Oxidative Addition of Methyl Iodide to Dicarbonylrhodium(I) Complexes

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Oxidative addition of MeI to $[Rh(CO)_2I_2]^-$ in aprotic solvents, the 'rate-determining' step in the carbonylation of methyl acetate and methyl halides (to acetic anhydride and acyl halides, respectively), is substantially promoted by iodide and bases (L, e.g. 1-methylimidazole).

The industrially important homogeneously catalysed carbonylation of methanol to acetic acid [equation (1)] uses a rhodium–iodide plus methyl iodide promoted catalyst system.[1] There has been considerable interest in the extension of this reaction, using the same catalyst, to the production of acetic anhydride by carbonylation of either dimethyl ether or methyl acetate [equation (2)],[2,3] and of acetyl halides by carbonylation of the methyl halide in an inert solvent [equation (3)].[4] These reactions, which are carried out under

$$MeOH + CO = MeCO_2H \qquad (1)$$

$$MeO_2CMe + CO = MeCO \cdot O \cdot OCMe \qquad (2)$$

$$MeX + CO = MeCOX \qquad (3)$$

Table 1. Activation parameters for the oxidative addition of MeI to [Ph$_4$As][Rh(CO)$_2$I$_2$] in different solvents.

Solvent	$\Delta G^{\ddagger}$ (298 K) /kJ mol^{-1}	$\Delta H^{\ddagger}$ /kJ mol^{-1}	$\Delta S^{\ddagger}$ /kJ mol^{-1}
Methanol	96.4	69	−92
Chloroform	97.3	53	−152
Tetrahydrofuran	98.8	52	−154
Methyl acetate	99.4	47	−176

aprotic conditions, require promoters (for example, iodide and Lewis bases, often as their quaternary ammonium or phosphonium salts) in order to make the rates useful.

Forster has shown that the 'rate-determining' step (*i.e.*, the step which, under normal conditions, controls the overall rate of the catalytic cycle) in the methanol carbonylation is the oxidative addition of methyl iodide to *cis*-[Rh(CO)$_2$I$_2$]$^-$ (**1**).[1a] This has also recently been shown to be the case for methyl iodide carbonylation in methyl acetate.[5]

We have measured the rates of oxidative addition of methyl iodide to (**1**) and related species in methanol, and in the aprotic solvents chloroform (or dichloromethane), tetrahydrofuran, and methyl acetate,†,‡ and have evaluated $\Delta G^{\ddagger}$ $\Delta H^{\ddagger}$, and $\Delta S^{\ddagger}$ (Table 1). The pattern observed is similar to that reported for the oxidative addition of methyl iodide to [Ir(PPh$_3$)$_2$(CO)Cl] in polar and non-polar solvents.[6] For the oxidative addition to (**1**) in methanol $\Delta G^{\ddagger}$ at 298 K was smaller by 3 kJ mol^{-1} than in methyl acetate leading to the observed difference in rates of a factor of 3.5.

By extrapolation, at 450 K there will be a difference of some 16 kJ mol^{-1} in $\Delta G^{\ddagger}$ leading to an expected rate difference of a factor of *ca.* 70 between the two solvents. We suggest that this underlies the need to use promoters in the catalytic carbonylation reactions in aprotic solvents at working temperatures (450 K).

We have therefore examined the effects of a variety of additives, reported to improve the rates of the catalytic reaction (2), on the rates of oxidative addition of MeI to (**1**). For solubility reasons, most experiments were carried out in dichloromethane. Addition of increasing amounts of tetra-butylammonium iodide caused a rate acceleration which reached a maximum of a factor of *ca.* 2 when 40 equiv. of iodide per equiv. of (**1**) had been added (Figure 1). This appears to arise from a general salt effect since a roughly comparable enhancement of rate is found on adding Bu$_4$NI to the reaction of 1-methylimidazole (meim) and methyl iodide to form the 1,3-dimethylimidazolium (me$_2$im) iodide.

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† It should be emphasised that species such as (**1**) will exist almost entirely (>99%) in ion paired (or higher) aggregates in aprotic solvents such as chloroform, dichloromethane, or methyl acetate at the concentration levels used here. The general salt effects noted here may well arise from changes in the degrees of aggregation or ion-pairing of the reactants. Similar (small) accelerations were found on addition of water.

‡ The rates of decrease of the v(CO) of (**1**) were measured at constant temperature in the presence of an excess of methyl iodide using a Perkin-Elmer 684 i.r. spectrometer equipped with a 3600 Data Station programmed to record automatically and subtract electronically signals of the reference containing all the reagents except (**1**) from a spectrum of the reaction solution. Separate experiments showed excellent Beer's law behaviour for the system and that the reaction was first order in both (**1**) (introduced as the tetraphenylarsonium salt) and methyl iodide, and also served to demonstrate the reliability of the approach.
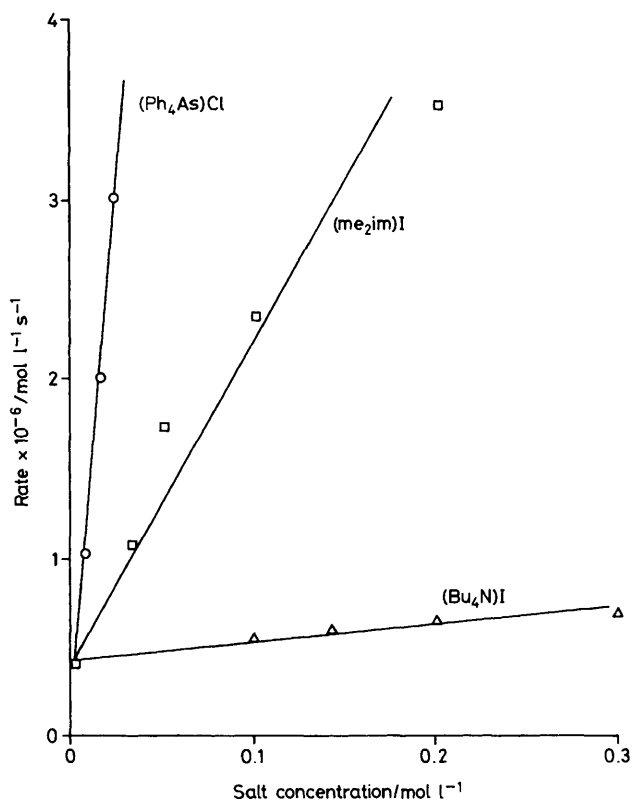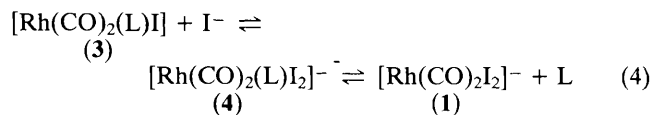

Figure 1. Variation of rates of oxidative addition, MeI + [Rh(CO)$_2$I$_2$]$^-$ (5 × 10^{-3} mol l^{-1}), in dichloromethane in the presence of various salts. [The values for (Ph$_4$As)I were similar to, but smaller than those for the chloride.]

However, other quaternary salts, most notably tetraphenylarsonium, showed very much larger accelerations which we ascribe to a specific salt effect. Addition of excess of bases (L) such as meim caused an even more substantial (ten-fold) increase in rate, again not due to a general salt effect.

$$cis\text{-}[Rh(CO)_2I_2]^- \qquad [Rh_2(CO)_4I_2] \qquad [Rh(CO)_2(L)I]$$
$$(\mathbf{1}) \qquad\qquad (\mathbf{2}) \qquad\qquad (\mathbf{3})$$
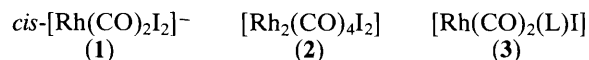
The i.r. spectra showed that the only species present on addition of iodide to [Rh$_2$(CO)$_4$I$_2$], (**2**), was (**1**) [v(CO) 1984, 2057 cm^{-1}]. Similarly, addition of L (meim or other bases) to (**2**) gave only [Rh(CO)$_2$(L)I] (**3**) [v(CO) 2001, 2072 cm^{-1}]. Addition of an excess of iodide to (**3**) gave the characteristic spectrum of the ionic species (**1**), while addition of meim and MeI to (**2**) gave spectra showing the presence of both (**1**) (as the me$_2$im$^+$ salt) and (**3**). These data are consistent with equilibria (4), involving a five-co-ordinate intermediate (**4**) present in low concentration, as is normal for square planar d^8 substitution reactions.[7]

$$[Rh(CO)_2(L)I] + I^- \rightleftharpoons$$
$$(\mathbf{3})$$
$$[Rh(CO)_2(L)I_2]^- \rightleftharpoons [Rh(CO)_2I_2]^- + L \qquad (4)$$
$$(\mathbf{4}) \qquad\qquad (\mathbf{1})$$

However, neither [me$_2$im][Rh(CO)$_2$I$_2$] nor (**3**), when tested individually in oxidative addtions with MeI, showed the fast rates observed above and therefore they cannot be the most active species present.

The presence of a species [v(CO) 1980, 2055 cm^{-1}] at low concentration in solutions containing (**1**) and excess of iodide

Table 2. Carbonylation of methyl iodide in methyl acetate using $[Ph_4As][Rh(CO)_2I_2]$ as catalyst.[a]

Additive (mmol)		Acetic anhydride (T/N)[b]	Acetic acid (T/N)[b,c]
None		trace	2
Bu₄NI	(1.75)	17	7
	(3.5)	24	9
	(17.5)	30	16
meim	(1.75)	3	2
	(3.5)	5	7
Bu₄NI	(3.5) +		
meim	(3.5)	46	20

[a] Conditions: methyl iodide (26 mmol), $[Ph_4As][Rh(CO)_2I_2]$ (0.35 mmol), in methyl acetate (15 cm³, 189 mmol) for 6 h at 160 °C and 54 atm CO. [b] T/N, turnover number: moles of product per mole of catalyst. [c] Formed by hydrolysis of MeCOI.

could be detected by accumulating and averaging large numbers of spectra. The positions of the bands (though not their intensities) were independent of the cation. One explanation is that they arise from the five-co-ordinate (**4**, L = I⁻). A five-co-ordinate complex {either $[Rh(CO)_2I_3]^{2-}$ or $[Rh(CO)_2LI_2]^-$}, which reacts more rapidly with MeI than (**1**), (**2**), or (**3**) is also quite consistent with our rate data on oxidative addition reactions (and implies that MeI is being attacked in an S_N2 mode). This proposal extends the finding by Forster that the mono-anionic $[Rh(Ph_3E)COI_2]^-$ are much better nucleophiles towards MeI than the neutral $[Rh(Ph_3E)_2COI]$ (E = P, As, or Sb).[8]

Although the i.r. measurements were carried out in dichloromethane at 298 K, they reflect rather well the situation in the catalytic carbonylation. Thus, a series of runs in a rocking autoclave at 433 K in which methyl acetate (and methyl iodide) were carbonylated (Table 2) showed that the maximum rate was obtained when a ratio of (**1**) : Bu₄N⁺I⁻ : meim of 1 : 10 : 10 was used. The rate enhancement in the catalytic formation of acetic anhydride in the presence of iodide and meim could then be due to the participation of five-co-ordinate species such as (**4**) also under these conditions.

References

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