	Ru(CO) <sub>4</sub> I <sub>2</sub>	2:1	7.02	23.06	5.80	15.23
11	301	Os <sub>3</sub> (CO) <sub>4</sub> I <sub>12</sub>	2:1	7.00	23.12	5.70	8.5
12	300	W(CO) <sub>6</sub>	2:1	7.05	23.04	5.70	7.5

The key function for all of the promoters can be summarized first as a competitive removal of HI to prevent entry into a rate limiting Ir catalyzed water–gas shift reaction and second as for abstraction of iodide from the anionic resting state of the Ir catalyst.

### 2- Effect of ruthenium concentration in carbonylation rate

The batch autoclave for different concentrations of

ruthenium as a promoter of iridium catalyst was shown in Table 4. With the same operation conditions, as the concentration of ruthenium increased, the reaction rate enhanced. Promoters, such as ruthenium, can therefore be used to increase the reaction selectivity by allowing a lower iridium catalyst concentration to be utilized to achieve a given reactor productivity [19]. This effect was illustrated in Figure 7.

Table 4 Effect of Ru concentration in presence of Ir catalyst in carbonylation rate; Reaction condition: 190°C, 28 barg and 1000 rpm; Carbonylation rate measured at 20 % conversion of methyl acetate.

Experiment	[Ir] (ppm)	Additive	Additive: Ir (ppm / ppm)	[MeI] (% W/W)	[MeOAc] (%W/W)	[H <sub>2</sub> O] (%W/W)	Carbonylation Rate*1000 (mol/min)
1	306	None	0	7.09	2304	5.73	7.09
13	302	Ru(CO) <sub>4</sub> I <sub>2</sub>	1:1	7.10	23.05	5.73	9.05
10	301	Ru(CO) <sub>4</sub> I <sub>2</sub>	2:1	7.20	23.06	5.80	15.23
14	301	Ru(CO) <sub>4</sub> I <sub>2</sub>	3.5:1	7.00	23.00	5.70	15.78
7	300	Ru(CO) <sub>4</sub> I <sub>2</sub>	5:1	7.07	23.03	5.75	16.15
15	301	Ru(CO) <sub>4</sub> I <sub>2</sub>	7.5:1	7.00	23.07	5.75	20.55

### 3- Effect of water concentration in carbonylation rate

A distinctive feature of the iridium based catalyst system used in Cativa™ is its behavior with water concentration. As the water concentration is reduced the reaction rate increased. This is illustrated in Figure 8 for a ruthenium promoted iridium catalyst.

For a Cativa™ system, the reaction rate increase by decreasing water content and a maximum value is reached at around 5-6 weight percent (figure 8). Studies show that the catalyst to be operating predominantly in the anionic catalyst regime when the reaction rate is increasing with reducing water concentration; [Ir(CO)<sub>2</sub>I<sub>3</sub>Me]<sup>-</sup> and [Ir(CO)<sub>2</sub>I<sub>4</sub>]<sup>-</sup> are

observed in the reaction solution [13]. At very low water concentration, when the reaction rate is declining with reducing water concentration, studies show the catalyst to be operating in the neutral catalyst regime and  $[\text{Ir}(\text{CO})_3\text{I}]$  and  $[\text{Ir}(\text{CO})_3\text{I}_3]$  are observed in the reaction solution [13]. Some experiments have been done with different water concentration in presence of ruthenium (Table 5) in the same operation conditions.

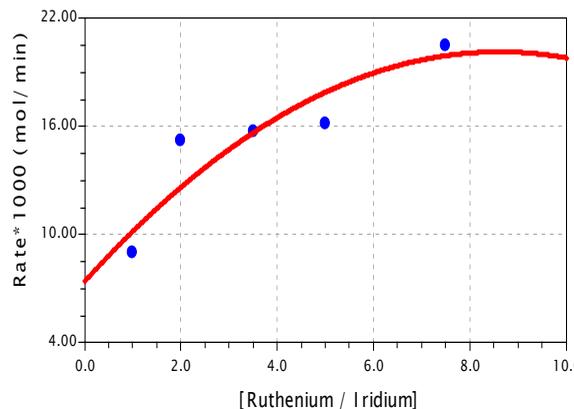


Figure 7 The Effect of the ruthenium concentration in carbonylation rate.

Table 5 Effect of water concentration in presence of Ir–Ru, in carbonylation rate; Reaction condition: 190°C, 28 barg and 1000 rpm; Carbonylation rate measured at 8 % conversion of methyl acetate. Carbonylation rates at 20 % conversion of methyl acetate is 9.3, 15.22 and 10.13 for run 17, 10 and 18 respectively.

Experiment	[Ir] (ppm)	Additive	Additive: Ir (ppm / ppm)	[MeI] (% W/W)	[MeOAc] (%W/W)	[H <sub>2</sub> O] (%W/W)	Carbonylation Rate*1000 (mol/min)
16	301	$\text{Ru}(\text{CO})_4\text{I}_2$	2:1	7.05	23.06	1.00	0.67
17	300	$\text{Ru}(\text{CO})_4\text{I}_2$	2:1	7.30	23.05	2.70	11.60
10	301	$\text{Ru}(\text{CO})_4\text{I}_2$	2:1	7.20	23.06	5.80	16.60
18	302	$\text{Ru}(\text{CO})_4\text{I}_2$	2:1	7.04	23.00	8.00	10.45

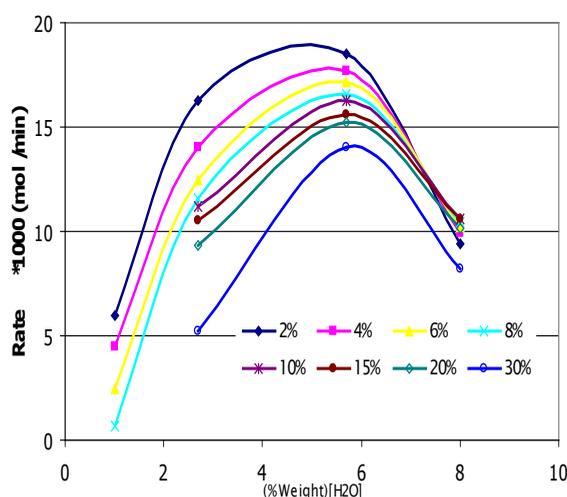


Figure 8 Effect of water concentration on carbonylation rate by a ruthenium promoted iridium catalyst in different conversion of methyl acetate.

## Conclusion

The use of a specific promoter enhanced the rate of the migratory insertion reaction and it can be increased the yield on carbon monoxide. The net effect of using different promoters is:

- The carbonylation rate enhanced by factors of 1.4 for  $\text{ZnI}_2$ ,  $\text{HgI}_2$  and  $\text{GaI}_3$ ; 1.04 for  $\text{CdI}_2$  and  $\text{InI}_3$ ; 2.3 for  $\text{Ru}(\text{CO})_4\text{I}_2$ ; 1.6 for  $\text{Ru}(\text{CO})_4\text{I}_2/\text{ZnI}_2$ ; and 2.6 for  $\text{Ru}(\text{CO})_4\text{I}_2/\text{InI}_3$ .

By using some carbonyl complexes such as ruthenium, tungsten and osmium and keeping the same conditions except than a promoter: iridium mass ratio 2:1, it was observed that the carbonylation rate enhanced by factors of 2.1 for  $\text{Ru}(\text{CO})_4\text{I}_2$ ; 1.2 for  $\text{Os}_3(\text{CO})_{12}$ ; and 1.07 for  $\text{W}(\text{CO})_{12}$ . Ru is the most

effective in carbonylation rate.

- By decreasing water content, the reaction rate is increased with up to a maximum value about 5-6 weight percent and then by decreasing the water level, the carbonylation rate is decreased.

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