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Factors influencing the oxidative addition of iodomethane to $[\text{Rh}(\text{CO})_2\text{I}_2]^-$, the key step in methanol and methyl acetate carbonylation

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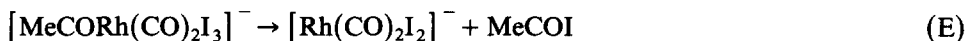
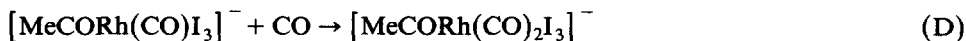
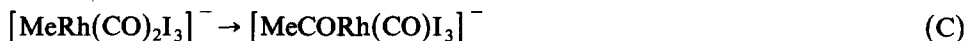
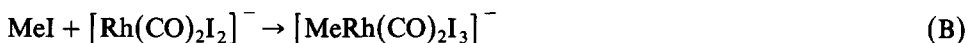
Abstract

The oxidative addition of MeI to $\text{A}^+ [\text{Rh}(\text{CO})_2\text{I}_2]^-$ [$\text{A} = \text{n-Bu}_4\text{N}$, Ph_4P , and Ph_4As], the rate determining step in the Rh and I^- catalysed conversion of methanol into acetic acid and of methyl acetate into acetic anhydride, is second order overall, first order in both complex and methyl iodide. The reaction is slower in less polar solvents (k_2 $1.9 \times 10^{-5} \text{ M}^{-1} \text{ s}^{-1}$ in MeOAc, 3.1×10^{-5} in THF, and $10.0 \times 10^{-5} \text{ M}^{-1} \text{ s}^{-1}$ at 298 K, in MeOH). Protic solvents accelerate the reaction; e.g. addition of ca. 3% water quadruples the rate in THF. Values of $\Delta G^\ddagger$ have been measured in MeOH and MeOAc between 288 and 318 K, and values of $\Delta H^\ddagger$ [60 (MeOH), 46 (MeOAc) kJ mol^{-1}], and $\Delta S^\ddagger$ [–120 (MeOH), –180 (MeOAc) $\text{J mol}^{-1} \text{ K}^{-1}$] calculated from them; these numbers are very close to those for the catalytic carboxylation. Iodide also accelerates the reaction in methyl acetate up to two-fold, for addition of 20 equivalents of $[\text{I}^-]$; this may be due to a “general” salt effect, stabilising the transition rather than the ground state. LiOAc behaves analogously; this is due to the reaction, $\text{MeI} + \text{LiOAc} \rightleftharpoons \text{MeOAc} + \text{LiI}$, which increases the LiI concentration, not to the formation of acetato-complexes of unusual reactivity. $\text{n-Bu}_4\text{NBF}_4$ has no effect on the reaction in methyl acetate. The oxidative addition is insensitive to the nature of the counter-ion except for $\text{C}_{12}\text{H}_{25}\text{NH}_3^+ [\text{Rh}(\text{CO})_2\text{I}_2]^-$ in less polar solvents, where the IR spectra and also the slower rates of oxidative addition are consistent with some form of interaction, probably a $\text{N} \cdots \text{H} \cdots \text{Rh}$ hydrogen-bond.

Introduction

Forster and his collaborators have described the probable cycle for the rhodium and iodide-catalysed carbonylation of methanol to acetic acid in some detail [1]; this scheme, reactions A–F, is generally accepted. The oxidative addition, step (B), is normally the slowest and determines the overall rate; since migration (C) is much

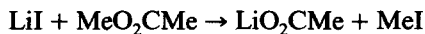
faster, $[\text{MeRh}(\text{CO})_2\text{I}_3]^-$ has never been detected. Subsidiary processes, for example oxidation to $[\text{Rh}(\text{CO})_2\text{I}_4]^-$, which must be reversed to retain catalyst activity, complicate the picture.



The carbonylation of methyl acetate to acetic anhydride appears to be very similar but the selectivity, rate, and catalyst stability are all poor. Promoters therefore need to be used, and a wide variety has been claimed in Patents [2]. The commonest is iodide in very large excess, with counter-cations such as R_4N^+ , R_4P^+ , and Li^+ . Some information on the industrial processes has been given in the open literature [3,4].

Luft and Schrod reported that Rh is the most active metal, that methyl acetate carbonylation is first order in both Rh and MeI concentrations, and that the species present under reaction conditions were $[\text{Rh}(\text{CO})_2\text{I}_2]^-$ and $[\text{Rh}(\text{CO})_2\text{I}_4]^-$, the latter being replaced by the former when hydrogen was added to the gas feed [5]. However that study was complicated by the presence of triphenylphosphine and chromium hexacarbonyl as extra promoters. Comparative data for various iodides as promoters for the methanol carbonylation at low water levels have been given [4c]; LiOAc was claimed to be a better promoter than LiI. Activation parameters for the methanol to acetic acid and for the promoted methyl acetate to acetic anhydride reactions are similar, again suggesting similar cycles [3,4c,6].

Suggestions put forward to account for the promoting effects of water, of iodide, and of acetate, include, i) changes of aggregation of the ion-paired reactants [7], ii) formation of a five-coordinate species of higher charge and hence higher nucleophilicity, $[\text{Rh}(\text{CO})_2\text{I}_2(\text{X})]^{2-}$ ($\text{X} = \text{I}$ or OAc) [4b,7], and iii) the formation of a mixed species, $[\text{Rh}(\text{CO})_2(\text{OAc})\text{I}]^-$, of higher reactivity [4b]. Other workers, noting that the overall catalysis behaved differently at high iodide and at low iodide levels, proposed that the iodide was used in a key organic step [3],



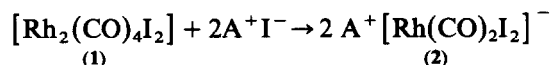
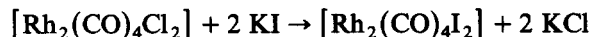
and that at low iodide, the rate-limiting step is possibly the reaction of lithium acetate with acetyl iodide.

Since the slowest (rate determining) step of the catalytic cycle is the oxidative addition of MeI to $[\text{Rh}(\text{CO})_2\text{I}_2]^-$ (e.g. step (B) above), the Sheffield group has examined the effects of different solvents and promoters on this reaction. We have reported, in a preliminary communication, that the rates of oxidative addition (in aprotic model solvents) were increased i) by addition of soluble $[\text{I}^-]$, and ii) by protic solvents, water being especially effective [7].

Results

The synthesis and properties of the salts A[Rh(CO)₂I₂]

The salts A[Rh(CO)₂I₂], (**2**, A = *n*-Bu₄N, Ph₄P, Ph₄As, Li, and C₁₂H₂₅NH₃) were made from the dimer (**1**) (a modification of the original route [8,9]); this allowed the salts to be isolated easily and free from excess halide.

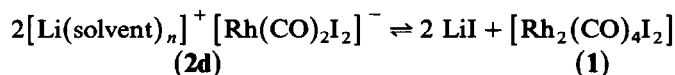


(a, A = *n*-Bu₄N; b, A = Ph₄P; c, A = Ph₄As; d, A = Li; e, A = C₁₂H₂₅NH₃)

(a) *Salts with n-Bu₄N, Ph₄P, and Ph₄As counterions.* These salts were obtained as air-sensitive pale yellow crystals and were stored under nitrogen at 0°C. The IR spectra of all these salts (Table 1) were cation-independent [e.g. in MeOH: 1990, 2060 (**2a**); 1992, 2062 (**2b**); 1992, 2061 (**2c**) cm⁻¹], and showed only small variations with solvent [e.g., for (**2a**): 1990, 2060 (MeOH), 1985, 2056 (MeOAc), and 1988, 2060 (CH₂Cl₂) cm⁻¹]. We conclude that the species are all very similar and that the interactions between cations and the metal in the anions are simply coulombic.

To check that the oxidative addition proceeded as expected, the reactions of **2a** and **2c** with iodomethane were repeated on a preparative scale. The complexes *n*-Bu₄N[Rh(CO)(COMe)I₃] [10] and Ph₄As[Rh(CO)(COMe)I₃] were isolated and fully characterised.

(b) *Lithium salt.* In oxygenated solvents (methanol, methyl acetate, THF, diethyl ether, or acetone), anhydrous LiI and [Rh₂(CO)₄I₂] gave solutions with ν(CO) at 1990 and 2060 cm⁻¹, arising from [Li(solvent)_{*n*}]⁺[Rh(CO)₂I₂]⁻. Attempts to isolate such species led only to hygroscopic and unstable brown oils, and attempts to make the unsolvated **2d** in benzene, toluene, dichloromethane, or pentane were frustrated by the insolubility of LiI and the total lack of any reaction. Addition of one of these solvents to a solution of solvated **2d** caused the precipitation of white LiI and the reformation of the orange dimer **1**, indicating the existence of the mobile equilibrium,



Such disproportionation was not observed with the other salts.

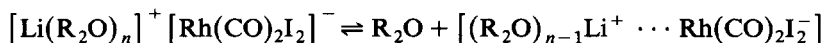
Table 1

IR spectral data of A[Rh(CO)₂I₂] [ν(CO) cm⁻¹]^a

Complex	2a	2b	2c	2d	2e
cation	ⁿ Bu ₄ N ⁺	Ph ₄ P ⁺	Ph ₄ As ⁺	Li ⁺	C ₁₂ H ₂₅ NH ₃ ⁺
MeOH	2060 1990	2061 1992	2062 1992	2060 1990	2060 1990
MeOAc	2056 1985	2054 1982	2053 1981	2054 1981	2063 1993
CH ₂ Cl ₂	2060 1988	2058 1986	2058 1986	^b	2071 2004

^a 2 cm⁻¹ resolution. ^b Insoluble.

At high concentrations (> 50 mM) in diethyl ether or THF the lithium salt (**2d**) showed two sets of $\nu(\text{CO})$. One [$\nu(\text{CO})$ 1976, 2048 cm^{-1} in THF] was due to the normal solvated species, (**2d**), while the other, at higher frequency [2002, 2074 cm^{-1}] must arise from other species which are favoured at very high concentrations. The probable formulation for the equilibrium is,



Quite a number of such interactions are known in transition metal carbonyl anions [11] and several different types have been defined. It could be directly between the Li^+ and the carbonyls, between the two metals directly, or between Li^+ and $\text{I}-\text{Rh}$. The first would be expected to reduce $\nu(\text{CO})$, but a $\text{Li}^+ \cdots \text{Rh}$ interaction would be consistent with the higher frequency $\nu(\text{CO})$ observed. The alternative, an interaction $\text{Li}^+ \cdots \text{I}-\text{Rh}$, should change the $\nu(\text{CO})$ substantially less. Some type of direct cation $\cdots \text{Rh}$ interaction is supported by the observation that $\nu(\text{CO})$ for the “high-frequency species” are very similar to those noted below for the $\text{C}_{12}\text{H}_{25}\text{NH}_3[\text{Rh}(\text{CO})_2\text{I}_2]$ salt and for $[\text{H}^+ \cdots \text{Rh}(\text{CO})_2\text{I}_2^-]$ [12].

These higher frequency bands disappeared on dilution of the ether solutions of **2d**, and they were not present at concentrations of the order of those used in the kinetic determinations (ca. 5 mM); it is unlikely that the species responsible play any role in our kinetic studies.

(c) *n*-Dodecylammonium salt. The primary and secondary ammonium salts could be prepared in situ. However, they were all very hygroscopic and unstable except for the dodecylammonium salt (**2e**) which could be isolated and characterised spectroscopically. This showed $\nu(\text{CO})$ bands in methanol similar to those of (**2a–c**) in that solvent, indicating similar anion–cation–solvent interactions. By contrast, in methyl acetate the bands were at higher frequency (1993, 2063 cm^{-1}) than those of salts (**2a–c**) (Table 1). There was also a pronounced shift to higher frequency in dichloromethane (2004, 2071 cm^{-1}). Very similar results were obtained for other salts (**2**) containing NH cations ($\text{A} = 4\text{-methylpyridinium}$, piperidinium, *N*-methylpiperidinium, and *N*-methyldodecylammonium), prepared in situ. These data are consistent with some additional bonding, probably between the amine N–H and the rhodium $[\text{R}_{3-n}\text{H}_n\text{N} \cdots \text{H} \cdots \text{Rh}(\text{CO})_2\text{I}_2]$. A useful model is offered by the salts $\text{R}_3\text{NH}^+[\text{Co}(\text{CO})_4]^-$ ($\text{R} = \text{Me}, \text{Et}$) where an X-ray structure determination shows the N–H to be on the three-fold rotation axis of the $\text{Co}(\text{CO})_4^-$, pointing directly at the cobalt [13]. Interactions of this type would cause a decrease in negative charge, and hence decrease back-bonding to the carbonyls.

Rate measurements

The rates of oxidative addition of iodomethane to $\text{A}[\text{Rh}(\text{CO})_2\text{I}_2]$ (determined by IR spectroscopy) showed overall second order kinetics, first order in MeI and in $\text{A}[\text{Rh}(\text{CO})_2\text{I}_2]$, in all the solvents and for all A^+ examined, according to,

$$-\text{d}[\text{Rh}(\text{CO})_2\text{I}_2]/\text{dt} = k_2[\text{Rh}(\text{CO})_2\text{I}_2^-][\text{MeI}]$$

where k_2 ($\text{M}^{-1} \text{s}^{-1}$) is the second order rate constant. The reaction was carried out in the presence of a large excess of iodomethane relative to $\text{A}[\text{Rh}(\text{CO})_2\text{I}_2]$; the rate equation then reduced to,

$$-\text{d}[\text{Rh}(\text{CO})_2\text{I}_2]/\text{dt} = k_1'[\text{Rh}(\text{CO})_2\text{I}_2^-]$$

Table 2

Rate constant ($k_2 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$) for the reaction of complex **2a** and MeI

Solvent	Temp (K)	Complex				
		2a n-Bu ₄ N ⁺	2b Ph ₄ P ⁺	2c Ph ₄ As ⁺	2d Li ⁺	2e C ₁₂ H ₂₅ NH ₃ ⁺
MeOH	288	3.75			3.9	3.4
	298	10.0	9.4	7.3	10.0	9.4
	308	21.3		19.4	20.6	19.4
	313			31.0		
	318			44.0		
MeOAc	288	1.15			1.15	0.45
	298	1.9		2.1	2	1.15
	303			2.6		
	308	4.9		3.75	4.15	2.0
	313			6.25		
	318			6.6		
CH ₂ Cl ₂	288	1.15				0.6
	298	2.5		5 ^b	^a	1.55
	303			7.2 ^b		
	308	5.25		11 ^b		2.7
	313			15 ^b		
	318			20 ^b		

^a Insoluble. ^b In CHCl₃.

where k_1' is the pseudo first order rate constant (s^{-1}). These have all been converted into the second order rate constants, k_2 ($\text{M}^{-1} \text{s}^{-1}$), by dividing by the concentration of methyl iodide (3.2 mol l^{-1} ; Table 2).

It was found that the terminal $\nu(\text{CO})$ of the $\text{A}[\text{Rh}(\text{CO})_2\text{I}_2]$ were always cleanly displaced by the bands characteristic of $[\text{MeCORh}(\text{CO})\text{I}_3]^-$ [10] [$\nu(\text{CO}_t)$ 2060; $\nu(\text{CO}_{\text{acyl}})$ 1712 (br) cm^{-1}]. Contrary to one proposal [1], none of the intermediate $[\text{MeRh}(\text{CO})_2\text{I}_3]^-$ could be detected, even in aprotic solvents.

The oxidative addition was solvent dependent, thus for **2a** ($\text{A} = \text{n-Bu}_4\text{N}$), k_2 was 1.9×10^{-5} (MeOAc) and 10.0×10^{-5} (MeOH) $\text{M}^{-1} \text{s}^{-1}$ at 25°C (Table 2). There were however no significant differences in rates for the salts **2a**, **2b**, **2c**, or **2d** in methanol, or between **2a**, **2c**, and **2d** in methyl acetate at temperatures between 288 and 318 K. This confirms the conclusions from the IR spectra, that the environments of the Rh in these solvents are very similar, irrespective of the cation (A). Measurements in dichloromethane indicated that **2a** reacted at the same rate as in methyl acetate, again consistent with the IR data.

The dodecylammonium salt $\text{C}_{12}\text{H}_{25}\text{NH}_3[\text{Rh}(\text{CO})_2\text{I}_2]$ (**2e**) (and related salts) prepared in situ, reacted more slowly in aprotic solvents than did (**2a–d**), though all their rates were very similar in methanol (Table 1). These data are consistent with the IR spectra (above) and suggest that in aprotic solvents there is some special anion–cation contact in **2e** which leads to an increase in positive charge at the metal. Such a change at the metal centre would lead to a decrease in backbonding to the carbonyls and to a decrease in the nucleophilicity of the metal centre, which in turn leads to a decrease in the rate of oxidative addition.

Table 3

Free energies of activation ($\Delta G^\ddagger$, kJ/mol) for the reaction of complex **2** and MeI

Solvent	Temp (K)	Complex			
		2a n-Bu ₄ N ⁺	2b Ph ₄ P ⁺	2d Li ⁺	2e C ₁₂ H ₂₅ NH ₃ ⁺
MeOH	288	94.7		94.6	94.9
	298	95.6	96.4	95.6	99.8
	308	97	97.2	97.1	97.2
	313		97.6		
	318		98.3		
MeOAc	288	97.5		97.5	99.8
	298	99.7	99.5	99.6	101
	303		100.7		
	308	100.8	101.4	101.2	103
	313		101.8		
	318		103.3		
CH ₂ Cl ₂	288	97.5			99
	298	99.1	97.3 ^b	^a	100.2
	303		98.1 ^b		
	308	100.6	98.7 ^b		102.3
	313		99.5 ^b		
	318		100.4 ^b		

^a Insoluble. ^b In CHCl₃.

In addition to the detailed rate measurements given in Table 2, the rates in some other solvents and solvent mixtures were determined for the reaction of complex **2c** with MeI. At 25°C $k_2 \times 10^5$ was found to be 6.3 (EtOH), 5.6 (i-PrOH), 4.9 (HOAc), 4.4 (MeNO₂, CHCl₃), 3.1 (THF), 2.5 (Ac₂O, CH₂Cl₂), and 2.3 (MeOAc) M⁻¹ s⁻¹. There was no correlation with dielectric constant; for example, the reaction had the same rates in CH₂Cl₂ (ϵ 9) and acetic anhydride (ϵ 22), and the same rates in chloroform (ϵ 5) and nitromethane (ϵ 36). Addition of water considerably accelerated the reaction; for example, k_2 increased by a factor of 4 on addition of water (1.7 mol l⁻¹; 3% v/v) to THF; similarly, addition of water (6.9 mol l⁻¹; 12% v/v) increased k_2 in methanol by a factor of 3.

Free energies of activation were measured for the reactions of MeI with **2a**, **2c**, **2d** and **2e** in methanol and in methyl acetate, from the rates between 288 and 318 K (Table 3). The temperature range available was restricted, since MeI volatilises above 318 K, and the reactions were too slow below 288 K. From the values of $\Delta G^\ddagger$ we calculate $\Delta H^\ddagger$ as 60 (MeOH) and 46 (MeOAc) kJ mol⁻¹, and $\Delta S^\ddagger$ as -120 (MeOH) and -180 (MeOAc) J mol⁻¹ K⁻¹. The values of $\Delta H^\ddagger$ and the strongly negative $\Delta S^\ddagger$ are quite reminiscent of those for the oxidative addition of MeI to [Ir(PPh₃)₂(CO)X] [14] and are consistent with an S_N2 attack by [Rh(CO)₂I₂]⁻ on the carbon of MeI. This is again analogous to the Menshutkin (amine quaternisation) reaction.

The rate of reaction of **2a** in dichloromethane was significantly slower and led to larger $\Delta G^\ddagger$; the same is true for the reactions of the dodecylammonium salt **2e** in

both methyl acetate and dichloromethane. This suggests a loss of nucleophilicity, perhaps due to an increase in tight ion-pairing, in both cases.

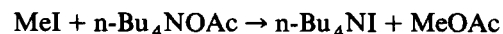
The effect of iodide on the reaction of iodomethane and $[\text{Rh}(\text{CO})_2\text{I}_2]^-$

We have also examined the effect of adding iodide (as $n\text{-Bu}_4\text{NI}$, LiI , or $n\text{-C}_{12}\text{H}_{25}\text{NH}_3\text{I}$), and of acetate (as $n\text{-Bu}_4\text{NOAc}$) to the reaction of $[\text{Rh}(\text{CO})_2\text{I}_2]^-$ with MeI . Since LiI is insoluble in CH_2Cl_2 , and both $n\text{-Bu}_4\text{NI}$ and $n\text{-C}_{12}\text{H}_{25}\text{NH}_3\text{I}$ are insoluble in methyl acetate, comparative data for all of these and for $n\text{-Bu}_4\text{NOAc}$ (see below) were obtained in dry mixtures ($\text{CH}_2\text{Cl}_2/\text{MeOAc}$, 1:1 v/v) of the two. The k_2 's increased linearly on progressive addition of $n\text{-Bu}_4\text{NI}$ to the reaction of $n\text{-Bu}_4\text{N}[\text{Rh}(\text{CO})_2\text{I}_2]$ up to a maximum of ca 2x at $[\text{I}^-]/[\text{Rh}]$ ratios of ca 20:1. Further addition had no effect. A precisely similar result was found on addition of LiI to $\text{Li}(\text{solv})_x[\text{Rh}(\text{CO})_2\text{I}_2]$; however addition of $n\text{-Bu}_4\text{N}[\text{BF}_4]$ to $n\text{-Bu}_4\text{N}[\text{Rh}(\text{CO})_2\text{I}_2]$ gave no rate enhancement. Addition of LiI or $n\text{-Bu}_4\text{NI}$ to the reaction of $\text{Ph}_4\text{As}[\text{Rh}(\text{CO})_2\text{I}_2]$ with MeI in methanol caused a rate enhancement similar to those in methyl acetate or dichloromethane.

Addition of $n\text{-C}_{12}\text{H}_{25}\text{NH}_3\text{I}$ to $n\text{-C}_{12}\text{H}_{25}\text{NH}_3[\text{Rh}(\text{CO})_2\text{I}_2]$ (measured in dichloromethane because of solubility problems) showed a very small reduction in rate. The rate of oxidative addition of MeI to $n\text{-C}_{12}\text{H}_{25}\text{NH}_3[\text{Rh}(\text{CO})_2\text{I}_2]$ in that solvent was only about 60% of that for the same reaction using $n\text{-Bu}_4\text{N}[\text{Rh}(\text{CO})_2\text{I}_2]$. This result is consistent with the proposal that $\text{C}_{12}\text{H}_{25}\text{NH}_3^+$ forms a tight ion pair with $[\text{Rh}(\text{CO})_2\text{I}_2]^-$, which would again lower the charge and decrease the nucleophilicity of the rhodium towards the oxidative addition. One might also expect that, if the $n\text{-C}_{12}\text{H}_{25}\text{NH}_3$ blocked one side of the Rh completely and oxidative addition only occurred from the other, the rate would be halved; a result close to that observed.

The effect of acetate on the reaction of iodomethane and $[\text{Rh}(\text{CO})_2\text{I}_2]^-$; the equilibrium, $\text{MeI} + \text{A}^+\text{OAc}^- \rightleftharpoons \text{A}^+\text{I}^- + \text{MeOAc}$

Addition of $n\text{-Bu}_4\text{NOAc}$ to the reaction of MeI and $n\text{-Bu}_4\text{N}[\text{Rh}(\text{CO})_2\text{I}_2]$ in $\text{CH}_2\text{Cl}_2/\text{MeOAc}$ (1:1) caused an increase in rate, identical to that found on adding the same amount of $n\text{-Bu}_4\text{NI}$. As the anhydrous salts were insoluble in it, reactions in neat methyl acetate could not be tried. However, a rapid reaction occurred between (neat) MeI and $n\text{-Bu}_4\text{NOAc}$, giving $n\text{-Bu}_4\text{NI}$ and methyl acetate, according to,



The formation of methyl acetate was confirmed by GC analysis of a separate reaction in dichloromethane (0.08 mmol of MeI and of $n\text{-Bu}_4\text{NOAc}$ in 10 cm^3), and by the appearance ($t_{1/2} 10^3\text{ s}$) of the characteristic $\nu(\text{CO}_2)$ at 1743 cm^{-1} ; all the $n\text{-Bu}_4\text{NOAc}$ [$\nu(\text{CO}_2) 1579\text{ cm}^{-1}$] reacted.

Spectroscopic investigation of the interaction of $[\text{Rh}(\text{CO})_2\text{I}_2]^-$ and I^-

One possible explanation for the rate enhancement of the oxidative addition in the presence of iodide is that this is a general salt effect. This proposal is still the one we favour.

Another possibility [6] (also put forward by others [4b]), is that $[\text{Rh}(\text{CO})_2\text{I}_3]^{2-}$ is formed at high $[\text{I}^-]$ levels; as that carries a higher negative charge than $[\text{Rh}(\text{CO})_2\text{I}_2]^-$ it could be a better nucleophile in the oxidative addition. We have therefore

examined in some detail the IR spectra of solutions of $[\text{Rh}(\text{CO})_2\text{I}_2]^-$ containing large additional amounts of iodide (up to 100 equivalents). By spectral subtraction techniques we found two additional weak bands at very high iodide levels. For example, $\text{Li}[\text{Rh}(\text{CO})_2\text{I}_2]$ in methyl acetate showed bands at 1981, 2054 cm^{-1} ; in the presence of 60 equivalents of LiI , subtraction revealed two small bands at 1988 and 2059 cm^{-1} . Similarly $n\text{-Bu}_4\text{N}[\text{Rh}(\text{CO})_2\text{I}_2]$ showed bands at 1988 and 2060 cm^{-1} in dichloromethane, and revealed two difference bands at 1986 and 2057 cm^{-1} in the presence of $n\text{-Bu}_4\text{NI}$ (50 equivalents).

However we also observed very similar changes in the presence of $n\text{-Bu}_4\text{NBF}_4$: thus on adding 60 equivalents of $n\text{-Bu}_4\text{NBF}_4$ to a solution of $n\text{-Bu}_4\text{N}[\text{Rh}(\text{CO})_2\text{I}_2]$ in dichloromethane, difference bands were again seen, at 1987 and 2057 cm^{-1} , very close to those noted above. We also found that there were no differences between the solid state IR spectrum of $n\text{-Bu}_4\text{N}[\text{Rh}(\text{CO})_2\text{I}_2]$ in a KI disc (i.e. in a very high iodide environment) and that in either Nujol or a KBr disc. We conclude that the observed difference bands probably arise from a medium effect and that, under ambient conditions, there is no unequivocal spectroscopic evidence for the presence of species such as $[\text{Rh}(\text{CO})_2\text{I}_3]^{2-}$. However, further studies at higher temperatures, both on the effect of excess iodide on the rates and on other species present, are needed.

Discussion

Data from our investigations of the oxidative addition of $[\text{Rh}(\text{CO})_2\text{I}_2]^-$ and MeI run parallel in three ways to data available about the overall carbonylation. Both reactions are i) favoured by protic (rather than merely polar) solvents, ii) strongly promoted by quite small amounts of water, and iii) promoted by iodide.

A significant result is that the $\Delta H^\ddagger$ (60 kJ mol^{-1}) and $\Delta S^\ddagger$ ($-120 \text{ J mol}^{-1} \text{ K}^{-1}$) found for the oxidative addition reaction in methanol are quite close to the values reported for the catalytic carbonylation of methanol ($\Delta H^\ddagger$ 63.6 kJ mol^{-1} , $\Delta S^\ddagger$ $-116 \text{ J mol}^{-1} \text{ K}^{-1}$) [6] and to those for the lithium iodide promoted catalytic carbonylation of methyl acetate in acetic acid ($\Delta H^\ddagger$ 60.3 kJ mol^{-1} , $\Delta S^\ddagger$ $-113 \text{ J mol}^{-1} \text{ K}^{-1}$) [3]. This strongly supports the view that the oxidative addition is the step in the carbonylation cycle which determines the overall rate.

From the values of $\Delta G^\ddagger$ measured between 288 and 318 K for the oxidative addition in methanol and in methyl acetate, values of $(\Delta G^\ddagger)_{453}$ of 114 (MeOH) and 128 (MeOAc) kJ mol^{-1} can be extrapolated for 453 K, the actual temperature at which the carbonylation processes are operated. The difference of 14 kJ mol^{-1} in $\Delta G^\ddagger$ suggests that the oxidative addition reaction in methanol should be ca. 60 times faster than in methyl acetate at 453 K. Since this step appears to control the overall carbonylation, one would anticipate a factor of this order between the unpromoted reactions run in these two solvents.

Analysis of the $\Delta H^\ddagger$ [60 (MeOH) and 46 (MeOAc) kJ mol^{-1}] and of $\Delta S^\ddagger$ [-120 (MeOH) and -180 (MeOAc) $\text{J mol}^{-1} \text{ K}^{-1}$] for oxidative addition in the two solvents indicates that the reaction in methanol is favoured at higher temperature because the entropy term becomes dominant. This may be because the ordering process in going to the transition state is less disfavoured in methanol, perhaps because it is assisted by some outer-sphere H-bonding, and that this overcomes the

more unfavourable enthalpy of activation in that solvent. Water presumably plays a strongly promoting role for a similar reason.

The cation A generally plays no role in oxidative addition reactions in methanol or methyl acetate, though there is a significant slowing down for the salt **2e** in methyl acetate and in dichloromethane. Thus in oxygenated solvents, quaternary ammonium (or phosphonium or arsonium) cations are similar to solvated lithium in their influence on this reaction. This is shown most easily by the IR spectra, $\nu(\text{CO})$, and also by the rate studies; the evidence is that the environment of the rhodium is very similar in each case. Since various papers and patents indicate that cation effects are manifested in the carbonylation of methanol at low water levels or of methyl acetate, they presumably arise from different causes.

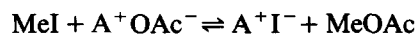
We have sought evidence to explain the effect of iodide on the oxidative addition. The formation of dianions (and hence potentially better nucleophiles) such as $[\text{Rh}(\text{CO})_2\text{I}_3]^{2-}$ has not been spectroscopically detectable under ambient conditions, though we cannot rule them out at higher temperatures. Based upon the currently available evidence, we favour the iodide stabilising the transition state for nucleophilic substitution*.

We have found $n\text{-Bu}_4\text{NOAc}$ to react readily with MeI to give methyl acetate and $n\text{-Bu}_4\text{NI}$. Thus also the acceleration caused by addition of some acetates will arise from the formation of iodide. However, oxidative addition reactions in the presence of very large amounts of $n\text{-Bu}_4\text{NOAc}$ will cause corresponding reductions in the concentrations of iodomethane; this effect must be allowed for in calculating k_2 from the pseudo first order rate constants. When this is done, it is found that the effect of $n\text{-Bu}_4\text{NOAc}$ is the same as that of $n\text{-Bu}_4\text{NI}$, and that there is no specific acetate effect.

It is plausible to speculate that the effects of lithium acetate on the catalytic carbonylation may be due to similar reactions with MeI.

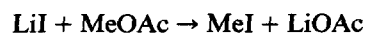
Although no reaction was detected (over 10^4s) when $n\text{-Bu}_4\text{NI}$ was mixed with MeOAc in dichloromethane, we have confirmed that solid LiI undergoes an exothermic reaction with neat methyl acetate, giving MeI and LiOAc [4]. In solution that reaction is slow, slower than the one between $n\text{-Bu}_4\text{NOAc}$ and MeI.

We conclude that for,



the position of the equilibrium, and the rate at which it is attained, are very much a function of the nature of A^+ , and of the solvent, since ion-aggregation must obviously play a major role.

The Celanese workers also found that iodide accelerated the oxidative addition; however they noted that the same degree of acceleration was not always shown by different batches of LiI [4]. It is possible that this arises from the slow generation of methyl iodide by the (known exothermic) reaction,



* *Note added in proof.* Iodide catalysis in nucleophilic organic substitution reactions has recently been discussed [B.A. McCortney, B.M. Jacobson, M. Vreeke, and E.S. Lewis, J. Am. Chem. Soc., 112 (1990) 3554]. The intimate mechanism for the iodide catalysis of the oxidative addition of MeI to $\text{A}[\text{Rh}(\text{CO})_2\text{I}_2]$ must however be different from that involved in the catalysis of exchange reactions such as $\text{R}_3\text{NMe}^+ + \text{R}'_3\text{N} \rightleftharpoons \text{R}'_3\text{NMe}^+ + \text{R}_3\text{N}$. Further studies are in progress.

Equivalent amounts of LiI and of MeI were generally used; thus, once this reaction has proceeded for long enough, sufficient methyl iodide will have been generated to affect the oxidative addition kinetics. This may vary between experiments.

The participation of mixed species such as $[\text{Rh}(\text{CO})_2\text{I}(\text{OAc})]^-$ has also been suggested. Attempts have been made to make this, without success. We have concluded that unsymmetrical salts of this type are very labile, and disproportionate to the more symmetrical anions, $[\text{Rh}(\text{CO})_2\text{I}_2]^-$ and $[\text{Rh}(\text{CO})_2(\text{OAc})_2]^-$.

Thus we may conclude that, to a first approximation, the oxidative addition of MeI to $[\text{Rh}(\text{CO})_2\text{I}_2]^-$ is a useful model for a study of the carbonylation process. However, higher temperature investigations, now in progress, are needed to confirm and extend this conclusion.

Experimental

All operations were carried out under dry nitrogen. Solvents were purified as described below, and then distilled under nitrogen immediately prior to use. Microanalyses were performed by the University of Sheffield microanalysis service. GC analyses were carried out on a Perkin Elmer 8700 chromatograph (f.i.d. detector/ H_2 carrier gas: DB1 wide bore capillary column (15 m) for liquid analyses; Porapak QS column (2.5 m) gas analyses).

Purification of reagents and solvents

Methanol (spectroscopic grade, 200 cm^3) and magnesium turnings (1 g) were placed in a flask under nitrogen. Iodine (0.1 g) was added and the mixture heated to initiate an exothermic reaction forming magnesium methoxide. The mixture was refluxed (24 h) and the pure solvent distilled before use. Ethanol was purified from magnesium ethoxide similarly.

THF, toluene and ether were pre-dried over molecular sieve (4Å) (24 h) and distilled from a purple solution of sodium/benzophenone before use. Dichloromethane and acetonitrile were distilled from calcium hydride; acetone from molecular sieve (4Å) or anhydrous sodium carbonate, and methyl acetate was distilled from anhydrous calcium sulphate. Iodomethane was pre-dried over molecular sieve (4Å) and cooled to -35°C at which point most of the water present crystallised out. The liquid was filtered by cannula into a foil wrapped Schlenk tube and stored over copper turnings. This method proved more effective than distillation from calcium hydride. NMR grade chloroform- d , acetone- d_6 and iodomethane- d_3 were distilled from molecular sieve (4Å); iodomethane- d_3 was then freeze-dried as described above.

Tetraphenylarsonium chloride was recrystallised from ethanol-ether; tetrabutylammonium chloride was vacuum dried (40°C , 30 min) before use; lithium iodide (anhydrous, Aldrich) was stored under dry nitrogen.

To purify hydriodic acid from iodine, hydriodic acid (100 cm^3) in a 3-necked 250 cm^3 flask under nitrogen, was stirred and heated almost to reflux (ca. 90°C). Hypophosphorous acid (10 cm^3) was added dropwise until the deep purple (iodine) colouration just disappeared. The pure acid was then distilled as a colourless azeotrope (b.p. 126°C) and stored in foil-wrapped bottles with hypophosphorous acid (ca. 2 cm^3 per 50 cm^3) as a stabiliser.

Description of kinetics experiments

In the oxidative addition of iodomethane to $[\text{Rh}(\text{CO})_2\text{I}_2]^-$ (**2**) to give $[\text{Rh}(\text{CO})(\text{COMe})\text{I}_3]^-$, the strong $\nu(\text{CO})$ in the IR spectrum at ca. 2060, 1988 cm^{-1} , are replaced by a new terminal and an acyl carbonyl absorption [$\nu(\text{CO})$ 2060, 1712 cm^{-1}]. The reaction was monitored by following the decrease in intensity of the 1988 cm^{-1} absorption of the $[\text{Rh}(\text{CO})_2\text{I}_2]^-$ anion.

A Perkin Elmer 684 grating IR spectrophotometer was used to record spectra which were stored electronically on a PE 3600 Data Station. The IR cell (0.2 mm spacing) with calcium fluoride windows was fitted with a thermostatted jacket to maintain a constant temperature in the beam of the spectrophotometer. The IR spectra of the reaction solutions were recorded (2200–1700 cm^{-1}), the solvent spectrum was subtracted electronically and the resultant difference spectrum stored on disc. The intensity values of the carbonyl peaks were recorded in absorbance units, and this procedure was repeated at constant time intervals to give a data set of absorbance against time for each reaction.

Solutions were prepared (under nitrogen or argon, NOT carbon monoxide) by adding iodomethane (2 cm^3) to the other reactants in a 10 cm^3 graduated flask. The volume was made up to 10 cm^3 with solvent, the flask stoppered with a Suba seal and the solution was shaken. A portion (1 cm^3) was withdrawn by syringe to provide the reference solvent spectrum for the experiment. A second portion of the solution was added to the rhodium complex, e.g. $\text{Bu}_4\text{N}[\text{Rh}(\text{CO})_2\text{I}_2]$ (16.4 mg, 0.025 mol), in a 5 cm^3 graduated flask and the volume made up to 5 cm^3 . The reaction solution was then stoppered with a Suba seal and shaken to dissolve the rhodium complex. When the rhodium salts used were not isolable as solids, they were made in situ by the addition of a 10% excess of the iodide to $[\text{Rh}_2(\text{CO})_4\text{I}_2]$.

The Lambert–Beer law was shown to hold for **2** at least over the concentration range zero to $15 \times 10^{-3} \text{ mol l}^{-1}$ in dichloromethane, THF, methanol, and methyl acetate. Straight lines were obtained on plotting the rates ($\text{mol l}^{-1} \text{ s}^{-1}$) against the concentration of **2** between zero and $15 \times 10^{-3} \text{ mol l}^{-1}$ in all four solvents at constant $[\text{MeI}]$ (3.2 mol l^{-1}); similar straight lines were obtained in all four solvents on plotting the rates against $[\text{MeI}]$ from zero to 9 mol l^{-1} at constant **2**. These data indicated that the reaction was first order in both iodomethane and complex **2**, second order overall. Plotting the absorbances against time gave an exponential curve; however plotting $\ln(a/x)$ against time (t , a = initial peak height, x = peak height after time t), gave a straight line, the gradient of which gave the pseudo first order rate constant.

The rates found are accurate to $\pm 8\%$. The largest error is in the syringing of 2 cm^2 of iodomethane, which is accurate to 0.05 cm^3 . The first order fit to the data was very good with a correlation coefficient of 0.995 or better. The reproducibility of identical experiments was within the experimental error.

IR spectra were also recorded on PE-1710 and PE-1600 Fourier Transform spectrophotometers using a calcium fluoride solution cell (0.1 mm spacing) with electronic subtraction of solvent. Measurements were made at room temperature generally with 2 cm^{-1} resolution.

Synthetic procedure

Rhodium complexes. All the rhodium complexes were air sensitive to varying degrees and were stored under nitrogen or carbon monoxide in the refrigerator at

ca. 0 °C. The anionic rhodium(I) iodides and acetates had useful shelf lives of ca 1–2 months under these conditions. Samples showing some decomposition (shown by darkening of the originally pale yellow material) were recrystallised (under carbon monoxide) immediately prior to use.

[Rh₂(CO)₄I₂] (I). An orange solution of [Rh₂(CO)₄Cl₂] [15] (0.73 g, 3.8 mmol Rh) in n-hexane (50 cm³) was stirred over KI (3.9 g, 24 mmol) under CO (1 atm, 20 °C, 24 h). The resulting deep red solution was filtered (Hyflo) and the volume reduced in vacuo until the product began to precipitate out as an orange powder. The mixture was sealed under carbon monoxide, warmed to dissolve the solid and left to crystallise at 0 °C. The product was filtered off as deep red needles and the filtrate reduced again and recrystallised as described above at –30 °C to yield a second crop of red crystals of complex 1: 0.92 g, 86%. (Analysis, found: C, 8.3; H, 0.0; I, 44.1. C₂IO₂Rh calc.: C, 8.4; H, 0.0; I, 44.4%). $\nu(\text{CO})$ 2095, 2079, 2068, 1997 cm^{–1} (n-hexane).

A[Rh(CO)₂I₂] salts (2a–c). Complex 2a, and the others, were prepared by a modification of the method of Vallarino [8]. An orange solution of [Rh₂(CO)₄I₂] (0.24 g, 0.84 mmol Rh) in methanol (6 cm³) was treated with a solution of Bu₄NI (0.36 g, 0.97 mmol) in methanol (5 cm³) with stirring under CO (1 atm, 20 °C). The resulting pale yellow solution was filtered (Hyflo) and reduced in vacuo until a pale yellow solid began to separate. The solution was sealed under CO and left to crystallise at 0 °C. The yellow crystals formed were isolated by filtration and the filtrate reduced again and cooled to –30 °C to afford a second crop of crystals. The product was dried in vacuo. Yield 0.39 g, 70% of Bu₄N[Rh(CO)₂I₂] (2a). (Analysis found: C, 32.9; H, 5.6; N, 2.0; I, 38.8. C₁₈H₃₆I₂NO₂Rh calc.: C, 33.0; H, 5.5; N, 2.1; I, 38.7%). m/z 413 (M^-), 385 ($M - \text{CO}$), 357 ($M - 2\text{CO}$). $\nu(\text{CO})$ 2060, 1988 cm^{–1} (CH₂Cl₂). Ph₄P[Rh(CO)₂I₂] (2b), 74%, (Analysis, found: C, 41.9; H, 2.9; I, 33.8. C₂₆H₂₀I₂O₂PRh calc.: C, 41.5; H, 2.9; I, 33.8%). m/z 413 (M^-), 385 ($M - \text{CO}$), 357 ($M - 2\text{CO}$). $\nu(\text{CO})$ 2058, 1986, cm^{–1} (CH₂Cl₂). Ph₄As[Rh(CO)₂I₂] (2c), 83%, (Analysis, found: C, 39.7; H, 2.6; I, 32.1. C₂₆H₂₀AsI₂O₂Rh calc.: C, 39.2; H, 2.5; I, 31.9%). m/z 413 (M^-), 385 ($M - \text{CO}$), 357 ($M - 2\text{CO}$). $\nu(\text{CO})$ 2058, 1986 cm^{–1} (CH₂Cl₂).

n-Bu₄N[Rh(COME)(CO)I₃]. A pale yellow solution of Bu₄N[Rh(CO)₂I₂] (0.4 g, 0.61 mmol) in methanol/iodomethane (10 cm³, 1:1 v/v) was stirred at room temperature under nitrogen in a foil-wrapped flask (76 h). The resulting dark red/purple solution was filtered (Hyflo) and reduced to dryness in vacuo. The brown residue was dissolved in a minimum volume of dichloromethane, filtered (Hyflo) and recrystallised by addition of ether. On standing at –30 °C a crop of deep red crystals was obtained. (Yield 0.39 g, 80%). Bu₄N[Rh(CO)(COME)I₃]. (Analysis, found: C, 28.4; H, 5.0; N, 1.7; I, 48.1. C₁₈H₃₉NI₃O₂Rh calc.: C, 28.6; H, 4.9; N, 1.8; I, 47.8%). $\nu(\text{CO})$ 2060, 1735sh, 1712br cm^{–1} (CH₂Cl₂). δH (250 MHz, CDCl₃); 3.48 (8H, t, NCH₂), 3.10, 3.14 (6H, 2 × s, COCH₃), 1.89 (8H, q, NCH₂CH₂), 1.48 (8H, sxt, N(CH₂)₂CH₂), 1.04 (12H, t, N(CH₂)₃CH₃). Ph₄As[Rh(CO)(COME)I₃]. (Analysis, found: C, 34.6; H, 2.6; I, 40.7. C₂₇H₂₃AsI₂O₂Rh calc.: C, 34.5; H, 2.5; I, 40.6%). $\nu(\text{CO})$ 2060, 1734sh, 1712br cm^{–1} (CH₂Cl₂). δH (250 MHz, CDCl₃) 7.63, 7.85 (40H, m, C₆H₅As), 3.10, 3.14 (6H, 2 × s, COCH₃).

Dodecylammonium iodide. Dry gaseous HI was passed through a refluxing solution of n-dodecylamine (1.1 g, 5.9 mmol) in ether (100 cm³) for 10 min and the solution refluxed (20 min). A fine white precipitate was isolated, and was recrystal-

lised from the minimum volume of hot ethanol, to yield white leaflets of dodecylammonium iodide, yield 1.6 g, 86%. $C_{12}H_{25}NH_3I$ (Analysis, found: C, 45.9; H, 9.3; N, 4.3; I, 40.0. $C_{12}H_{28}NI$ calc.: C, 46.0; H, 8.9; N, 4.5; I, 40.6%) δH (250 MHz, $CDCl_3$) 7.58 (3H, br, NH_3), 3.12 (2H, t, CH_2N), 1.88 (2H, q, CH_2CH_2N), 1.28 (18H, br, $CH_3(CH_2)_9CH_2N$), 0.9 (3H, t, $CH_3(CH_2)_{11}N$).

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