

IODIDE AND ACETATE PROMOTION OF CARBONYLATION OF METHANOL TO ACETIC ACID: MODEL AND CATALYTIC STUDIES

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Summary

Iodide and acetate salts increase the rate of reaction of $\text{Li}[\text{RhI}_2(\text{CO})_2]$ with MeI at 25°C in acetic acid solution, a model of the rate-determining step in catalytic methanol carbonylation. The effects of water, LiBF_4 , and other additives are also reported. Iodide salts also promote catalytic methanol carbonylation at low water concentrations. In the case of LiI promoter, lithium acetate is produced in catalytic solutions via the reaction of LiI with methyl acetate. The promotional effects of iodide and acetate on both the model and catalytic systems are rationalized in terms of iodide or acetate coordination to $[\text{RhI}_2(\text{CO})_2]^-$, to yield five-coordinate Rh^{I} anions as reactive intermediates for rate-determining reactions with MeI .

Introduction

The rhodium/iodide catalyzed carbonylation of methanol to acetic acid is typically carried out in the presence of considerable quantities of water [1], which promote both the activity [2] and stability [3] of the rhodium catalyst. Because of the significant energy and capital savings (related to the separation of water from acetic acid product) which could derive from methanol carbonylation at relatively low water concentrations, we undertook a search for additives which would promote and/or stabilize Rh methanol carbonylation catalysts at low water levels. It was discovered [3] that the addition of certain iodide salts (particularly lithium iodide) to Rh/I methanol carbonylation catalysts gave highly productive and stable catalysts under low-water conditions.

In an attempt to understand the chemistry involved in the low-water methanol carbonylation catalyst systems, we have carried out a number of catalytic and model kinetic investigations. A preliminary account of our room temperature kinetic studies of the reaction of $\text{Li}[\text{RhI}_2(\text{CO})_2]$ (1) with MeI , a model for the rate-determining step of methanol carbonylation, has recently appeared [4]. In that communication, kinetic evidence for iodide and acetate promotion of the oxidative

addition of MeI to **1** was reported. In this contribution we wish to expand and more fully report our results with model kinetic studies, and also report some results from batch catalytic studies which show evidence for iodide and acetate promotion of methanol carbonylation at low water concentrations. A more complete study of catalytic carbonylation reactions under a wide range of conditions will be published elsewhere [3,5].

Experimental

Model kinetic studies

Glacial acetic acid (AcOH), J.T. Baker, was distilled under nitrogen before use. Methyl iodide (MeI) was distilled, then stored over copper turnings in brown, foil wrapped bottles. Deionized water was degassed by extended alternate cycles of vacuum and nitrogen purge. All the liquids were stored inside a nitrogen purged glovebox. $[\text{RhCl}(\text{CO})_2]_2$ (Strem), anhydrous LiI (98%, Alfa), $\text{Li}[\text{O}_2\text{CCH}_3] \cdot 2\text{H}_2\text{O}$ (Aldrich) and $\text{Li}[\text{BF}_4]$ (Aldrich) were used as received. *N*-methyl-picolinium iodide (NMPI) was prepared from 3-picoline (Aldrich) by reaction with excess MeI, followed by vacuum removal of excess MeI from the precipitated NMPI. NMR spectra of the product showed no evidence for the presence of free picoline or other impurities.

“Stock” solutions of $\text{Li}[\text{RhI}_2(\text{CO})_2]$ (**1**) for kinetic runs were typically prepared inside the glovebox by dissolving $[\text{RhCl}(\text{CO})_2]_2$ in acetic acid solutions containing 2.5 equiv. of LiI per Rh at 25°C. The solutions of yellow **1** are usually tinged purple (presumably due to trace oxidation to $\text{Li}[\text{RhI}_4(\text{CO})_2]$), but no metal carbonyl species other than **1** are detected by IR, and the concentration of **1** is reproducible to about 5%. The solutions were used within 4 d, but are stable for extended periods in the absence of O_2 or MeI. Additives for kinetic runs were dissolved in appropriate volumes of AcOH/ H_2O , then **1** was added from the stock solution. Methyl iodide was added at time zero (in large excess compared to Rh). Standard ZnSe or CaF_2 solution IR cells with 0.1 mm pathlengths were rinsed twice with the reacting solution, then filled and the Luer hubs sealed with tight fitting 5 mm rubber septum caps. The IR cells were removed from the glovebox and placed in an N_2 purged Nicolet MX-1 FT-IR spectrometer for the duration of each run. Rigorous temperature control was not possible, but the temperature within the sample chamber was not observed to vary from 25°C by more than 1°C.

IR spectra of the solution reacting within the IR cell were periodically scanned and the strong solvent background subtracted via computer over the region of 2300–1900 cm^{-1} (virtually all other regions of the IR spectrum are obscured by strong absorptions of the AcOH solvent). The disappearance of **1** was monitored via band area measurements of its 1988 cm^{-1} absorption (Figs. 1 and 2). Most runs were followed for two half-lives, and typically showed good first order disappearance of **1** as evidenced by the linearity of plots of $\ln(A_0/A_t)$ vs. time (Fig. 3). Pseudo-first order rate constants for the disappearance of **1** were obtained from least-squares fits of such plots. Some deviation (toward accelerating rates of disappearance of **1**) is found in the presence of lithium acetate promoter after approximately 1.5 half-lives (Fig. 3). First order fits are much better than second order or higher fits. Accurate measurement of IR band areas after two half-lives was not possible in the presence of higher concentrations of acetate due to the poor

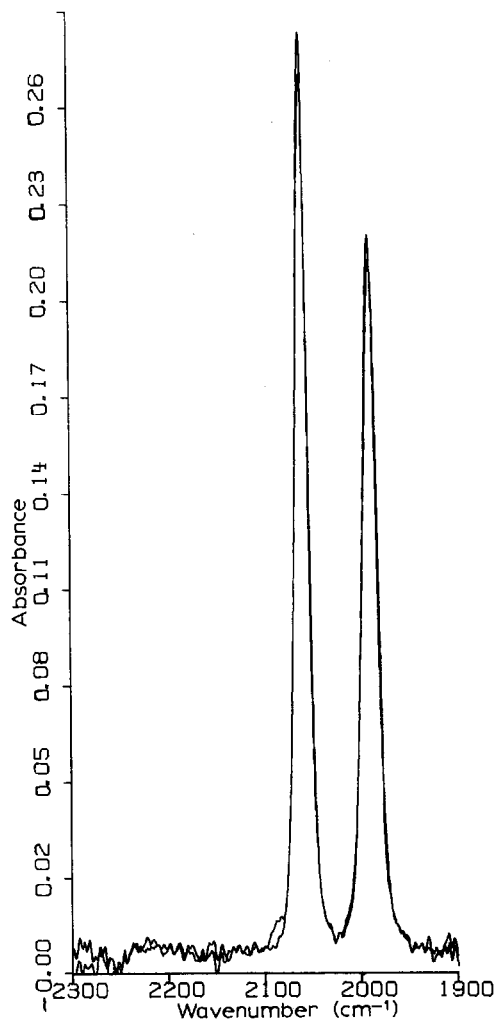


Fig. 1. Overlaid IR spectra of $\text{Li}[\text{RhI}_2(\text{CO})_2]$ and $\text{NMP}[\text{RhI}_2(\text{CO})_2]$ prepared via addition of LiI or NMPI to $[\text{RhCl}(\text{CO})_2]_2$ in acetic acid solutions containing 2 wt% H_2O , see text.

signal-to-noise ratios which result from the high optical density of the acetate/acetic acid solvent.

Catalytic experiments

RhI_3 and $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ (Engelhardt) were used as catalyst precursors. Carbon monoxide was purchased from Matheson. All other chemicals were commercial products and were used without further purification.

Catalytic experiments were carried out in stirred, electrically heated 300 ml Hastelloy-B or Hastelloy-C autoclaves (Autoclave Engineers) provided with gas and liquid feed and take-off lines. Constant total reaction pressure was maintained during a run by feeding carbon monoxide on demand from a high pressure reservoir. The autoclave was charged with rhodium catalyst precursor (generally RhI_3), water,

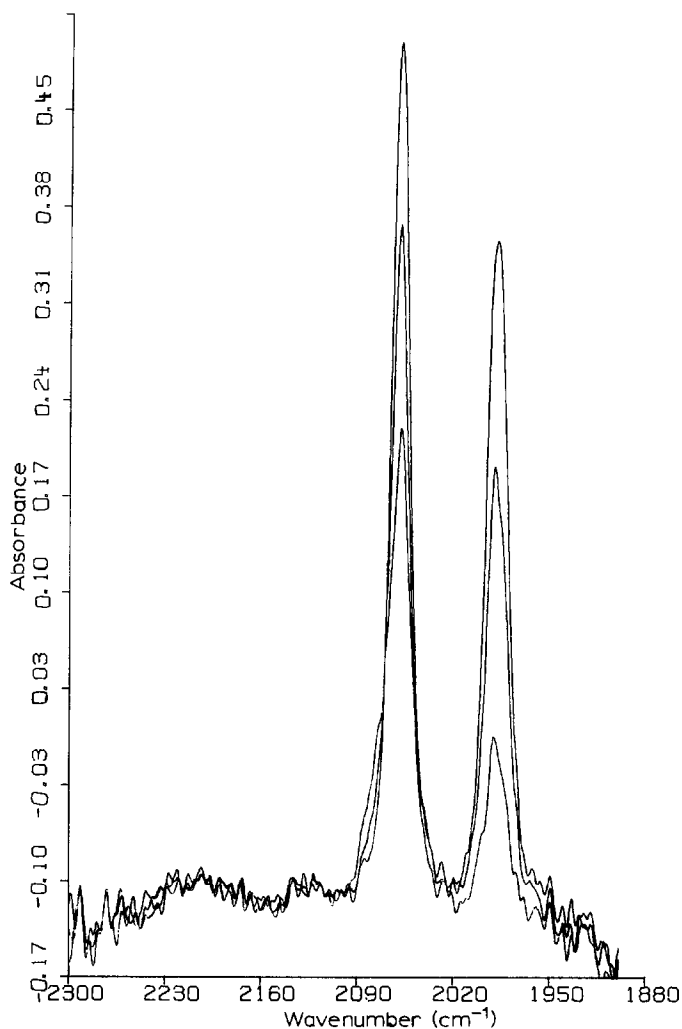


Fig. 2. IR spectra from the reaction of $\text{Li}[\text{RhI}_2(\text{CO})_2]$ with 1.63 *M* MeI in AcOH solvent containing 0.459 *M* lithium acetate and 2 wt% H_2O .

methyl iodide, iodide salt, and acetic acid, sealed, and purged twice with 50 psi CO. The reactor pressure was brought to 150 psig CO, and heated with slow stirring to reaction temperature (usually 190°C). Methanol or methyl acetate (0.36 mol unless otherwise specified) was injected into the autoclave at time zero via a pressurized bomb, fast stirring started and total pressure increased with CO to 400 psig. The initial rate of catalytic carbonylation was determined by measuring the quantity of carbon monoxide consumed (as calculated from the pressure drop in the carbon monoxide reservoir) vs. time.

When methanol is charged to a hot batch reactor containing acetic acid solvent, rapid (and essentially quantitative) esterification produces water and methyl acetate [2]. The water produced is then gradually consumed during the run by the hydrolysis

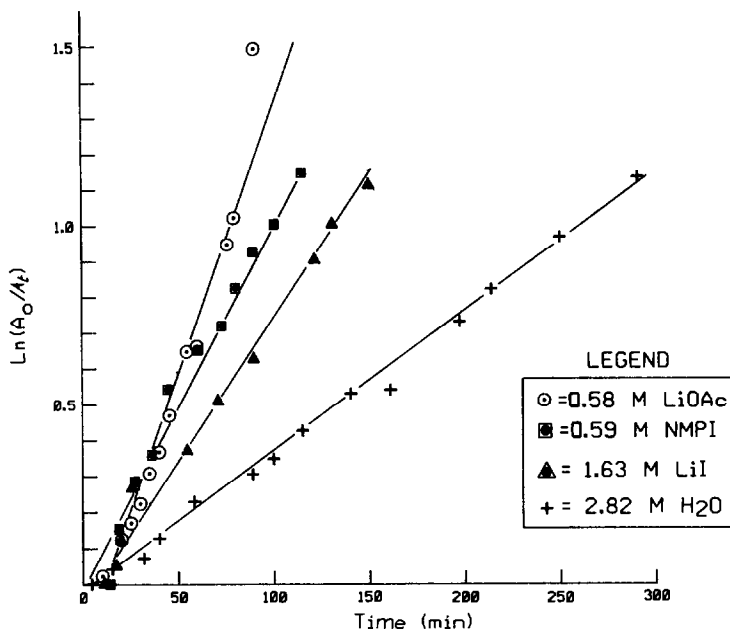
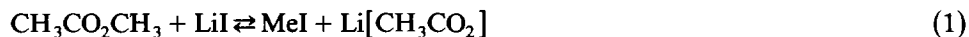


Fig. 3. First order plots for reaction of $\text{Li}[\text{RhI}_2(\text{CO})_2]$ with 1.63 M MeI in the presence of additives in acetic acid solutions containing 2 wt% H_2O .

of acetyl iodide. In low-water carbonylation runs methyl acetate was charged in place of methanol in order to avoid in-situ formation of large concentrations of water during the initial period of the reaction when rates are measured. In control experiments at equivalent high water concentrations no difference in initial carbonylation rate was observed between the use of methanol and methyl acetate charges.

In our batch autoclave experiments containing lithium iodide, we observed that considerable quantities of MeI and lithium acetate (LiOAc) can be generated under reaction conditions via the reaction of LiI with methyl acetate (eq. 1). In contrast NMPI did not react with methyl acetate to produce detectable quantities of acetate salts (Table 3). Such equilibria are known [6], and have been observed in anhydrous systems for methyl acetate carbonylation [7].



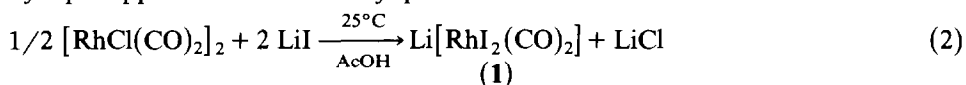
Furthermore, density changes caused by the presence of large concentrations of iodides, and volatilization of liquid reagents into the reactor headspace can cause substantial variations in reactant concentrations compared to the cold reactor charge. In order to determine the concentration of each reagent at actual reaction conditions, in separate experiments the autoclave was charged with all reagents except rhodium and heated and pressurized to reaction conditions. A hot liquid aliquot was rapidly drained into a volumetric flask dipped in a CO_2 acetone bath, instantly freezing the liquid sample. The sample was quickly thawed and analyzed by GLC for methyl acetate, methyl iodide, and acetic acid, and for inorganic iodides and acetates by titration. The observed rates reported here are for the initial period of each run where reagent concentrations are reliably known. Rhodium concentra-

tion was calculated based on rhodium charged. The observed rates were then normalized to equivalent concentrations of methyl iodide and Rh catalyst.

Results

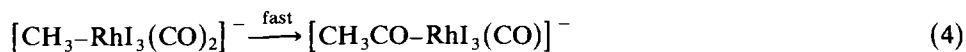
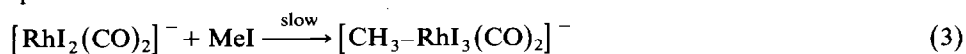
Synthesis, characterization, and reactions of $[\text{RhI}_2(\text{CO})_2]^-$

Stable acetic acid solutions of **1** can be rapidly prepared [4] by treating $[\text{RhCl}(\text{CO})_2]_2$ with LiI according to eq. 2. Two IR bands at 2059 and 1988 cm^{-1} are observed (Fig. 1) whose energies and relative band intensities closely match those reported for other salts of $[\text{RhI}_2(\text{CO})_2]^-$ [8–10], and those from our catalyst solutions. When less than 2 equiv. of LiI per Rh were present, complex IR spectra in the carbonyl stretching region were observed, indicating mixtures of species. The *N*-methyl-picolinium salt of $[\text{RhI}_2(\text{CO})_2]^-$ was similarly obtained by substitution of NMPI for lithium iodide. Overlaid spectra of **1** and NMP $[\text{RhI}_2(\text{CO})_2]$ obtained by treating two aliquots of $[\text{RhCl}(\text{CO})_2]_2$ dissolved in AcOH containing 2 wt% H_2O with 2.1 equiv. of LiI or NMPI per Rh are shown in Fig. 1. The reaction represented by eq. 1 appears to be essentially quantitative.



The energies of the IR bands of **1** vary only 3–4 wavenumbers as excess quantities of water, nitromethane, or hexamethylphosphoramide (HMPA) are added to AcOH solutions of **1**. Similarly, addition of large excesses of salts such as LiI, lithium acetate (LiOAc) and LiBF_4 resulted in no significant changes in the $\nu(\text{CO})$ band energies or intensities of **1**, even at elevated temperatures. Air oxidation of pure **1** is slow at 25°C and produces no detectable carbonyl containing products, but is rapid in the presence of iodide salts, cleanly producing solutions of $[\text{RhI}_4(\text{CO})_2]^-$ (2088 cm^{-1}). This reaction presumably results from O_2 oxidation of I^- to I_2 followed I_2 oxidative addition [11] to **1**. No reaction between **1** and iodide or acetate salts were observable in the absence of O_2 or MeI.

Acetic acid solutions of **1** react smoothly with excess MeI (eqs. 3, 4) over several hours at room temperature in a manner essentially similar to a previous report [9a] for other salts of $[\text{RhI}_2(\text{CO})_2]^-$. In both promoted and non-promoted experiments, the 1988 cm^{-1} band of **1** completely disappears, and the 2059 cm^{-1} band of **1** also disappears, but the apparent decrease in absorption is slower because the 2059 cm^{-1} band is simultaneously replaced by the less intense and overlapping absorptions of the product acyl complexes near 2060 cm^{-1} (Fig. 2). Precipitation of the products of non-promoted and iodide promoted runs with $[\text{N}(\text{C}_2\text{H}_5)_4][\text{ClO}_4]$ gave a reddish brown salt whose IR and ^1H NMR spectra match that of the expected Rh-acyl complex [9,12], $[\text{CH}_3\text{CO-RhI}_3(\text{CO})_2]^{2-}$. In the presence of lithium acetate, the major absorption of the final product(s) is at 2057 cm^{-1} , with a small shoulder at 2075 cm^{-1} . Attempted isolation of the products of acetate promoted reactions via precipitation with $[\text{N}(\text{C}_2\text{H}_5)_4][\text{ClO}_4]$ gave red-brown solids whose KBr-IR and solution IR and ^1H NMR spectra indicated the presence of acetate, and Rh-acyl species.



Model kinetic studies

Quantitative studies of the reaction of $[\text{RhI}_2(\text{CO})_2]^-$ with MeI (eq. 3) were carried out using FT-IR measurements of the band area of the 1988 cm^{-1} absorption of **1** (Fig. 2). Most kinetic runs reported here were conducted in solutions containing 2 wt% (1.16 M) H_2O in order to simulate as accurately as possible the conditions of the catalytic methanol carbonylation runs reported below. In the presence of excess MeI, the disappearance of **1** followed first order kinetics as evidenced by the linearity of plots of $\ln(A_0/A_t)$ vs. time (Fig. 3).

In the absence of iodides or acetates pseudo-first order rate constants for the disappearance of **1** were directly proportional to MeI concentration (Table 1) indicating first order dependence on MeI. Water concentration had only very small effects on the rate of reaction (Table 1). Nitromethane and methyl acetate were also found to have very small promotional effects on the rate of reaction 3.

The effects of iodide and acetate salts on the rate of reaction 3 are substantially larger than those induced by H_2O , nitromethane, methyl acetate, or $\text{Li}[\text{BF}_4]$. The reactions still exhibit first order behavior with respect to Rh and MeI (vide infra). From the base-case rates obtained without additives in solutions containing 2 wt% H_2O , rates increase substantially in direct proportion to the concentrations of LiI, NMPI, LiOAc and sodium acetate (Fig. 4 and Table 2).

The rate increases attributed to LiI in our initial communication [4] (based on three runs) were approximately twice as large as the ones reported here. The rates previously obtained for the unpromoted reaction, and the reaction promoted by LiOAc, and LiBF_4 are experimentally equivalent to the rates obtained now. The early work with LiI was conducted with a LiI lot which is no longer available from the manufacturer. Although we cannot specifically attribute the lower rates we now observe with LiI to the material used in the earlier study, the rates we now obtain in

TABLE 1
EFFECT OF POLAR ADDITIVES ON THE RATE OF REACTION OF $\text{Li}[\text{RhI}_2(\text{CO})_2]$ AND MeI ^a

Additive	[Additive] (mol l ⁻¹)	[Rh] ₀ (mol l ⁻¹)	[MeI] (mol l ⁻¹)	<i>k</i> _{obs} (× 10 ⁴) ^b (s ⁻¹)	Rate (× 10 ⁶) ^c (mol l ⁻¹ s ⁻¹)
H ₂ O	0.075	0.014	1.63	0.710(0.012)	0.994
H ₂ O	1.16	0.014	1.63	0.630(0.022)	0.882
H ₂ O	1.16	0.014	1.63	0.622(0.023)	0.871
H ₂ O	1.16	0.014	1.63	0.687(0.027)	0.962
H ₂ O	1.16	0.028	1.63	0.663(0.027)	0.928
H ₂ O	1.16	0.014	1.23	0.542(0.012)	0.759
H ₂ O	1.16	0.014	0.82	0.348(0.023)	0.487
H ₂ O	2.49	0.028	1.63	0.630(0.010)	0.882
H ₂ O	2.82	0.028	1.63	0.662(0.013)	0.927
H ₂ O	3.38	0.028	1.63	0.908(0.038)	1.271
CH ₃ NO ₂	0.72	0.014	1.63	0.767(0.038)	1.074
CH ₃ CO ₂ CH ₃	0.48	0.014	1.63	0.700(0.022)	0.980

^a 25°C, acetic acid solvent, 2 wt% (1.16 M) H_2O (unless otherwise stated). ^b Pseudo-first order rate constants (and standard deviations) calculated from least-squares fits of plots for first order disappearance of **1**. For averaged values of equivalent runs (and calculated standard deviations), see Fig. 4.

^c Rates normalized to 0.014 M Rh.

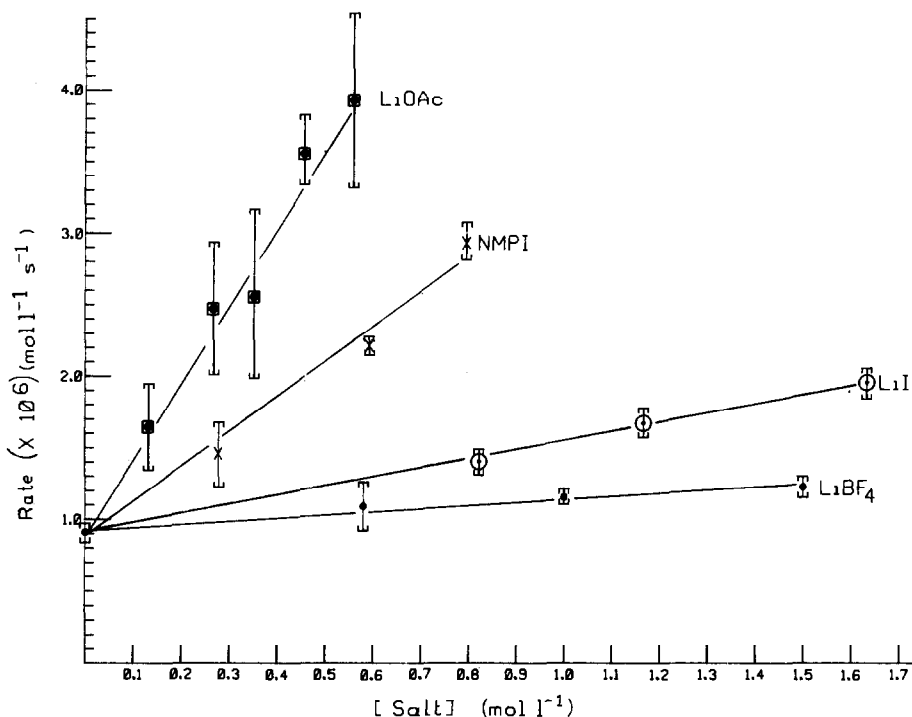


Fig. 4. Effect of salt additives on rate of reaction of $\text{Li}[\text{RhI}_2(\text{CO})_2]$ with 1.63 M MeI at 25°C in acetic acid solutions containing 2 wt% H_2O . Data points represent means and \pm one standard deviation for equivalent experiments (calculated from data in Table 2).

the presence of different lots of LiI are equivalent and reproducible and we are confident of our current experimental results.

Some deviation from first order disappearance of **1** is noted after 1.5 half-lives in the presence of acetate (see Fig. 3 and the experimental section). We attribute the increased scatter which is apparent in our acetate data to this deviation and to the generally poorer quality of the IR spectra obtained in the presence of acetate (which substantially decreases the already small transmission of IR energy through the solution in the region of interest). We do believe that the reaction between **1** and MeI in the presence of both iodides and acetate is first order in **1**. The reactions are approximately first order in methyl iodide as illustrated by Fig. 5 and Table 2.

Catalytic methanol carbonylation

At low water levels carbonylation rates were found to increase substantially as iodide salts were added. See Table 3. We discovered however that in the presence of high concentrations of methyl acetate and LiI, the equilibrium reaction illustrated in eq. 1 produces significant quantities of lithium acetate (LiOAc), and significantly increases MeI concentrations relative to those found in the absence of LiI. Table 3 illustrates the LiI and LiOAc concentrations detected in samples taken from reaction solutions under catalytic conditions (see experimental section). *N*-methyl-picolinium iodide (NMPI) did not react with methyl acetate to produce detectable quantities of acetate salts.

TABLE 2

RATE DATA FOR OXIDATIVE ADDITION OF MeI TO $\text{Li}[\text{RhI}_2(\text{CO})_2]$ IN THE PRESENCE OF SALTS ^a

Salt	[Salt] (mol l ⁻¹)	[Rh] ₀ (mol l ⁻¹)	[MeI] (mol l ⁻¹)	<i>k</i> _{obs} (× 10 ⁴) ^b (s ⁻¹)	Rate (× 10 ⁶) ^c (mol l ⁻¹ s ⁻¹)
LiBF ₄	0.58	0.014	1.63	0.866(0.030)	1.21
LiBF ₄	0.58	0.028	1.63	0.690(0.017)	0.97
LiBF ₄	1.00	0.028	1.63	0.838(0.022)	1.17
LiBF ₄	1.00	0.028	1.63	0.820(0.015)	1.15
LiBF ₄	1.50	0.028	1.63	0.838(0.020)	1.17
LiBF ₄	1.50	0.028	1.63	0.908(0.027)	1.27
LiI	0.82	0.028	1.63	0.958(0.010)	1.34
LiI	0.82	0.028	1.63	1.050(0.033)	1.47
LiI	1.17	0.028	1.63	1.148(0.017)	1.61
LiI	1.17	0.028	1.63	1.248(0.017)	1.75
LiI	1.63	0.028	1.63	1.343(0.028)	1.88
LiI	1.63	0.028	1.63	1.458(0.076)	2.04
NMPI	0.28	0.014	1.63	0.925(0.063)	1.30
NMPI	0.28	0.014	1.63	1.161(0.057)	1.62
NMPI	0.59	0.014	1.63	1.550(0.100)	2.17
NMPI	0.59	0.014	1.63	1.615(0.040)	2.26
NMPI	0.797	0.014	1.63	2.033(0.056)	2.85
NMPI	0.797	0.014	1.63	2.166(0.048)	3.03
NMPI	0.797	0.014	1.13	1.583(0.096)	2.22
LiOAc	0.137	0.028	1.63	1.021(0.025)	1.43
LiOAc	0.137	0.014	1.63	1.325(0.090)	1.86
LiOAc	0.275	0.028	1.63	1.448(0.067)	2.03
LiOAc	0.275	0.028	1.63	1.523(0.055)	2.13
LiOAc	0.275	0.014	1.63	2.150(0.213)	3.01
LiOAc	0.275	0.028	1.63	1.950(0.028)	2.73
LiOAc	0.275	0.014	0.88	0.983(0.080)	1.38
LiOAc	0.350	0.028	1.63	1.383(0.132)	1.94
LiOAc	0.350	0.028	1.63	1.916(0.158)	2.68
LiOAc	0.350	0.028	1.63	2.233(0.181)	3.12
LiOAc	0.459	0.028	1.63	2.433(0.120)	3.41
LiOAc	0.459	0.028	1.63	2.683(0.085)	3.76
LiOAc	0.583	0.028	1.63	2.383(0.122)	3.34
LiOAc	0.583	0.028	1.63	2.600(0.085)	3.64
LiOAc	0.583	0.014	1.63	2.833(0.122)	3.97
LiOAc	0.583	0.014	1.63	3.400(0.108)	4.76
LiOAc ^d	0.583	0.028	1.63	2.233(0.103)	3.13
NaOAc ^e	0.583	0.28	1.63	3.083(0.348)	4.25

^a 25°C, acetic acid solvent, 2 wt% (1.16 M) H₂O (unless otherwise stated). ^b Pseudo-first order rate constants (and standard deviations) calculated from least-squares fits of plots for first order disappearance of 1. For averaged values of equivalent runs (and calculated standard deviations), see Fig. 4.

^c Rate normalized to 0.014 M Rh. ^d Glacial acetic acid (approx. 0.1 wt% H₂O) solvent. ^e Lithium acetate (LiOAc) added as Li[CH₃CO₂]·2H₂O, sodium acetate (NaOAc) added as Na[CH₃CO₂]·3H₂O.

Solution density and MeI concentration vary somewhat in different runs due to the addition of substantial quantities of iodide salts. Therefore we found it desirable to normalize rates to constant MeI and Rh concentrations and plot the resulting normalized rates vs. total salt concentration (Fig. 6). Because acetate is generated in

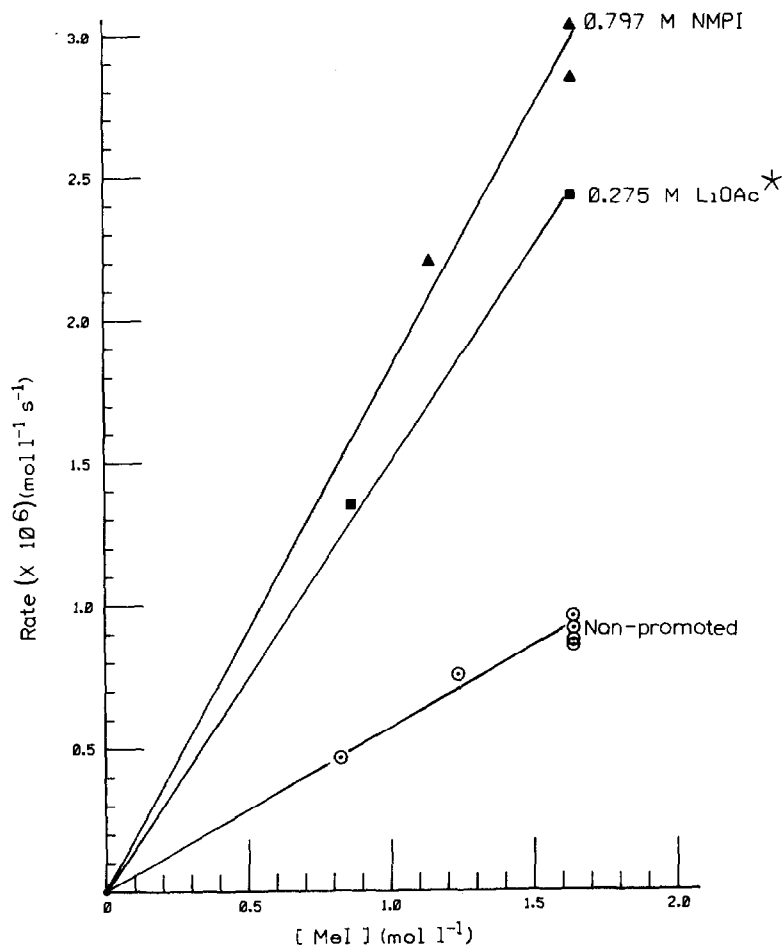


Fig. 5. Rates of reaction of $\text{Li}[\text{RhI}_2(\text{CO})_2]$ with MeI as a function of MeI concentration in the presence of salts. * = average value calculated from Table 2.

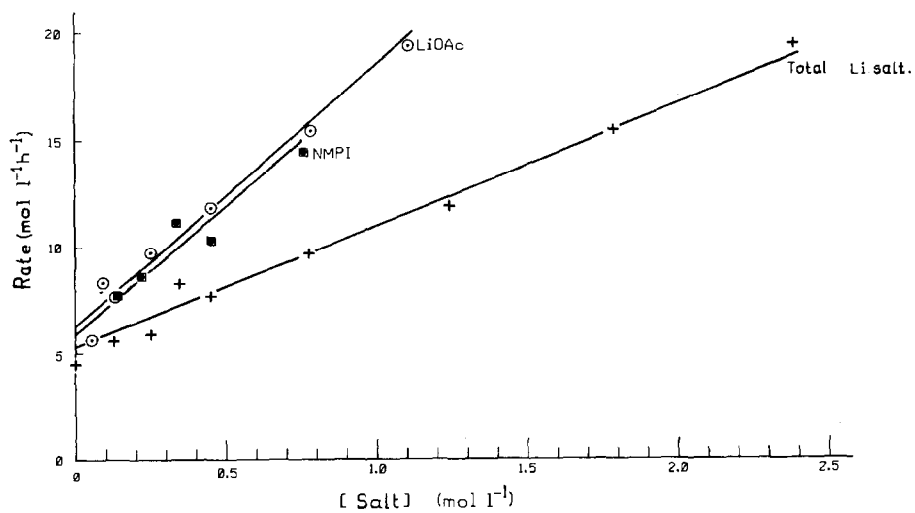


Fig. 6. Rates of catalytic methanol carbonylation as a function of promoter concentration. Conditions and data listed in Table 3.

TABLE 3
RATES OF METHANOL CARBONYLATION vs. PROMOTER CONCENTRATIONS ^a

Promoter (charged)	Moles (charged)	Observed		Rate _{obs} (mol l ⁻¹ h ⁻¹)	Rate (normalized) ^b (mol l ⁻¹ h ⁻¹)
		[I ⁻] (mol l ⁻¹)	[CH ₃ CO ₂ ⁻] (mol l ⁻¹)		
none	0.0	–	–	3.97	4.40
LiI	0.015	0.123	0.040	6.70	6.67
LiI	0.023	0.178	0.062	7.00	6.90
LiI	0.034	0.248	0.097	9.00	8.19
LiI	0.045	0.316	0.139	8.40	7.84
LiI	0.076	0.530	0.254	12.20	9.85
LiI	0.110	0.780	0.460	16.60	11.90
LiI	0.149	1.000	0.790	21.10	15.50
LiI	0.194	1.280	1.11	28.50	19.40
NMPI	0.015	0.14	ND ^c	6.92	7.70
NMPI	0.023	0.22	ND	7.93	8.79
NMPI	0.034	0.33	ND	10.12	11.10
NMPI	0.045	0.45	ND	9.56	10.30
NMPI	0.085	0.77	ND	13.60	14.50

^a 190°C, 400 psig total pressure. 19.0 g MeI and 27.0 g CH₃CO₂CH₃ and 2.0 g H₂O charged with AcOH solvent to give 2 wt% H₂O/AcOH. ^b Rates normalized for changes in solution Rh concentration (constant 4.59 × 10⁻⁴ mol RhI₃ charged) due to density changes induced by iodide salts, and for MeI concentration (to 1.00 M) because of solution equilibria, see text. ^c ND = None detected.

the LiI runs, and our model studies suggest that acetate is the more effective promoter, we also plotted normalized rate vs. observed acetate concentration (Fig. 6). Both plots show a linear increase in carbonylation rate with increasing salt concentration. In our NMPI promoted catalytic system, carbonylation rates also increase approximately linearly with NMPI concentration. Figure 6 suggests that first order promotional effects are obtained as iodide and acetate salts are added to methanol carbonylation catalysts at low-water concentrations.

Discussion

The general mechanism of traditional rhodium/iodide catalyzed methanol carbonylation is well-known [2,9,13]. The observed kinetic dependences of the catalytic system (first order in Rh, first order in MeI, and zero order in CO) were cited [9] as evidence that the rate-determining step is oxidative addition of MeI to [RhI₂(CO)₂]⁻. In view of the industrial importance of the catalytic [RhI₂(CO)₂]⁻/MeI system, it is somewhat surprising that no model kinetic studies of the proposed rate-determining step, the reaction of [RhI₂(CO)₂]⁻ with MeI, have been reported until very recently [4,10].

Kinetic studies of the oxidative addition of MeI to Li[RhI₂(CO)₂]

It is known that salts of [RhI₂(CO)₂]⁻ are obtained on treatment of [RhX(CO)₂]₂ (X = Cl, Br, I) with iodide salts [8,10]. We find that treatment of acetic acid solutions of [RhCl(CO)₂]₂ with LiI according to eq. 2 produces apparently quantitative yields of the AcOH soluble alkali metal salt, Li[RhI₂(CO)₂] (1). The ease of this

preparation enabled us [4] to carry out quantitative studies (via FT-IR spectroscopy) of the reactions of **1** with MeI in aqueous acetic acid, the solvent medium most relevant to the actual practice of catalytic methanol carbonylation.

The oxidative addition of alkyl halides to transition metal complexes in general, and square-planar, d^8 complexes in specific are well-known and have been extensively studied [14]. In acetic acid solvent containing 2 wt% H_2O , we find the unpromoted reaction between **1** and MeI (eq. 3) to be cleanly first order in both **1** and MeI (Tables 1, 2, Figs. 3, 5). The product isolated from the reaction was $[CH_3CORhI_3(CO)]_2^{2-}$ (which is a product of presumably fast rearrangements of the initially formed methyl-Rh complex [9]). These observations indicated that our IR technique measures accurately the rate of oxidative addition of MeI to **1**, and are consistent with a mechanism involving rate-determining nucleophilic attack of **1** on MeI. These observations also support the conclusion [2a,9,13] that the reaction of $[RhI_2(CO)_2]^-$ with MeI is rate-determining in catalytic methanol carbonylation.

Iodide and acetate promotion of oxidative addition

Lithium iodide, NMPI, LiOAc and sodium acetate all increased the rate of reaction of MeI with **1** by amounts measurably larger than did H_2O , $LiBF_4$, CH_3NO_2 or $CH_3CO_2CH_3$ (Fig. 4, Tables 1 and 2). From a base-case rate obtained in acetic acid containing 2 wt% H_2O , rates increase linearly with the concentration of iodide or acetate salts. Hickey and Maitlis [10] have obtained similar results in their study of amine and halide salt promotion of oxidative addition of MeI to $[As(C_6H_5)_4][RhI_2(CO)_2]$. Figures 4 and 5 suggest that the oxidative addition reaction follows an empirical two term rate law (eq. 5). One term involves direct reaction of **1** with MeI, and gives the non-zero intercept observed in Fig. 4. The other term involves first order iodide or acetate promotion of the oxidative addition, and gives rate increases directly proportional to salt concentration.

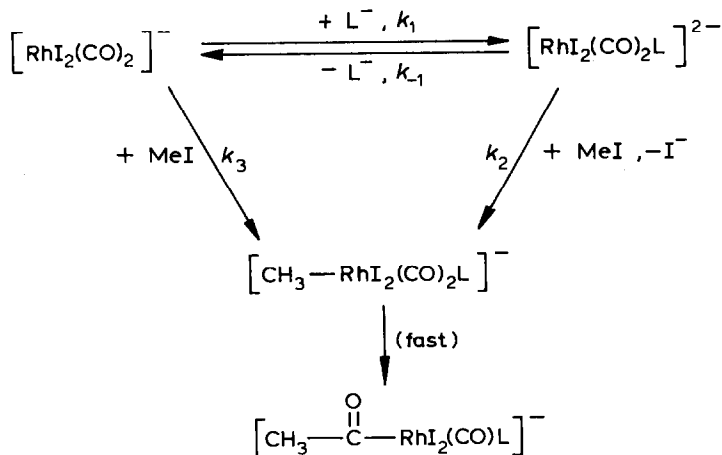
$$-\frac{d[RhI_2(CO)_2^-]}{dt} = (k' + k''[\text{salt}])[RhI_2(CO)_2^-][MeI] \quad (5)$$

We suggest that iodide and acetate salts may be significantly better promoters than $LiBF_4$ or polar solvent molecules because of the ability of the iodide or acetate anions to serve as ligands for $[RhI_2(CO)_2]^-$. The $[RhI_2(CO)_2]^-$ anion is a sixteen electron, coordinatively unsaturated, four-coordinate complex, and may be in equilibrium with steady-state concentrations of five-coordinate dianionic complexes in which iodide or acetate is a fifth ligand (eq. 6). The $[RhI_2(CO)_2L]^{2-}$ complexes formed, (**2**, L = iodide or acetate) would be electronically analogous to $[Mn(CO)_5]^-$ and other similar species, and might be expected to behave as strong S_N2 nucleophiles toward MeI. Hickey and Maitlis [10] propose a similar explanation for their results with halide salt promoters for reaction of $[RhI_2(CO)_2]^-$ with MeI in other solvents, and also propose that amines such as methyl-imidazole may react with $[RhI_2(CO)_2]^-$ to give reactive five-coordinate species.



(L = I^- or $CH_3CO_2^-$)

Five-coordinate intermediates are commonly postulated as intermediates in ligand substitution reactions of square planar d^8 complexes [15], and substitution of halide



SCHEME 1

anions for neutral phosphine and arsine ligands [16] is proposed to increase the reactivity of Rh^I complexes toward MeI. A number of stable, five-coordinate Rh^I complexes are known [17], and carboxylate [17,18] and other sp^2 -hybridized carbonyl oxygen atoms are well-known as potential ligands for Rh^I complexes. For the species we are considering, the increased nucleophilicity of five-coordinate species (relative to four-coordinate species) might be more important than steric bulk during an S_N2 attack on MeI. The steric demands of the ligands in the five-coordinate intermediates we propose would be relatively small. Baker, Hendrickson, and Eisenberg [19] have proposed the five-coordinate dianion **2** (where $L = I^-$) as an intermediate in the oxidative addition of HI to $[RhI_2(CO)_2]^-$. Five-coordinate intermediates have been proposed [20] and isolated [21] in the oxidative addition of hydrogen halides to square-planar Ir^I complexes. Hickey and Maitlis [10] report observation of weak IR bands in iodide-containing solutions of $[RhI_2(CO)_2]^-$ which they attribute to five-coordinate species, although we were unable to detect similar bands in either iodide or acetate containing acetic acid solutions of **1**.

The iodide or acetate effects on reaction 3 illustrated in Fig. 4 can be rationalized as a competition between four-coordinate and five-coordinate pathways for rate-determining oxidative addition of MeI to **1** (Scheme 1).

The steady-state rate law derived from Scheme 1 (eq. 7) readily rationalizes Fig. 4. A non-promoted pathway (k_3) gives a non-zero intercept in the plot of rate vs. salt concentration, and a ligand-promoted pathway (k_2) provides rate increases directly proportional to promoter concentration. At constant MeI concentration the empirical rate law (eq. 5) can be derived from eq. 7. In the case of iodide promotion, displacement of iodide during an S_N2 attack on MeI would produce the same intermediate methyl rhodium complex as the non-promoted pathway. In an acetate-promoted reaction, an acetate-substituted Rh complex would initially result (which might be able to reductively eliminate acetic anhydride in the presence of CO). It is interesting to note that eq. 7 predicts that MeI dependence may be less than first order if $k_2[MeI]$ is sufficiently large relative to k_{-1} . Although our very limited MeI dependence data at room temperature suggests the MeI dependence of the iodide

and acetate promoted reactions are close to first order, we cannot rule out the possibility that some curvature is present. Pertinent evidence on this matter from our catalytic systems will be presented in a future publication [5].

$$\frac{-d[\text{RhI}_2(\text{CO})_2^-]}{dt} = \left\{ \frac{k_1 k_2 [\text{L}]}{k_{-1} + k_2 [\text{MeI}]} + k_3 \right\} [\text{RhI}_2(\text{CO})_2^-] [\text{MeI}] \quad (7)$$

Solvent and ion-pairing effects

We believe that contact ion-pairing effects are not a significant factor in the reactivity of **1** toward MeI in aqueous acetic acid and they are not responsible for the promotional effects of iodide and acetate salts. The similarity of the IR spectra of the Li^+ and NMP^+ salts of $[\text{RhI}_2(\text{CO})_2]^-$ in acetic acid solution containing 2 wt% H_2O (Fig. 1) suggests that contact ion-pair formation between Li^+ and $[\text{RhI}_2(\text{CO})_2]^-$ is not significant in this medium. Furthermore, water, nitromethane, or HMPA (which might be expected to coordinate Li^+ and break up contact ion pairs [22]) had very little effect on the IR spectra of **1** dissolved in acetic acid. Similarly, addition of LiBF_4 , LiI , or LiOAc did not significantly effect the IR spectra of **1** in aqueous acetic acid. We also find that water or LiBF_4 concentration has very little effect on the rate of the unpromoted reaction between **1** and MeI.

The observed small changes in the rate of reaction 3 caused by H_2O , nitromethane and LiBF_4 (Table 1) may be attributable to the effects of these polar agents on equilibria between various classes of "solvent-separated" ion pairs and multiple ions (which are not expected to change reactivity dramatically). Alternatively, the small observed effects of water, nitromethane, and LiBF_4 on the rate of reaction 3 could be explained by polarity induced stabilization of an $S_{\text{N}}2$ transition state for the attack of d^8 complexes on MeI [14a]. Such stabilization is not expected to be large for attack of an anionic Rh^{I} complex on MeI.

In the case of the iodide and acetate-promoted reaction between **1** and MeI, we can only speculate about why NMPI appears to be a more effective promoter than LiI. General solution or ion-pairing effects may be responsible. Many simple salts (including LiI and LiOAc) are heavily ion paired in acetic acid solvent [23]. Formation of dimeric aggregates of alkali metal halides is also known to be significant [23]. There may be substantial differences in the concentrations of "effective" iodide between similar solutions of LiI and NMPI. It is also possible that while $[\text{RhI}_2(\text{CO})_2]^-$ does not appear to be highly involved in intimate associations with its cations (vide supra), dianionic species such as $[\text{RhI}_3(\text{CO})_2]^{2-}$ may be more prone to intimate ion-pairing interactions with its cations. Contact ion-pairing of a Li^+ cation with dianionic, five-coordinate species such as **2** might effect their $S_{\text{N}}2$ reactivity by both steric and "electronic" effects.

Alternative explanations for acetate promotion of the reaction of **1** with MeI are possible. For example, actual substitution of acetate for an iodide of $[\text{RhI}_2(\text{CO})_2]^-$ could occur, yielding non-detectable concentrations of $[\text{RhI}(\text{CO})_2(\text{OAc})]^-$ species. Such species could have either a monodentate or bidentate acetate ligand and might be more reactive than $[\text{RhI}_2(\text{CO})_2]^-$. It is clear that a similar substitution mechanism cannot apply to the case of iodide promotion of the reaction of **1** with MeI. Finally, we cannot completely exclude the possibility that radical processes could somehow be involved in our reactions, although such possibilities seem remote with only a primary alkyl halide (MeI) as substrate.

Implications of the catalytic results

Both *N*-methyl-picolinium iodide and LiI were found to promote the rate of batch methanol carbonylation under low water conditions (Table 3). It is important to note that significant equilibrium concentrations of acetate and MeI were generated (Table 3) in catalytic solutions containing LiI. Therefore it is necessary to interpret the results in terms of all species that are present under reaction conditions. Figure 6 shows that from a base-case rate obtained in the absence of salt promoters, rates increase approximately linearly with total salt concentration. Although extrapolation of the results and conclusions of our model kinetic study to an operating catalytic system is risky, it is apparent that the kinetic rate law (eq. 7) derived from Scheme 1 can also be used to rationalize Fig. 6. We therefore propose that iodide and acetate salts can promote catalytic methanol carbonylation via the intermediacy of five-coordinate species in a rate-determining nucleophilic attack on MeI.

Because of the equilibrium represented by eq. 1, it is difficult to distinguish kinetically the promotional effects of iodide and acetate in the lithium-containing catalytic system. Therefore, Fig. 6 shows a plot of rate vs. total salt concentration for the Li-containing system. On the basis of our model kinetic study, where lithium acetate is approximately ten times more effective (on a molar basis) than lithium iodide, we speculate that acetate provides the more significant effect in the catalytic system. Therefore, in Fig. 6 we also plot catalytic rates vs. the concentration of lithium acetate present. It should be emphasized that effective concentrations of acetate are present only when both LiI and methyl acetate concentrations are high. NMPI and methyl acetate do not significantly react to produce acetate under our conditions. It is clear in the case of the NMPI promoted system that iodides alone can provide a promotional effect.

The generation of acetate salts has also been observed in Rh/I catalyzed systems for the carbonylation of methyl acetate to acetic anhydride [7]. Under anhydrous conditions, it has been proposed [7b] that the formation of acetic anhydride from acyl iodide can become rate-determining, and that acetate salts can promote that process. Kinetic orders of zero for Rh and MeI are observed under those conditions. We are confident that acyl iodide hydrolysis is not rate-determining in our catalytic systems, which contain relatively low, but still significant concentrations of water. Data on the effect of Rh (first order) and MeI in our catalytic system to support this claim will be published later [5].

Because of the importance of the rate-determining step of a catalytic system, we conducted the model studies described above. In low-water methanol carbonylation there is much interesting chemistry with many practical consequences that does not directly involve the rate-determining step. The role of water, methyl acetate, and promoter concentrations in the maintenance of active, stable catalysts and the interrelations of those variables to the rate-determining processes will be the subject of a future paper [5].

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