THE RHODIUM-CATALYZED METHANOL CARBONYLATION TO ACETIC ACID AT LOW WATER CONCENTRATIONS: THE EFFECT OF IODIDE AND ACETATE ON CATALYST ACTIVITY AND STABILITY

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(Received April 1, 1986; accepted June 10, 1986)

Summary

Addition of iodide salts to rhodium catalyst solutions for methanol carbonylation at low water concentrations (<2 M) promotes the rate of carbonylation and stabilizes the rhodium catalyst. Some iodide salts also react with methyl acetate to form acetate salts which also act as promoters. We suggest that promotion by acetate and iodide ions can be explained by their coordination with Rh(I), generating catalyst species which are more active towards oxidative addition of methyl iodide. Rate dependences on water and methyl acetate concentrations are explained by their role in increasing the steady-state concentration of Rh(I) via the water–gas shift process. Catalyst stabilization is rationalized by formation of soluble rhodium complexes that prevent precipitation of RhI₃. By choosing the proper iodide salt and methyl acetate concentrations, the same rate and catalyst stability observed at high water concentrations can be obtained at much lower water concentrations with improved CO selectivity to acetic acid. Operation with lower water concentrations can provide significant savings in the commercial acetic acid process.

Introduction

The role of water in rhodium-catalyzed methanol carbonylation to acetic acid is more important than might be expected from the traditional view of the mechanism [1]. A water dependence in the rate law below ca. 10 M water was reported by Hjortkjaer and Jensen [2]. Paulik et al. report that for methanol carbonylation to acetic acid, a substantial quantity of water is necessary to attain high reaction rates [3]. We have found that water concentration is also important for maintaining rhodium catalyst stability, especially when the partial pressure of carbon monoxide is low [4]. Though high reaction rates and increased catalyst stability at high water concentrations are attractive, the separation of the acid from appreciable quantities of water requires substantial expenditure of energy. Considerable cost savings...
can be realized by operating at low water concentrations if a way can be found to compensate for the decrease in the reaction rate and catalyst stability.

In a previous paper [5a, b], we reported preliminary evidence that iodide and acetate salts enhance the rate of methanol carbonylation to acetic acid at low water concentrations. In this paper, we report in detail our batch kinetic results, as well as some key results from a continuous carbonylation unit, to demonstrate that rhodium-catalyzed methanol carbonylation to acetic acid under low water concentrations can be achieved with high reaction rates and improved catalyst stability and product selectivity by the addition of an iodide salt and operation at significant concentrations of methyl acetate (MeOAc).

Experimental

Materials

RhI₃ and RhCl₃·3H₂O were used as catalyst precursors and purchased from Engelhardt. Carbon monoxide was purchased from Matheson. All other chemicals except N-methyl picolinium iodide (NMPI) are commercial products and were used without further purification. NMPI was prepared as follows: in a hood, 100 ml of methyl iodide (MeI) was placed in a 250 ml 3-necked flask with a teflon-coated stir bar and with attached reflux condenser, gas adapter and septum cap. The MeI was stirred while 17 ml (16.3 g) of 3-picoline (Aldrich) was added by syringe over a 10 min period, which caused the solution to become hot and begin to reflux. After a few minutes the refluxing stopped and the solution cooled, generally with resultant NMPI precipitation. The reflux condenser was replaced by a glass stopper and the MeI was removed under vacuum leaving behind the yellow solid NMPI. The NMPI was used without further purification.

Methods

Batch

Catalytic experiments were carried out in a 300 ml Hastelloy-B or Hastelloy-C autoclave (Autoclave Engineers) provided with an electrically-heated jacket, a magnetically driven agitator, and gas and liquid feed take-off lines. The autoclave was charged with the desired quantities of rhodium catalyst precursor (generally RhI₃ though others were possible [6a, b]), water, methyl iodide, iodide salt and acetic acid. The autoclave was then sealed, pressure tested and purged twice with 50 psig CO. The reactor pressure was increased to 150 psig CO, and with slow stirring (85 rpm) heated to 190 °C. Once reaction temperature was reached, methanol or methyl acetate (0.36 mol unless otherwise specified) was injected into the autoclave via a pressurized bomb, the stirrer speed increased to 610 rpm and the pressure increased with CO to 400 psig. As the CO in the reactor was consumed by carbonylation, more CO was introduced to the reactor from a CO reservoir by way of a regulator which maintained the reactor pressure at a constant 400 psig.
total pressure. The rate of carbonylation was generally determined by monitoring the rate of CO consumption as calculated from the pressure drop in the carbon monoxide reservoir. This is justified since the rate of CO consumption was shown in our continuous unit to approximate the rate of acetic acid (HOAc) production (the CO inefficiency to by-products is small). Unless otherwise indicated, rate data is reported as space–time–yield (STY) in mol CO uptake h⁻¹ l⁻¹. Although we were unable to conduct ‘on-line in situ’ infrared studies of our system due to equipment limitations, we did conduct limited IR studies in a static high-pressure cell. We found that the major rhodium species at the temperature and CO pressure of our catalyst system was \([\text{Rh}(\text{CO})_2\text{I}_2]^-\) and \([\text{Rh}(\text{CO})_2\text{I}_4]^-\), consistent with literature reports [6c]. Most of the iodide salts screened in this study were soluble in the reaction solution (0.75 M \(\text{I}^-\)) at 190 °C but rapidly precipitated from solution while solutions cooled to room temperature, Table 1. Both LiI and NaI remained soluble at room temperature and in the case of LiI, room temperature acetic acid solutions of 50 wt.% LiI and 2 wt.% water could be prepared without precipitation.

The general procedure for the carbonylation experiments as described above consists of charging the autoclave with known amounts of each reagent. However, at operating temperature, a considerable amount of each liquid reagent is volatilized to the autoclave head space, thus the concentration of each component in solution was not the same as at room temperature. Also, due to the equilibrium shown in eqn. (1), addition of iodide salts generally produces MeI. Because of eqn. (1), changes in the concentration of iodide salts or MeOAc will affect the concentration of methyl iodide, which has a direct effect on reaction rate. This results in a higher concentration of MeI than that initially charged in the batch autoclave experiments.

\[
\text{I}^- + \text{MeOAc} \rightleftharpoons \text{MeI} + \text{OAc}^-(1)
\]

In order to determine the concentration of each reagent at run temperature and pressure, in separate experiments the autoclave was charged with all reagents except rhodium and heated and pressurized to the conditions described above. A hot liquid aliquot was then drained from the autoclave into a volumetric flask dipped in a \(\text{CO}_2/\text{acetone}\) bath, instantly freezing the liquid sample. The sample was quickly thawed and analyzed by GLC for water, methyl iodide, methyl acetate and acetic acid concentrations. The iodide and acetate concentrations were determined as discussed in the analytical section. Rhodium concentration was calculated from the rhodium charged. Solution water concentration also varies during a batch run. When methanol is blowcased into the autoclave, rapid esterification with acetic acid produces one equiv of water which is gradually consumed during the run [1b]. For most of the batch experiments at low water concentrations, it was necessary to use methyl acetate in place of methanol in order to obtain the desired low initial water concentration. In control experiments at high water concentrations, no difference in initial carbonylation rates was observed between the use of methanol and methyl acetate charges.
<table>
<thead>
<tr>
<th>Salt Added</th>
<th>8 M H₂O</th>
<th>1.0 M H₂O</th>
<th>2.0 M H₂O</th>
<th>Comment</th>
</tr>
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<td>none</td>
<td>13.1</td>
<td>4.2</td>
<td>-</td>
<td>b</td>
</tr>
<tr>
<td>LiI</td>
<td>12.2</td>
<td>14.8</td>
<td>-</td>
<td>b</td>
</tr>
<tr>
<td>NaI</td>
<td>8.8</td>
<td>-</td>
<td>b</td>
<td></td>
</tr>
<tr>
<td>KI</td>
<td>11.2</td>
<td>13.2</td>
<td>c</td>
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<td>RbI</td>
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<tr>
<td>CsI</td>
<td>-</td>
<td>-</td>
<td>e</td>
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<tr>
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<td>-</td>
<td>3.5</td>
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<td>Bu₄N⁺I⁻</td>
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<td>-</td>
<td>b</td>
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</tr>
<tr>
<td>NH₄⁺I⁻</td>
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<td>-</td>
<td>e</td>
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<td>LiBF₄</td>
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<td>LiCF₃SO₃</td>
<td>4.5</td>
<td>-</td>
<td>f</td>
<td></td>
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</table>

aCharge: 1.0 M MeI, 4.0 × 10⁻³ M RhI₃, 3.0 M MeOAc, 0.75 M added salt. No normalization was done for any MeI produced due to the reaction described in eqn. (1).
bSoluble.
cPartially soluble.
dPoor solubility.
eInsoluble.
f1.1 M added salt.

Kinetic data and observed rates for the variable studies are reported for the initial period of each run where reliable reagent concentrations are known. Batch kinetic rates were reproducible to within ±12%. The error is somewhat high, due to the difficulty in accurately determining the concentration of each reagent at the reaction temperature. Because the methyl iodide concentration varied from run to run due to eqn. (1), for comparative purposes rates were normalized to equivalent concentrations of methyl iodide, using the methyl iodide dependence described in Fig. 1. Rates were also normalized to equivalent rhodium concentrations assuming a first-order reaction.
dependence in rhodium, Fig. 2. In most of the figures presented here the concentration of lithium salt is given as the sum of LiI + LiOAc.

The values for the equilibrium constant for the reaction represented by eqn. (1) are very dependent on the water concentration. For example, charging LiI to catalyst solutions at 190 °C containing 7.0 M water, an equilibrium constant of 0.01 - 0.03 was determined, but an equilibrium constant of 0.1 - 0.2 was measured under similar conditions at 1.0 M water. Table 2 lists the amount of acetate ion formed when various amounts of LiI were added to acetic acid solutions containing ca. 3 M MeOAc and 7.0, 4.0 and 1.0 M water.
TABLE 2
Determination of equilibrium constant for the reaction of LiI with MeOAc at 190 °C

<table>
<thead>
<tr>
<th>[LiI] (M)</th>
<th>[MeOAc] (M)</th>
<th>[LiOAc] (M)</th>
<th>[MeI] (M)</th>
<th>K_eq</th>
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<td>7.0 M H₂O</td>
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<tr>
<td>0.41</td>
<td>2.7</td>
<td>0.013</td>
<td>0.9</td>
<td>0.01</td>
</tr>
<tr>
<td>0.80</td>
<td>2.8</td>
<td>0.03</td>
<td>1.0</td>
<td>0.01</td>
</tr>
<tr>
<td>1.07</td>
<td>2.9</td>
<td>0.06</td>
<td>1.1</td>
<td>0.02</td>
</tr>
<tr>
<td>1.45</td>
<td>3.2</td>
<td>0.12</td>
<td>1.3</td>
<td>0.03</td>
</tr>
<tr>
<td>4.0 M H₂O</td>
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<td></td>
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<td></td>
</tr>
<tr>
<td>0.39</td>
<td>3.13</td>
<td>0.04</td>
<td>1.1</td>
<td>0.04</td>
</tr>
<tr>
<td>0.75</td>
<td>3.06</td>
<td>0.09</td>
<td>1.07</td>
<td>0.04</td>
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<td>0.17</td>
<td>1.13</td>
<td>0.06</td>
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<tr>
<td>1.46</td>
<td>2.8</td>
<td>0.30</td>
<td>1.20</td>
<td>0.09</td>
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<tr>
<td>1.0 M H₂O</td>
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</tr>
<tr>
<td>0.12</td>
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<tr>
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<td>0.10</td>
<td>1.1</td>
<td>0.14</td>
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<td>0.46</td>
<td>1.5</td>
<td>0.30</td>
</tr>
<tr>
<td>1.0</td>
<td>3.0</td>
<td>0.79</td>
<td>1.6</td>
<td>0.42</td>
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</table>

Continuous process experimental

The equipment used for the studies of the continuous process will be detailed in a future publication [7], but simply described it consists of three parts: (a) a liquid-phase carbonylation reactor, (b) a 'flasher', or a column for initial product/catalyst separation, and (c) a column to separate the methyl iodide from the acetic acid. The carbonylation reactor was a one-gallon stirred autoclave in which the reacting liquid contents are maintained automatically at a constant level. Fresh methanol, water, carbon monoxide, recycled catalyst solution from the flasher base, and recycled methyl iodide and methyl acetate from the overhead of the methyl iodide–acetic acid splitter column were continuously introduced into the carbonylation reactor. A small gaseous purge stream was vented from the head of the reactor to prevent buildup of gaseous byproducts and to maintain a constant carbon monoxide partial pressure at a given total reactor pressure. The temperature of the reactor was controlled automatically, and the carbon monoxide was introduced at a rate sufficient to maintain a constant total reactor pressure. Liquid product was drawn off from the carbonylation reactor and was introduced into the flasher. The catalyst solution in the base of the flasher was recycled to the reactor (predominantly acetic acid containing the rhodium and the iodide salt along with lesser quantities of methyl iodide, and water). The overhead of the flasher was comprised largely of the product acetic acid, methyl iodide, methyl acetate and water.
along with gaseous byproducts such as methane, hydrogen, and CO\textsubscript{2} exit from the top of the flasher. The product from the flasher overhead was introduced into the methyl iodide–acetic acid splitter column. The product acetic acid, along with water, was drawn from the base of the methyl iodide–acetic acid splitter column, while the overhead from the methyl iodide–acetic acid splitter, consisting mainly of methyl iodide and methyl acetate, was recycled to the carbonylation reactor.

Although lengthier and mechanically more complex, experiments in the continuous unit were easier to evaluate than the batch experiments because the concentrations of all the reagents could be better controlled to the desired value at a given set of conditions. Therefore fewer corrections were needed on the observed rates. For this reason, confirmation of batch trends with the continuous unit was very important. Kinetic rates for the continuous process were reproducible to within ±5%. All the data obtained with the continuous unit will be reported in a future publication [7]; however, in this paper we present continuous unit data to support our findings from batch experiments concerning what we believe to be the more critical variables (H\textsubscript{2}O, Li salts). The figures presented here are for batch experiments unless otherwise indicated.

\textit{Catalyst stability experiments}

Catalyst stability experiments were performed in an apparatus prepared from thick-walled 2 in glass pipe. Conditions were similar to those found in the flasher of the continuous unit, where the catalyst environment would be lowest in CO partial pressure and the rhodium catalyst precipitation to RhI\textsubscript{3} would be most severe. These experiments were performed behind a Plexiglass\textsuperscript{®} shield. The vessel was charged with RhI\textsubscript{3} (600 - 1100 ppm), H\textsubscript{2}O (0 - 10 M), HI (0 - 0.14 M), iodide salt (0 - 2.5 M) and enough acetic acid for the total charge to equal 200 g. The glass vessel was pressurized to 27 psig with CO and heated in an oil bath to 130 °C. The CO was bubbled into the solution (47 ml min\textsuperscript{-1}) by means of a teflon gas-inlet tube, while constant pressure was maintained via a back-flow regulator. After 1 h, all of the RhI\textsubscript{3} had dissolved and was converted to [RhI\textsubscript{2}(CO)\textsubscript{2}]\textsuperscript{−}. The CO was then replaced with N\textsubscript{2} and the total pressure was reduced to 15 psig (reflux pressure). Under these conditions the rhodium complex loses CO and generates RhI\textsubscript{3}. Samples were removed via a sampling port, centrifuged 5 - 10 min and analyzed for Rh content. First-order rate constants for catalyst precipitation were obtained from linear plots of In [Rh]/[Rh], vs. time. The rate of Rh precipitation is expressed as ppm h\textsuperscript{-1}, which is calculated by multiplying the first-order rate constant times the initial rhodium concentration.

\textit{Analytical methods}

Product solutions were analyzed for MeI, MeOAc, water and acetic acid by gas chromatography (Varian 1400, Sigma 3B or Hewlett-Packard 4790 with a thermal conductivity detector; 6 ft, 1/8 in Ni alloy column packed with Porapak T 100/120 mesh; 175 °C column temperature). Iodide concen-
tration was determined by iodide titration with AgNO₃ using an iodide-specific electrode as sensing device. LiOAc concentration was determined by titration with standard perchloric acid solutions. Rh concentration was determined by atomic absorption spectroscopy.

Results

Reaction kinetics

Batch experiments were important since they could be designed to quickly screen a wide range of conditions and reagent concentrations and to guide the more informative but more time-consuming experiments with the continuous process unit. Figures presented here are from batch data except where otherwise indicated. For conventional methanol carbonylation (without added iodide salt), water concentration is typically maintained at a level high enough so that no water dependence is observed [8, 2]. As shown in Fig. 3, this represents about 8 M. Our data shows that reduction of water concentration from 8 to 1 M results in a rate decrease of about 75%, consistent with the water effect reported in the literature [2, 9], Fig. 3. Also, catalyst stability decreases significantly (see below) as water concentration decreases. Thus, even though energy savings can be realized by operating under low water concentrations, the penalty from rate and catalyst losses is severe.

We have found that rate loss due to decreasing water concentration can be overcome by the addition of certain iodide salts, Fig. 3. To determine the salts which are both soluble and show the best promotional effect on rate, a screening test with various inorganic and organic iodides was performed, with results listed in Table 1. Table 1 shows the STY values obtained at two water concentrations for runs containing added inorganic or organic iodide salts.

Fig. 3. H₂O dependence with and without Li salts (LiI + LiOAc). [MeI] = 0.62 M, [MeOAc] = 3.0 M, [Rh] = 1.0 x 10⁻³ M, 185 °C, 400 psig.
where the amount of iodide salt added was the same for each run (0.75 M I\(^-\)).

Also shown is the rate at 8 M water without added iodide salt. In nearly every case, the addition of an iodide salt resulted in rate enhancement, and in some cases (e.g. LiI) rates at 1.0 M H\(_2\)O were comparable with rates observed at 8 M water in the absence of iodide salt. Batch runs with LiCF\(_3\)SO\(_3\) and LiBF\(_4\) showed much slower rates (Table 1) than runs with LiI, suggesting that the rate enhancement was due to the iodide anion rather than the cation or to a simple salt effect.

Figure 4 shows the good agreement between batch and continuous unit data for the effect of water on the rate of methanol carbonylation in the presence of LiI. Figure 4 also shows that at conditions of 0.6 - 0.9 M MeOAc and 1.6 - 1.9 M LiI the carbonylation rate decreases about 30% as the water concentration decreases from 4 to 1 M water, and then drops more rapidly below 1 M water. Therefore even in the presence of LiI, the carbonylation rate is still dependent on water concentration, although not as much as with no LiI.

![Figure 4](image_url)

Fig. 4. Comparison of water concentration dependence data for batch and continuous units. [Rh] = 3.9 \times 10^{-3} M, [MeI] = 1.0 M, [MeOAc] = 0.6 - 0.9 M, [LiI + LiOAc] = 1.6 - 1.9 M, 190 °C, 400 psig total pressure; ● batch, □ continuous.

We examined in more detail the rate dependence of LiI and NMPI, since these two compounds showed good solubility properties, and allow for comparison between organic vs. inorganic iodide salts, Figs. 5 and 6. As shown in Fig. 5, which is a plot of the rate vs. total lithium salt analyzed (LiI + LiOAc), the rate is first order in total salts, although the slope of each line decreased as water concentration increased. At carbonylation temperatures and pressures, a considerable amount of acetate is formed according to eqn. (1) and Table 2, with more acetate formed at low water concentrations where the promotional effect of the added salt was greatest. Since the difference in slopes observed in Fig. 5 could be due to a promotional effect by LiOAc greater than that by LiI [5a, b], the carbonylation rate was also plotted as a
Fig. 5. Rate dependence on total Li salts (LiI + LiOAc) at various H2O concentrations. [Rh] = 4.0 \times 10^{-3} \text{ M}, [\text{MeI}] = 1.0 \text{ M}, [\text{MeOAc}] = 2.9 \text{ M}, 190 \degree \text{C}, 400 \text{ psig total pressure}; \bigcirc 1.0 \text{ M H2O}, \square 3.5 \text{ M H2O}, \bigtriangleup 7.0 \text{ M H2O}.

Fig. 6. Rate dependence on NMPI concentration at 1.0 M H2O concentration. [Rh] = 4.0 \times 10^{-3} \text{ M}, [\text{MeI}] = 1.0 \text{ M}, [\text{MeOAc}] = 3.0 \text{ M}, 190 \degree \text{C}, 400 \text{ psig total pressure}.

function of LiOAc concentration (Fig. 7), which shows a linear dependence with similar slopes at the various water concentrations. This suggests, as we observed in our model studies, that LiOAc is a better rate promoter than LiI.

Figure 8 compares the effect of total lithium salts from batch runs at 1.0 M water and 2.9 M MeOAc to continuous unit runs at 2.0 M water and 0.5 M MeOAc. At the above conditions, the amount of LiOAc produced in the continuous unit runs is small due to the effect of the higher water and lower MeOAc concentrations on the reaction represented by eqn. (1). The amount of LiOAc produced in the batch operation is much higher (one major advantage of a continuous unit over a batch unit is that a broad range
Fig. 7. LiOAc dependence at various H₂O concentrations. [Rh] = 4.0 × 10⁻³ M, [MeI] = 1.0 M, [MeOAc] = 3.0 M, 190 °C, 400 psig total pressure; ○ 1.0 M H₂O, □ 3.5 M H₂O, ● 7.0 M H₂O.

Fig. 8. Effect of [LiI + LiOAc] on rate of continuous and batch carbonylations. □ Continuous experiments: [Rh] = 4.0 × 10⁻³ M, [MeI] = 1.0 M, [MeOAc] = 0.6 M, [H₂O] = 2.2 M (4 wt.%). ● Batch experiments: [Rh] = 4.0 × 10⁻³ M, [MeI] = 1.0 M, [MeOAc] = 0.6 M, [H₂O] = 2.2 M (2 wt.%) 190 °C, 400 psig total pressure.

of MeOAc concentrations can be employed, while the batch unit requires high concentrations of MeOAc to allow for sufficient run length). As expected, the slope from the batch data (which contained much more LiOAc per LiI added) was greater than that observed from the continuous runs. However, a plot of the rate vs. LiOAc concentration for the above runs showed slopes which are similar, again supporting the idea that the rate is enhanced more by LiOAc than LiI, Fig. 9.

Although the carbonylation rate is enhanced only to a small extent by LiI, promotion due to iodide was observed using NMPI as iodide source (no acetate ion was detected with 0.8 M NMPI at 1.0 M water, Fig. 6).
Fig. 9. Effect of [LiOAc] on the rate of continuous and batch carbonylations. Continuous experiments: [Rh] = 4.0 \times 10^{-3} M, [MeI] = 1.0 M, [MeOAc] = 0.6 M, [H_2O] = 2.2 M. Batch experiments: [Rh] = 4.0 \times 10^{-3} M, [MeI] = 1.0 M, [MeOAc] = 3.0 M, [H_2O] = 1.0 M, 190 °C, 400 psig total pressure.

The effect of temperature on the rate was determined in the continuous unit over the temperature range 185 - 200 °C under conditions of 2.3 M H_2O, 0.4 M MeOAc, 0.87 M MeI, 1.5 M LiI and 4.5 mM Rh. The activation parameters determined from a plot of ln(k/T) vs. 1/T were $E_a = 14.9 \pm 1.1$ kcal mol$^{-1}$, $\Delta H^\ddagger = 14.2 \pm 1.1$ kcal mol$^{-1}$, and $\Delta S^\ddagger = -23.0 \pm 2.3$ e.u. (95% confidence level).

In addition to studying the effect of water and salts on the rate of methanol carbonylation, we examined the effects of rhodium, methyl acetate, methyl iodide and CO partial pressure. We found that CO partial pressure had no effect on the rate of carbonylation at 2.0 M H_2O above 50 psi.

Fig. 10. Effect of MeOAc concentration on rate. [Rh] = 2.4 \times 10^{-3} M, [MeI] = 1.0 M, 190 °C, 400 psig total pressure.
CO pressure [7]. This is consistent with the literature at high water concentration [9]. Figure 2 shows the first-order dependence on rhodium catalyst at three different lithium concentrations. The methyl acetate effect at variable water and lithium concentrations is seen in Fig. 10, which shows a significant dependence on methyl acetate concentration when methyl acetate is below ca. 1.0 M but a much smaller effect above ca. 1.0 M. In the presence of 1.8 M LiI at 1.2 M water, the rate increases by 500% from 0.2 M to 1.0 M MeOAc, Fig. 10. Also, at low water concentrations, a high concentration of Li salts is needed to obtain the high rates observed with 8 M water (Fig. 10), therefore maximum rate at low water concentrations required both high concentrations of MeOAc and Li salts. By selecting the proper concentrations of LiI and MeOAc, rates obtained with high water concentrations can be obtained at low water concentrations without changing the Me1 and rhodium concentrations. This is demonstrated further by Fig. 11, which compares the water dependence obtained in the continuous unit at 0.1 - 0.15 M MeOAc and no LiI with runs at 0.5 - 0.8 M MeOAc and 1.4 - 1.6 M LiI. As seen in Fig. 11, the same rate obtained at 8 M water can be obtained at 2 M water if ca. 1.5 M LiI is added and the MeOAc concentrations is raised to ca. 0.5 - 0.8 M.

![Fig. 11. Water concentration dependence in the continuous carbonylation unit. [Rh] = 4.0 x 10^{-3} M, [MeI] = 1.0 M, 190 °C, 400 psig total pressure.](image)

The methyl iodide dependence obtained from solutions containing 0.15 and 1.6 M Li salt at 1.0 M water is given in Fig. 1, and shows a non-linear increase in STY with an increase in MeI concentration. This differs from the first-order behavior we and others [9] observed under conditions without LiI at 8 M water. Similar results for the methyl iodide dependence as well as the other reagents were obtained in the continuous unit and are reported elsewhere [4, 7].
TABLE 3
Comparison of CO₂ and H₂ make rates from the continuous unit at high and low water concentrations

<table>
<thead>
<tr>
<th>Rxn H₂O (M)</th>
<th>Rxn I⁻ (M)</th>
<th>CO₂ STY (mol l⁻¹ h⁻¹)</th>
<th>H₂ STY (mol l⁻¹ h⁻¹)</th>
<th>CO₂ (mol (100 mol HOAC)⁻¹)</th>
<th>H₂ (mol (100 mol HOAC)⁻¹)</th>
<th>IIOAc STY (mol l⁻¹ h⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.0 a</td>
<td>none</td>
<td>0.4</td>
<td>0.3</td>
<td>2.3</td>
<td>1.9</td>
<td>13.1</td>
</tr>
<tr>
<td>2.2 b</td>
<td>1.4 c</td>
<td>0.04</td>
<td>0.01</td>
<td>0.2</td>
<td>0.1</td>
<td>12.3</td>
</tr>
</tbody>
</table>

a 0.1 M MeOAc, 3.5 mM Rh, 1.0 M MeI, 190 °C, 400 psig.
b 6.1 M MeOAc, 3.5 mM Rh, 1.0 M MeI, 190 °C, 400 psig.
c Inorganic iodide, added as LiI.

Selectivity improvements
A definite advantage of operating at low water concentrations in the presence of lithium salts and significant MeOAc concentrations is the decrease in CO inefficiency due to the major byproducts CO₂ and H₂. As demonstrated in the continuous unit [4, 7], gaseous byproducts stemming from the water-gas shift process decrease as water concentration decreases, Table 3.

Catalyst stability studies
Rhodium catalyst stability is aided by high CO partial pressure [8]. However, the effect of water concentration on catalyst stability at low CO partial pressure is not generally recognized. Figure 12 shows the effect of H₂O on the rate of precipitation of the rhodium catalyst from acetic acid solutions under N₂. The rate of RhI₃ precipitation increases as the water concentration decreases. We have previously reported that precipitation can

Fig. 12. Effect of water and LiI on the rate of Rh precipitation. [HI] = 0.24 M, [Rh]ₗᵢ₉ = 8.8 × 10⁻³ M (1000 ppm), 130 °C, 15 psig total N₂ pressure.
be significantly slowed down by addition of LiI or other alkali metal iodides, and also HI [4]. Figure 12 illustrates that catalyst stability obtained at 10 M water can be realized at ≤1.0 M water if LiI (0.24 M) is added. The rate of precipitation of the catalyst also increases with increasing temperature, Fig. 13, but precipitation due to high temperature can also be reduced by LiI addition.

Discussion

Effect of iodide and acetate on rate

In our previous papers [5a, b], we proposed that iodide and acetate increased the rate of reaction by increasing the rate of oxidative addition of methyl iodide to [RhI₂(CO)_2]−. We also proposed that such a rate increase could be due to the formation of a five-coordinate intermediate [RhI₂(CO)_2(L)]⁻² (L = I⁻ or OAc⁻). Such a dianionic complex might be expected to react more rapidly with MeI than would [RhI₂(CO)_2]−. Ion-pairing effects or changes in solvent polarity could explain the enhanced reaction rate with lithium salt addition, but we found that polar solvents such as water, HMPA or nitromethane (solvents which might be expected to break up ion pairs) had very little effect on the IR spectra of [RhI₂(CO)_2]− or on the rate of oxidative addition of MeI to [RhI₂(CO)_2]− [5a, b]. Poorly coordinating salts such as LiBF₄ or LiCF₃SO₃ did not affect the IR spectra of the rhodium complex, nor did their addition increase the rate of carbonylation significantly. It is also difficult to explain the non-linear MeI dependence with a salt effect argument (see below). Though the production of a five-coordinate dianionic complex is speculative, a similar explanation was proposed for halide salt promotion for the reaction of [RhI₂(CO)_2]− with MeI in other solvents [5c]. Baker et al. have proposed the dianion [RhI₃(CO)_2]²− as
the intermediate in the oxidative addition of HI to \([\text{RhI}_2(\text{CO})_2]^-\) \cite{10}. Thus, our evidence suggests two possible pathways through which the oxidative addition could proceed, Scheme 1:

\[
[\text{RhI}_2(\text{CO})_2]^- + \text{L}^- \xrightleftharpoons[k_{-1}]{k_1} [\text{RhI}_2(\text{CO})_2\text{L}]^- \\
\xrightarrow{k_3} \text{MeI} \\
\xrightarrow{k_2} \text{MeI}, \text{L}^- \xrightarrow{-\text{L}} [\text{Me-RhI}_3(\text{CO})_2]^- 
\]

Scheme 1. Two proposed pathways for the oxidative addition of MeI to \([\text{RhI}_2(\text{CO})_2]\). The rate law derived from a steady-state treatment for the two-pathway process of Scheme 1 is given in eqn. (2).

\[
\text{Rate} = [\text{RhI}_2(\text{CO})_2^-][\text{MeI}] \frac{k_1 k_2 [\text{L}^-]}{k_{-1} + k_2 [\text{MeI}]} + k_3 \tag{2}
\]

The effect of MeI on rate

Figure 1 shows that at conditions of low water and high lithium salt concentrations, the MeI dependence is not linear. This deviation from first-order MeI kinetics cannot be explained by the traditional view that for methanol carbonylation the rate-determining step is a simple oxidative addition of MeI to \([\text{RhI}_2(\text{CO})_2]\). The methyl iodide dependence as described by eqn. (2) does not have to be linear, and may not be linear at conditions of high \(\text{L}^-\) concentration where \(k_3\) could be smaller than \(k_1 k_2 [\text{L}^-]/(k_{-1} + k_2 [\text{MeI}])\). To consider the value of \(k_3\) small in eqn. (2) compared to the ligand-promoted pathway allows eqn. (2) to be rearranged to eqn. (3).

\[
\frac{1}{\text{Rate}} = \frac{k_{-1}}{k_2 k_1 [\text{Rh(CO)}_2\text{I}_2^-][\text{L}^-][\text{MeI}]} + \frac{1}{k_1 [\text{Rh(CO)}_2\text{I}_2^-][\text{L}^-]} \tag{3}
\]

The linear plot and non-zero intercept of 1/rate vs. 1/[MeI], Fig. 14, provides support for Scheme 1. The absolute rate constants cannot be calculated exactly from Fig. 14 because the Rh(I) complex is in equilibrium with various Rh(II) species, but assuming the Rh(I) concentration is close to the total rhodium charged (a reasonable assumption at high concentrations of \(\text{L}^-\), see section below on effect of \(\text{L}^-\) on Rh(I) concentration), the \(k_1\) obtained from the intercept of Fig. 14 would be about \(10^4 \text{ M}^{-1} \text{ s}^{-1}\) at 190 °C. From the slope, \(k_{-1}/k_2\) would be about 2.0 M\(^{-1}\). Assuming \(k_{-1}\) is more than 10 times faster than \(k_1\) (we have not seen \([\text{RhI}_2(\text{CO})_2(\text{L}^-)]^2^-\) spectroscopically), a lower limit for the value of \(k_2\) would be about \(5 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}\). Substitution of the values for the above-described rate constants into eqn. (2) shows that \(k_1 k_2 [\text{L}^-]/(k_{-1} + k_2 [\text{MeI}])\) is greater than \(k_3\) by a factor of about 5 - 10 times, thus our rearrangement of eqn. (2) to eqn. (3) is probably reasonable.
Some of the curvature observed in Fig. 1 at high MeI concentrations may be due to the fact that LiOAc (a promoter) concentration decreases as MeI concentration increases, eqn. (1). Thus the LiOAc concentration is less at the higher MeI regime. However, by using Fig. 7 one can determine that the maximum decrease in rate that would be attributable to decreases in LiOAc concentration is only ca. 10%. Therefore, we believe that the promoted oxidative addition reaction is less than first-order in MeI.

**Effect of water and MeOAc on rate and selectivity**

Water concentration was found to have very little effect on the rate of oxidative addition of MeI to \([\text{RhI}_2(\text{CO})_2]^-\) at 25 °C [5a, b]. This suggests that the rate dependence on water concentration in the catalytic process is not due to any interaction of water with the transition-state species of the rate-determining step. Instead, we believe the major effect of water is its effect on the concentration of rhodium existing in the active catalyst form as dictated by the water–gas shift reaction (WGS) [10]. The WGS process is the principle source of the major byproducts (CO₂ and H₂) from methanol carbonylation, and consists of the combination of an oxidation and a reduction process, eqns. (4) and (5).

\[
\begin{align*}
\text{[Rh(CO)₂I₂]}^- + 2\text{HI} & \rightleftharpoons \text{[Rh(CO)₂I₄]}^- + \text{H₂} \quad (4) \\
\text{[RhI₄(CO)₂]} + \text{H₂O} + \text{CO} & \rightleftharpoons \text{[Rh(CO)₂I₂]}^- + 2\text{HI} + \text{CO₂} \quad (5)
\end{align*}
\]

Steady-state kinetics for the WGS process has been investigated elsewhere [10] and the rate for the reduction and oxidation processes of eqns. (4) and (5) is described in eqns. (6) and (7).

**Rate for Rh(III) reduction**

\[
\text{Rate for Rh(III) reduction} = \frac{k[P_{\text{CO}}][\text{Rh}][\text{H₂O}]}{[\text{H}^+][\Gamma][P_{\text{CO}} + [\Gamma]/K_{eq})} \quad (6)
\]
Rate for Rh(I) oxidation = $k_{obs}[\text{Rh}][H^+]^2[I^-]^2$  \hfill (7)

where $[\text{Rh}]$ is the total rhodium charged and $K_{eq}$ is related to an equilibrium between di- and monocarbonyl Rh(III) species \([10]\). It can be seen from eqn. (6) that as $H_2O$ concentration increases the rate of Rh(III) reduction to Rh(I) also increases. If at steady-state conditions the rate of Rh(III) reduction increases relative to Rh(I) oxidation, the steady-state concentration of Rh(I) increases, and so will the rate of methanol carbonylation.

Methyl acetate concentration can increase the carbonylation rate in two ways: (1) by reacting with HI according to eqn. (8), and (2) by reacting with LiI to form LiOAc, eqn. (9). LiOAc can react with HI, eqn. (10), or act as a promoter for the carbonylation itself. A reduction in HI concentration decreases the rate of Rh(I) oxidation, eqn. (6), so that the Rh(I) concentration builds up relative to Rh(III), and the rate of methanol carbonylation

\begin{align*}
\text{HI} + \text{MeOAc} &\rightarrow \text{MeI} + \text{HOAc} \hfill (8) \\
\text{LiI} + \text{MeOAc} &\rightarrow \text{LiOAc} + \text{MeI} \hfill (9) \\
\text{LiOAc} + \text{HI} &\rightarrow \text{HOAc} + \text{LiI} \hfill (10)
\end{align*}

increases. Spectroscopic evidence reported in the literature \([11]\) shows that high MeOAc and water concentrations and low HI concentrations favor the build-up of $[\text{RhI}_2(\text{CO})_2]^-$. Likewise, in catalyst solutions with low MeOAc, low water and high HI concentrations, Rh(III) forms of the catalyst predominate \([11]\).

As mentioned above, an increase in LiOAc concentration will cause the equilibrium concentration of HI to decrease. This raises the question of whether carbonylation rate enhancement by LiI and/or LiOAc is due to coordination of an anionic ligand to $[\text{RhI}_2(\text{CO})_2]^- \rightarrow$ to generate a more nucleophilic rhodium species, or whether the promotion is due to LiOAc decreasing the HI concentration and thereby raising the steady-state concentration of Rh(I). In the catalytic system this question is difficult to answer, but in our previous model studies on the rate of oxidative addition of MeI to $[\text{Rh}(\text{CO})_2I_2]^- \rightarrow [5a, b]$ we observed a significant rate enhancement by LiOAc and to a lesser extent by LiI. Our model study was done in solutions in which essentially all of the rhodium was already in the form $[\text{Rh}(\text{CO})_2I_2]^-$. Thus rate enhancement, at least in our model study, occurs by an interaction of the LiOAc with the rhodium catalyst rather than by an increase in the Rh(I) concentration. Results from our model study also support the idea that under catalytic conditions the majority of the promotional effect observed when LiI is added to the catalyst solution is due to the formation of LiOAc, eqn. (1), rather than LiI. This is also suggested by the similarity in the slopes obtained from plots of LiOAc concentration vs. rate, Figs. 5 and 7. Therefore, reagent concentrations and reaction conditions which favor the formation of LiOAc (high MeOAc and LiI) will help improve the rate. LiI is, however, very important for maintaining catalyst stability, as will be discussed below.
Improvements in selectivity were also realized by operating at conditions of low water and high LiOAc concentrations (low III). Since the rate law for the reduction and oxidation steps for the WGS process, eqns. (6) and (7), contain dependences for water (reduction) and HI (oxidation), then maintaining both reagent concentrations at a low value would slow the production of the gaseous byproducts.

A general diagram is given in Scheme 2, which shows the interactions of the various reagents which affect methanol carbonylation at low water concentrations. This diagram includes the equilibria between the iodide and acetate species as well as the influence of the water–gas shift process on the concentration of the active Rh(I) and catalyst.

A recent presentation was given by Polichnowski [12] on the mechanism for the Rh-catalyzed methyl acetate carbonylation to acetic anhydride in the presence of LiI. In light of similarities between the rhodium-catalyzed acetic anhydride process and the acetic acid process, we need to make some comment. Polichnowski disclosed that at anhydrous conditions, the rate-determining step for MeOAc carbonylation at conditions of 0.19 M LiI concentration, was the oxidative addition of MeI with [Rh(CO)I₂]⁻ and little effect of LiI on rate was observed. At conditions of much lower LiI concentration (0.02 M), the rate-determining step became the reaction of LiI with MeOAc to form LiOAc. The LiOAc then reacts with acetyl iodide to form acetic anhydride. The lack of a Rh or MeI dependence at 0.02 M LiI concentration and a dependence in Rh and MeI at 0.19 M LiI were given as support for the change in the rate-determining step. Any effect on the rate of acetic anhydride production observed at concentration higher than 0.28 M LiI was not mentioned. In contrast to the anhydrous system, under our conditions of > 1.0 M water concentrations, a rhodium dependence is observed over a wide concentration range of lithium (0 - 2.0 M lithium salt tested) both in batch and continuous units. We also observe an NMPI dependence, although acetate ion is not detected. It is very doubtful, therefore, that the acetic acid process passes through similar steps in which acetic anhydride is formed and then hydrolyzed with water. For the anhydride process, NaI was found to be a less effective promoter than LiI, as was expected since the formation of NaOAc is much slower than the rate of formation of LiOAc. However, we found that the rate of methanol carbonylation to acetic acid is essentially the same using NaI or LiI as a promoter [4b, 7]. Therefore, we conclude that the effect of LiI in our system is completely different than in the system used to produce acetic anhydride. However, the ligand promotional effect that we observe may be detected in the anhydride system at higher ligand concentrations.

Effect of LiI on catalyst stability

Water concentration and CO partial pressure are important for maintaining catalyst stability and preventing catalyst precipitation. This is probably because water and CO help maintain the catalyst as [RhI₂(CO)₂]⁻, eqn. (6), which is very soluble under carbonylation conditions. Once the
Scheme 2. Diagram of the interactions of the various reagents involved in methanol carbonylation at low water concentrations.
rhodium catalyst is oxidized to \([\text{RhI}_4(\text{CO})_2]^-\) via eqn. (7), loss of one iodide atom and two CO molecules produces \(\text{RhI}_3\) which is insoluble and precipitates from solution. Loss of CO is especially likely during the product-recovery steps of the continuous process, where distillation for the purpose of recovering the acetic acid product tends to remove the carbon monoxide from the catalyst [8].

The addition of iodide to the catalyst solution effectively stabilizes the catalyst towards precipitation, as shown in Figs. 12 and 13, under an environment void of CO. Similar results were reported by Japanese researchers who found that the thermal stability of the rhodium catalyst is dependent upon the HI concentration in the catalyst solutions, with the Rh(I) catalyst decomposing to insoluble \(\text{RhI}_3\) when the HI concentration was less than 1% [13]. The improved stability of the rhodium catalyst in the presence of excess iodide is understandable in light of the interconvertability of various stable and soluble tetra- and penta-iodocarbonyl rhodium complexes which can be prepared by the reaction of \([\text{Rh(CO)}_2\text{I}_2]^-\) with HI [14]. It has also been reported that organic derivatives of pentavalent phosphorus, arsenic, antimony, nitrogen and bismuth [15] in liquid phase carbonylation of ethylenically unsaturated compounds, as well as halostannate [13], \(N, N, N',N'\)-tetramethyl-o-phenylenediamine and 2,3'-dipyridyl [8] for methanol carbonylation systems all act to retard precipitation of the rhodium catalyst under carbon monoxide-deficient conditions. This stabilization has been rationalized as probably being due to the formation of soluble rhodium complexes with the above additives [8].

Conclusion

Methanol carbonylation to acetic acid with catalyst solutions of low water concentrations can provide considerable savings in the commercial acetic acid process. The detrimental effect of low water concentrations on rate and catalyst stability can be overcome by the addition of an inorganic or organic iodide salt and operation at significant concentrations of methyl acetate. In fact, as shown above, the same high rates obtained at 8 M water can also be obtained at 2 M water by addition of 1.5 M LiI and 0.5 M MeOAc, with equal or better catalyst stability and better CO selectivities. We believe the iodide salt (most notably in this study LiI) is most important as a catalyst stabilizer, but it can promote the rate of carbonylation, mostly by its reaction with methyl acetate to produce LiOAc which is a more effective promoter. LiOAc also serves to decrease the HI concentration, which allows for a higher equilibrium concentration of Rh(I). Likewise, methyl acetate serves to lower the equilibrium concentration of HI and increase the amount of active Rh(I) catalyst.
Acknowledgement

We would like to thank Dr. G. A. Blay for his assistance in developing our analytical methods, and Celanese Chemical Company, Inc. for their support and permission to publish this work.

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7 Manuscript covering data obtained in a continuous unit is in preparation.


12 S. W. Polichnowski, *189th National ACS Meeting*, Miami, FL, April 28 - May 3, 1985. CHED 0135, preprint of article to be submitted for publication was given to us by S. W. Polichnowski.

