Kinetic and Spectroscopic Studies of the Carbonylation of Methanol with an Iodide-promoted Iridium Catalyst

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A mechanistic interpretation is proposed for the carbonylation of methanol in the presence of iridium halides as the catalyst precursor and methyl iodide as promoter. The scheme is based on a combination of kinetic observations, *in situ* spectral studies of reactions, and studies of the chemistry of the observed intermediates. It is shown that there are two principal catalytic cycles for the methanol carbonylation, one involving neutral iridium carbonyl iodide complexes and the other involving anionic iridium species. In addition, a competitive water–gas shift reaction is observed under many conditions. The catalytic cycle which predominates is influenced by iodide-ion level and hydrogen iodide concentration. These two factors are influenced by variables such as water, methanol, and methyl iodide concentrations as well as salt additives and temperature. The kinetic dependencies for the reaction are dramatically dependent on the catalytic cycle which predominates.

THE carbonylation of methanol to acetic acid using a homogeneous iodide-promoted rhodium catalyst system is now conducted on a large scale commercially.[1] A good understanding of the basic metal-complex chemistry involved in the process has been obtained.[1,2] It is known that iridium compounds will also act as catalysts for this reaction [3] with comparable reactivity to that displayed by the rhodium-containing system.[4,5] However, kinetic observations [4,5a] on the iridium-catalysed reaction have given indications of considerably greater mechanistic complexity than displayed by the rhodium catalyst.

I report here an attempt to gain some mechanistic insight into the iridium-catalysed reaction by using a combination of techniques.

EXPERIMENTAL

The preparations of the following compounds have been described elsewhere: $[AsPh_4][Ir(CO)_2I_2]$,[6] $[AsPh_4][Ir(CO)_2I_4]$,[7] $[AsPh_4][IrMe(CO)_2I_3]$,[8] $[AsPh_4][Ir(OCMe)(CO)_2Cl_3]$,[8] and $[IrH(CO)_2I_3]^-$.[8]

*(Cyclo-octa-*1,5-*diene)iridium*(I) *Iodide*.—This compound was prepared in variable purity by the technique described [9] for the analogous chloro-complex with the modification of using 50% more cyclo-octadiene (Found: C, 22.85; H, 2.85; I, 29.25. Calc. for $C_8H_{14}IIr$: C, 22.5; H, 2.85; I, 29.7%).

Tricarbonyliodoiridium(I).—This compound was originally described by Hieber *et al.*[10] but no spectroscopic characterization has been presented. We find that carbonylation of [Ir(cod)I] in a variety of non-co-ordinating solvents produces a soluble brown species with CO stretching frequencies at 2 074 and 2 046 cm^{-1}. This compound reacts immediately with quaternary ammonium iodide salts to give the $[Ir(CO)_2I_2]^-$ ion and also with iodine to give $[Ir(CO)_3I_3]$.[11,12]

The solutions appear to be somewhat unstable in the absence of an elevated pressure of CO and a pure solid of composition $Ir(CO)_3I$ was not isolated from solution.

Methanol-carbonylation Reactions.—Experiments were carried out at constant pressure in a Hastelloy C. Magnedrive autoclave (300 cm^3). The temperature of the reaction was measured with an internal thermocouple and regulated with a West Gardsman controller. The progress of the reaction was followed by automatically recording the pressure drop in a high-pressure reservoir employing a Foxboro model 40 pressure recorder.

Typical operating procedure. The iridium precursor (usually $IrCl_3 \cdot 4H_2O$), iodide promoter (usually MeI), and solvent (usually nonanoic acid or methyl acetate) were charged to the autoclave and heated to the desired temperature under *ca.* 15 atm † of carbon monoxide with stirring. After the reaction temperature had been reached, the autoclave was charged with the reactant (MeOH) from a pressurized charging bomb. The reactor pressure was brought up to the desired value with additional carbon monoxide.

Spectroscopic Studies.—Infrared spectral studies of the reaction solutions under operating conditions were performed using the high-pressure high-temperature cell described previously.[13] Reaction solutions were fed to the cell under pressure and the cell was maintained at the relevant reaction temperature and pressure while the spectrum was recorded. Reaction conditions were chosen such that the rate of reaction was relatively slow so that CO diffusion would not become the rate-limiting process in the time taken to record the spectrum (<1 min) in the non-agitated reaction medium inside the spectrophotometric cell. Nonanoic acid was chosen as the reaction solvent because of its low absorption in the metal carbonyl region of the infrared.

Low-pressure Carbonylation Reactions.—Reactions conducted under carbon monoxide pressures of <8 atm were carried out in Fischer–Porter aerosol compatibility tubes with magnetic stirring.

Analyses.—Reaction solutions were examined by a gas chromatographic (g.c.) technique using a stainless-steel column (10 ft × 0.125 in) packed with OV101. Gas analyses were obtained by a g.c. technique using dual columns of Carbowax 400-modified Porasil A and 13X molecular sieves.

RESULTS AND DISCUSSION

Preliminary investigations showed that a variety of species could be detected in the reaction media and the predominant form depended upon the reaction parameters chosen. It also became apparent that quite different kinetic dependencies were manifested as the conditions were varied. It is therefore convenient to break down the discussion of the process into these

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† Throughout this paper: 1 atm = 101 325 Pa.

recognizably different regimes, although in practice sharp break points are not observed.

Regime I: The Neutral Iridium Complex Catalytic Cycle.—Experiments performed with methyl iodide concentrations of <0.15 mol dm^{-3} at an iridium concentration of 0.01 mol dm^{-3}, in media in which low levels of water and ionic iodide are expected (*e.g.* methyl acetate with water pumped into the reactor such that the water level was maintained at *ca.* 3 wt. %),* are characterized by kinetics in which an inhibiting effect of carbon monoxide pressure is observed (see Table 1). Infrared spectra of reacting solutions taken under these conditions show strong metal-carbonyl stretching frequencies at 2 073 and 2 046 cm^{-1} (see Figure 1). If the samples from the autoclave are rapidly cooled, the species is stable in solution for some time under ambient conditions and when treated with quaternary ammonium iodides gives $[Ir(CO)_2I_2]^-$ and when treated with iodine gives $[Ir(CO)_3I_3]$. The species observed under reaction conditions is therefore $[Ir(CO)_3I]$.

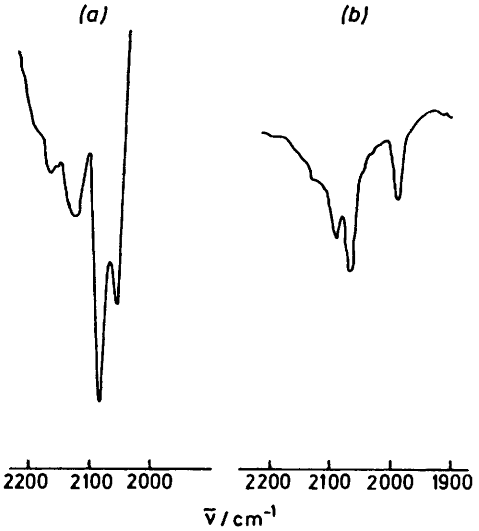

FIGURE 1 Infrared spectra of reacting solution at low methyl iodide levels: (*a*) observed at 160 °C and 33 atm pressure (CO partial pressure *ca.* 30 atm) for a reaction mixture consisting of 5 wt.% methanol and 2 wt. % water in nonanoic acid with [Ir] = 1.0×10^{-2} mol dm^{-3} and [MeI] = 4.0×10^{-2} mol dm^{-3}; (*b*) of solution (*a*) after cooling and releasing the carbon monoxide pressure, followed by treatment with tetraheptylammonium iodide

I have independently synthesized $[Ir(CO)_3I]$ and studied some of its reactions relevant to the methanol-carbonylation reaction. Thus a solution generated by the action of carbon monoxide on [Ir(cod)I] in CH_2Cl_2 reacts slowly (several hours at room temperature) with a large excess of methyl iodide to give two new species. The principal product has two strong carbonyl bands at 2 118 and 2 077 cm^{-1} and is immediately transformed by added iodide ion to $[IrMe(CO)_2I_3]^-$ without gas evolution [8] and is therefore formulated as $[IrMe(CO)_2I_2]$. This compound may be dimerized as is the corresponding chloro-complex; [14] however, the bridge between each component of the dimer must be very labile in view of the very rapid reaction with iodide ion. The lesser component in the reaction mixture is a species with carbonyl-stretching frequencies at 2 125, 2 090, and 1 710 cm^{-1} and is tentatively identified as $[\{Ir(OCMe)(CO)_2I_2\}_n]$ (n = 1 or 2) because of its immediate transformation into the $[Ir(OCMe)(CO)_2I_3]^-$ ion by treatment with iodide ion. The rate of reaction of $[Ir(CO)_3I]$ with MeI is far slower than the corresponding reaction with $[Ir(CO)_2I_2]^-$ and in view of the product observed may involve prior loss of carbon monoxide before reaction. This reactivity difference between the neutral and anionic iridium(I) halocarbonyl species is to be expected if the reaction pathway follows the anticipated nucleophilic attack of the metal species on the alkyl halide.[15,16]

The reaction between methyl iodide and $[Ir(CO)_3I]$ (in CH_2Cl_2 solvent) was also conducted under low pressures (3 atm) of carbon monoxide. At room temperature, a very slow reaction occurred and after *ca.* 19 h the sole species present had i.r. stretching frequencies at 2 176w, 2 116vs, and 1 712ms cm^{-1} and this compound was immediately transformed into $[Ir(OCMe)(CO)_2I_3]^-$ by addition of iodide ion. The species formed under pressure is tentatively identified as $[Ir(OCMe)(CO)_3I_2]$. When the reaction between MeI and $[Ir(CO)_3I]$ is carried out at 100 °C and 3 atm of carbon monoxide, in addition to the iridium species tentatively identified as $[Ir(OCMe)(CO)_3I_2]$ above, a strong band at 1 805 cm^{-1} is observed for the solutions. The species responsible for this band was identified as acetyl iodide both by the position of the carbonyl band and by its immediate reaction with methanol to give methyl acetate. It is thus apparent that a catalytic methanol-carbonylation cycle is possible when predominantly neutral iridium species are present in the medium. The strong inhibiting effect of carbon monoxide evident when $[Ir(CO)_3I]$ is the principal iridium species present in the catalytic reaction is probably caused by the existence of an equilibrium between the very weakly nucleophilic $[Ir(CO)_3I]$ and a more reactive dicarbonyl species.

$$e.g.\ [Ir(CO)_3I] \rightleftharpoons [\{Ir(CO)_2I\}_n]\ (n = 1 \text{ or } 2) + CO$$

$$[Ir(CO)_3I] \overset{I^-}{\rightleftharpoons} [Ir(CO)_2I_2]^- + CO$$

$$[Ir(CO)_3I] + MeI + H_2O \rightleftharpoons H[Ir(CO)_2I_2] + MeOH + CO$$

$$[Ir(CO)_3I] + L \rightleftharpoons [Ir(CO)_2I(L)] + CO$$

$$2\,[Ir(CO)_3I] + 2L \rightleftharpoons [Ir^{I}(CO)_2L_2][Ir^{I}(CO)_2I_2] + 2\,CO$$

where L = oxy-donor such as methanol or water

An extensive effort to distinguish among the various possibilities has not been made although it is noted that the $[Ir(CO)_2I_2]^-$ ion in $MeNO_2$ was not measurably converted into $[Ir(CO)_3I]$ under 35 atm of carbon monoxide when observed in the high-pressure spectrophotometric cell at room temperature.

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* Similar kinetic behaviour and spectroscopic observations were noted in media with *ca.* 10% methanol but no added water with MeI : Ir ratios as high as 60 : 1.

The kinetic dependence on methyl iodide concentration for this regime was not determined since the observation of [Ir(CO)$_3$I] as the principal iridium species is only found over a very narrow range of methyl iodide concentration. In addition, as the water or methanol level is raised at low I$^-$: Ir ratios, a substantial amount of the products of the water–gas shift reaction (*i.e.* $CO + H_2O \longrightarrow CO_2 + H_2$) is noted in gas samples and an i.r. spectrum taken under reaction conditions (Figure 2) shows that the principal form of iridium has changed to a species with a strong CO stretching frequency at 2 099 cm^{-1}. Samples containing this species are dark red and when treated with iodide ion,[IrH(CO)$_2$I$_3$]$^-$ is generated. A more extensive description of the identification of this species will be given elsewhere [12] and it suffices to note that the species is formulated as [IrH(CO)$_2$I$_2$(OH$_2$)] and can be produced by oxidative addition of HI to [Ir(CO)$_3$I] in the presence of low levels of water. This species is a logical intermediate in a water–gas shift cycle.

$$\textit{i.e.}\ \mathrm{Ir^{I} + HI \rightleftharpoons HIr^{III}I} \qquad (1)$$

$$\mathrm{HIr^{III}I + HI \rightleftharpoons Ir^{III}I_2 + H_2} \qquad (2)$$

$$\mathrm{Ir^{III}I_2 + CO + H_2O \longrightarrow Ir^{I} + CO_2 + 2HI} \qquad (3)$$

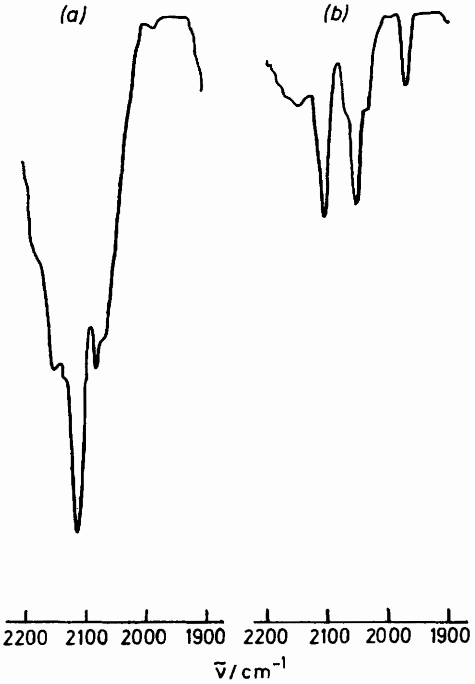

FIGURE 2 Infrared spectra of reacting solution with low methyl iodide and water levels: (*a*) observed at 150 °C and 33 atm total pressure (CO partial pressure *ca.* 30 atm) for the reaction mixture of run number 4 from Table 1; (*b*) of the solution (*a*) after cooling and releasing the carbon monoxide pressure, followed immediately by treatment with tetraheptylammonium iodide

The surprising feature about the observation of this species under reaction conditions (Figure 3) and the detection of CO$_2$ and H$_2$ in the gas phase is that the methanol-carbonylation reaction was proceeding at a considerably faster rate than the water–gas shift reaction while the hydridoiridium(III) species was the principal iridium species in solution. A similar situation exists in the anionic catalytic cycle described in a subsequent section. Discussion of this phenomenon will be reserved for this later section where more observations on the equilibria involving oxidative addition of HI to iridium(I) species will be presented.

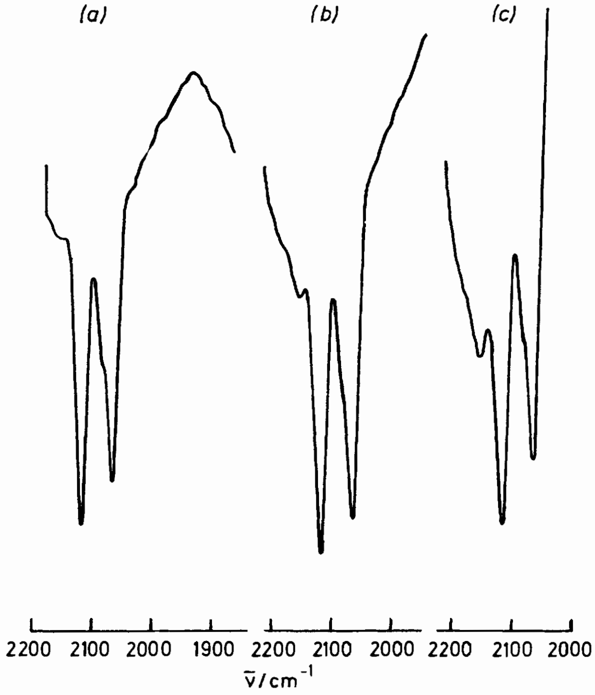

FIGURE 3 Infrared spectra of a reaction solution containing added salt: (*a*) observed at 160 °C and 30 atm partial pressure of carbon monoxide, run 6 from Table 1; (*b*) of run 7 under reaction condtions; (*c*) of run 8 under reaction conditions

Regime II: The Anionic Iridium Complex Catalytic Cycle.—In reactions conducted with the addition of low

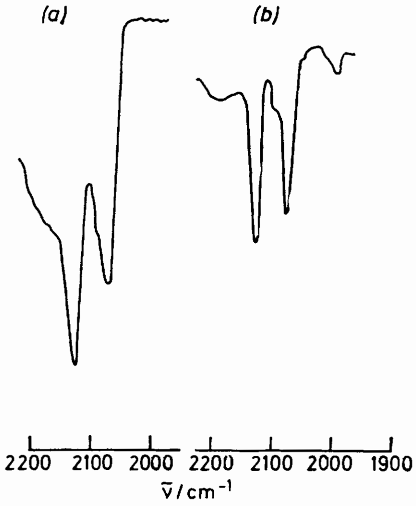

FIGURE 4 Infrared spectra of a reaction solution in regime III: (*a*) under reaction conditions of run 12 from Table 1; (*b*) of solution (*a*) after cooling and releasing the pressure

TABLE 1

Carbonylation of methanol with iodide-promoted iridium catalyst

Experiment	θ_c °C	CO pressure atm	Concentration/ mol dm^{-3} Ir	MeI	Solvent	Concentration/ mol dm^{-3} Initial Methanol	Charged water	Charged ^{a} I$^-$	Rate of MeOH carbonylation ^{b} mol dm^{-3} h^{-1}	Water–gas shift rate ^{c} mol dm^{-3} h^{-1}	Comments
Reactions where the predominant iridium species was $[Ir(CO)_3I]$											
1	175	23	0.01	0.01	Methyl acetate		2.2		2.7		
2	175	50	0.01	0.10	Methyl acetate		2.2		1.7	*ca.* 0.03	Small selectivity loss to CH_4
3	175	100	0.01	0.10	Methyl acetate		2.2		<0.2	Very low	
Reactions where the predominant iridium species was $[IrH(CO)_2I_2(OH_2)]$											
4	150	30	0.02	0.08	Nonanoic acid	2.47	1.7		0.6	*ca.* 0.5	4% of MeOH converted into CH_4
5	160	30	0.02	0.08	Nonanoic acid	2.47	1.7		2.2		
Reactions where the predominant iridium species was $[IrMe(CO)_2I_3]^-$											
6	160	30	0.02	1.0	Nonanoic acid	2.47		0.10	Very slow		
7	160	65	0.02	1.0	Nonanoic acid	2.47		0.10	*ca.* 0.06		
8	160	100	0.02	1.0	Nonanoic acid	2.47		0.10	0.10		
9	160	65	0.02	1.0	Nonanoic acid	2.47		0.04	0.16		
10	175	20	0.02	0.2	Methyl acetate	16		0.04	2.2		
11	175	50	0.02	0.2	Methyl acetate	16		0.04	8.0		10% of MeOH converted into CH_4
Reactions where the predominant iridium species was $[IrH(CO)_2I_3]^-$											
12	160	30	0.01	0.10	Nonanoic acid	1.2	1.1		*ca.* 0.15	*ca.* 0.04	
13	160	30	0.01	0.20	Nonanoic acid	1.2	1.1		0.8	*ca.* 0.12	
14	160	30	0.01	0.40	Nonanoic acid	1.2	1.1		1.1	*ca.* 0.12	
15	160	50	0.01	0.40	Nonanoic acid	1.2	1.1		1.05	*ca.* 0.12	
16	160	30	0.01	0.60	Nonanoic acid	1.2	1.1		1.3	*ca.* 0.17	
17	160	30	0.01	0.80	Nonanoic acid	1.2	1.1		1.7	*ca.* 0.3	
18	160	30	0.01	1.0	Nonanoic acid	1.2	1.1		1.3	*ca.* 0.3	
19	160	30	0.01	1.20	Nonanoic acid	1.2	1.1		1.2	*ca.* 0.3	

[a] Iodide added as $[N(C_7H_{15})_4]I^-$ or LiI. [b] Rate for initial 20% methanol conversion. [c] Determined by rate of gas uptake.

levels of salts (quaternary ammonium iodide or lithium iodide) the spectra of reacting solutions contain predominantly $[IrMe(CO)_2I_3]^-$ (see Figure 4). When this iridium species predominates the reaction rate increases with increasing carbon monoxide pressure (see Table 1, experiments 6—11) and decreases with increasing ionic iodide level. These results are compatible with the rate-determining step in a catalytic cycle being formation of a tricarbonyl(methyl)iridium(III) species by the dissociative substitution mechanism commonly found for octahedral d^6 metal species.*

$$\begin{tikzcd} \textit{i.e.}\ {[IrMe(CO)_2I_3]^-} \arrow[r, shift left] & {[IrMe(CO)_2I_2]} \arrow[l, shift left] \arrow[d, "CO"] & + I^- \\ & {[IrMe(CO)_3I_2]} & \end{tikzcd}$$

In agreement with this, $[IrMe(CO)_2I_3]^-$ can be converted into $[Ir(OCMe)(CO)_2I_3]^-$ by treatment with 5 atm of CO at 80 °C (4 h) in chlorobenzene. This transformation can be completely prevented by the addition of 5 mol of $[NBu_4]I$ per mol of iridium. In addition, the $[IrMe(CO)_2I_3]^-$ ion shows no tendency to isomerize to an acetyl species even on heating to 150 °C. This is in marked contrast with the corresponding rhodium system

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* I favour an equilibrium limitation on the overall rate of transformation to acyl species as indicated, not only because of the observed kinetic dependencies but because there is good reason to believe that the $[IrMe(CO)_2I_3]^-$ ion is highly labile at temperatures >100 °C. Thus the halide positions *trans* to the carbonyls in $[Ir(CO)_2X_4]^-$ are very labile even at room temperature (D. Forster, *Inorg. Chem.*, 1972, **11**, 1686) and this together with the high *trans*-labilizing effect of the methyl group should ensure that all of the iodide positions are labile.

where an acetyl species is formed from the reaction of methyl iodide with the $[Rh(CO)_2I_2]^-$ ion in the absence of carbon monoxide and with the species $[RhMe(CO)_2I_3]^-$ being an unstable intermediate.[2] Apparently, a tricarbonyl(methyl)iridium(III) species must form in order to induce alkyl migration in this system.

In support of this concept, it should be noted that $[\{IrMe(CO)_2Cl_2\}_2]$ is prepared by oxidative addition of acetyl chloride to an iridium(I) monocarbonyl species,[14] where it appears that alkyl migration occurs on an unstable intermediate, an iridium(III) acyl monocarbonyl complex.

In attempting to define the elimination step in the catalytic cycle, I studied the decomposition of $[Ir(OCMe)(CO)_2Cl_3]^-$ (ref. 8) in chlorobenzene and nitrobenzene, both with and without added methanol. In the absence of methanol, acetyl chloride and $[Ir(CO)_2Cl_2]^-$ were the decomposition products and with methanol present methyl acetate was formed. Methanol did not appear to affect the initial rate of formation of the $[Ir(CO)_2Cl_2]^-$ ion ($t_{\frac{1}{2}}$ *ca.* 15 min in chlorobenzene at 35 °C). It is concluded that solvolysis of the acetyl complex is not required to regenerate iridium(I).

Formation of methane and CO_2 becomes a very significant competing reaction under these carbonylation-reaction conditions, particularly at low MeI : Ir ratios and low carbon monoxide pressure. In several reactions no detectable hydrogen was produced although large amounts of methane were formed, implying a mechanism for cleavage of the methyliridium species involving either attack by a proton or a separate hydridoiridium species.

TABLE 2

Infrared spectra of iridium carbonyl species relevant to the methanol-carbonylation reaction

Complex [a]	Colour	Solvent	Carbonyl-stretching vibrations (cm^{-1}) [b]
$[Ir(CO)_2I_2]^-$	Yellow	nonanoic acid	2 048, 1 970
		nitromethane	2 051, 1 973
$[Ir(CO)_2I_4]^-$	Orange	nonanoic acid	2 110, 2 070
		nitromethane	2 115, 2 071
$[IrH(CO)_2I_3]^-$	Pale orange	nonanoic acid	*ca.* 2 160w,br [c] 2 101, 2 051
		nitromethane	*ca.* 2 160w,br [c] 2 107, 2 056
$[IrMe(CO)_2I_3]^-$	Yellow	nonanoic acid	2 096, 2 046
		nitromethane	2 102, 2 050
$[Ir(OCMe)(CO)_2I_3]^-$	Orange	nonanoic acid	2 108, 2 062
		chlorobenzene	2 110, 2 062, 1 685
$[Ir(CO)_3I]$	Dark brown	nonanoic acid	2 073, 2 046m
$[Ir(CO)_3I_3]$	Pale orange	benzene	2 186w, 2 170vw, 2 132
$[\{IrMe(CO)_2I_2\}_n]$ ($n = 1$ or 2)	Orange	benzene	2 116, 2 069
		methylene chloride	2 118, 2 077
$[\{Ir(OCMe)(CO)_2I_2\}_n]$ ($n = 1$ or 2)	Orange	benzene	2 125, 2 090, 1 710m
$[Ir(OCMe)(CO)_3I_2]$	Orange	methylene chloride	2 176w, 2 116, 1 712m
$[IrH(CO)_2I_2(OH_2)]$	Blood red	nonanoic acid	2 155w, 2 098vs

[a] The anionic species were studied as salts of the $[AsPh_4]^+$ cation. [b] All bands were very strong unless otherwise noted. [b] Ir–H stretch.

Regime III: Competition between the Water–Gas Shift Reaction and the Methanol-carbonylation Reaction.— Carbonylation reactions conducted at methyl iodide concentrations greater than 0.1 mol dm^{-3} at $[Ir] = 0.01$ mol dm^{-3} and with significant concentrations of water and/or methanol exhibit a different type of kinetic and spectroscopic behaviour. This is the regime where most of the previously published work [4,5a] was conducted and is characterized by an apparent first-order dependence on methanol concentration and an independence of carbon monoxide pressure (see Table 1 and refs. 4 and 5). Here, an optimum rate of reaction is found with respect to the methyl iodide concentration (see Table 1, experiments 12—19). Spectroscopically, a species with strong CO stretching bonds at 2 102 and 2 050 cm^{-1} is observed (Figure 4). This species dominates the spectra of reacting solutions over the whole range of MeI : Ir ratios. It is unchanged on cooling and releasing the CO pressure and it is not immediately changed on addition of ionic iodide, although it gradually transforms to a mixture of $[Ir(CO)_2I_4]^-$ with some $[Ir(CO)_2I_2]^-$. Further, by treating a reaction solution (MeI : Ir = 40 : 1) with PPh_3 a mixture of phosphine complexes precipitates. The i.r. spectrum of this mixture shows it to contain primarily $[IrH(CO)(PPh_3)_2I_2]$ [17] with a characteristic Ir–H stretch at *ca.* 2 215 cm^{-1} and $[Ir(CO)_2(PPh_3)_2I]$. A minor amount of a salt of the $[Ir(CO)_2I_4]^-$ ion * is also present. The predominant species in the reaction solutions thus appears to be the $[IrH(CO)_2I_3]^-$ ion. The reaction of PPh_3 with this ion, synthesized in $MeNO_2$ by reaction of a salt of $[Ir(CO)_2I_2]^-$ with aqueous HI, was studied and it was found that the reaction gave exclusively $[IrH(CO)(PPh_3)_2I_2]$ when the reaction was conducted with a large excess of HI, but a mixture of $[Ir(CO)_2(PPh_3)_2I]$ together with the hydride complex when the solutions contained little or no excess of HI.† It can be inferred from these experiments that the carbonylation-reaction solutions contain predominantly $[IrH(CO)_2I_3]^-$ and that little or no excess of HI is present. At high methyl iodide concentrations where the rate begins to slow down, significant amounts of $[Ir(CO)_2I_4]^-$ are observed in the spectra of the reacting solutions.

The water–gas shift reaction is also proceeding concurrently in these reactions although the rate is substantially slower than the methanol carbonylation rate (typically about a fifth of the methanol carbonylation rate). This slower rate appears unusual in view of the

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* This salt may contain the $[PMePh_3]^+$ cation formed by quaternization of some of the triphenylphosphine by the methyl iodide present. The finding of the $[Ir(CO)_2I_4]^-$ ion implies that this species is present in the reaction solution but is spectrally masked by the much higher concentration of $[IrH(CO)_2I_3]^-$.

† This is probably because of the rapidly established equilibrium between $[Ir(CO)_2I_2]^-$ and $[IrH(CO)_2I_3]^-$ which allows the phosphine to attack the more labile iridium(I) species.

observation of a hydridoiridium(III) species which would be a logical first step in a water–gas shift cycle.

$$\textit{e.g.}\ [Ir(CO)_2I_2]^- + HI \rightleftharpoons [IrH(CO)_2I_3]^- \quad (4)$$

$$[IrH(CO)_2I_3]^- + HI \rightleftharpoons [Ir(CO)_2I_4]^- + H_2 \quad (5)$$

$$[Ir(CO)_2I_4]^- + H_2O + CO \longrightarrow [Ir(CO)_2I_2]^- + CO_2 + 2\ HI \quad (6)$$

Thus in order to accommodate the observation of dominance of the $[IrH(CO)_2I_3]^-$ ion with the observed predominance of the methanol–carbonylation reaction in the system we have to propose that: (*a*) reaction (4) is readily reversible and probably occurs faster than methyl iodide addition; (*b*) reaction (5) is relatively slow; and (*c*) when methyl iodide addition occurs it is effectively non-reversible. In order to test these hypotheses several experiments were performed at ambient conditions. First, $[Ir(CO)_2I_2]^-$ was allowed to react with a small amount of aqueous hydriodic acid in nitromethane whereupon the $[IrH(CO)_2I_3]^-$ ion forms. The equilibrium for this reaction is very favorable at room temperature ($K > 50$ dm^3 mol^{-1}). A small amount of solid calcium carbonate when added to this solution immediately reverses the addition reaction and $[Ir(CO)_2I_2]^-$ reforms.

The oxidative-addition reactions of methyl iodide and hydrogen iodide with $[Ir(CO)_2I_2]^-$ were performed under competitive conditions. We found that if $[IrH(CO)_2I_3]^-$, prepared by the addition of slightly more than 1 mol of HI to $[Ir(CO)_2I_2]^-$ in $MeNO_2$, was treated with a large excess of MeI, the hydride was slowly transformed to $[IrMe(CO)_2I_3]^-$ over 60 min. In another experiment $[Ir(CO)_2I_2]^-$ was treated with a mixture of HI and MeI, each in a ten-fold excess. The $[IrH(CO)_2I_3]^-$ ion was the only species detected initially and over a period of 50 min it was transformed into $[Ir(CO)_2I_4]^-$. The comparative stability of the $[IrMe(CO)_2I_3]^-$ ion was confirmed in a separate experiment in which a $MeNO_2$ solution of a salt of this ion was heated to 100 °C in an open system (where MeI could escape) and no decomposition was evident after 10 min.

Thus the oxidative addition of HI is apparently much faster than that of methyl iodide, but the reversibility of the HI addition combined with the relative non-reversibility of the MeI addition means that $[IrMe(CO)_2I_3]^-$ can form in situations where there is little or no excess of HI. Obviously, if excess of HI is present, methyl iodide cannot compete, $[Ir(CO)_2I_4]^-$ forms, and under carbonylation-reaction conditions the water–gas shift reaction would predominate.

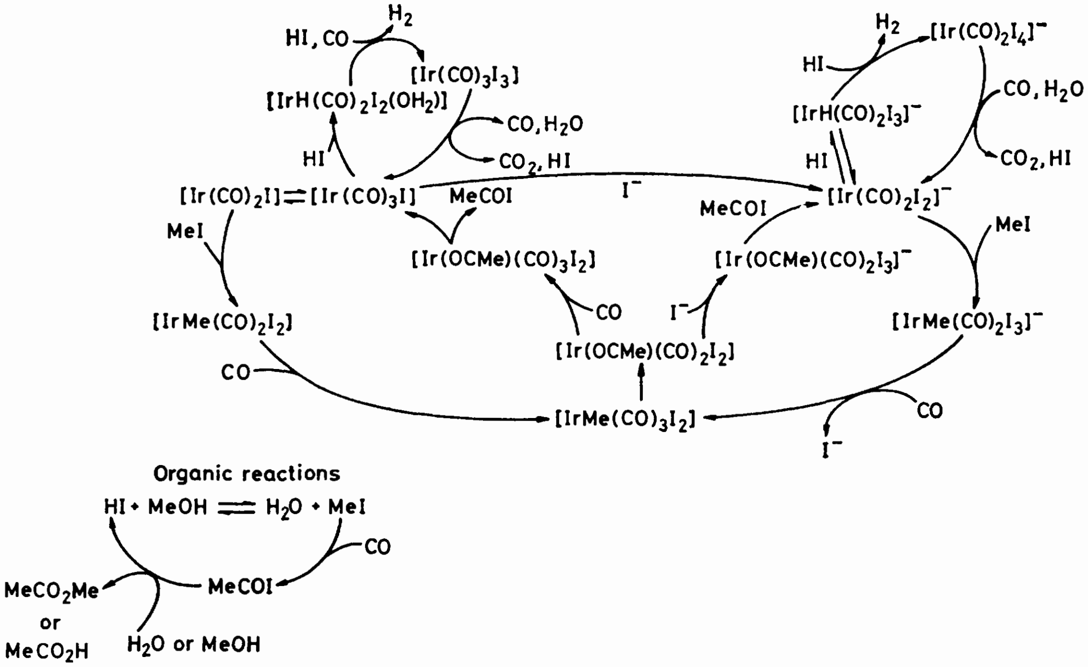
I therefore propose that in this regime of the carbonylation reaction the rate-determining step is methyl iodide addition to the low level of $[Ir(CO)_2I_2]^-$ which is in equilibrium with the $[IrH(CO)_2I_3]^-$ ion. The reaction rate should therefore show a positive dependence on methyl iodide level although the equilibrium $MeI + H_2O \rightleftharpoons MeOH + HI$ means that varying the methyl iodide independent of HI will be difficult in a practical situation, where ester formation also influences the methanol, water, and hence HI and methyl iodide levels. In my limited variation of the methyl iodide concentration (Table 1) it can be seen that there is an initial sharp drop in reaction rate which occurs as the catalyst system changes over from primarily iridium(I) species to the $[IrH(CO)_2I_3]^-$ ion and then the rate of the reaction increases with increasing MeI concentration up to a concentration of 0.80 mol dm^{-3} at [Ir] = 0.01 mol dm^{-3}, and then starts to decrease again. The dependence on methyl iodide concentration is somewhat less than first order over the range where the rate is showing a positive dependence on MeI concentration.

A detailed understanding of this kinetic phenomenon will require a knowledge of the various equilibrium constants under actual reaction conditions. However, it would appear that increasing methyl iodide would increase the HI level proportionately if the organic equilibria alone were controlling and hence that no positive dependence on methyl iodide should be observed. I tentatively propose that the amount of $[IrH(CO)_2I_3]^-$ present in the reacting solutions is not primarily a reflection of the amount of free HI involved in the organic equilibria alone, but rather reflects the rapid rate and large equilibrium constant of the reaction $HI + [Ir(CO)_2I_2]^- \rightleftharpoons [IrH(CO)_2I_3]^-$.

The experiments referred to earlier in which triphenylphosphine was added to the reaction solutions were interpreted as indicating little or no excess of HI in the solutions and experiments in Monsanto's Texas City laboratories on the equilibria involved in the methanol–acetic acid–water–hydriodic acid system suggest that the level of free HI in the experiments described herein should be very small.

Thus, if there is little or no excess of HI present in the reaction solutions, increasing the methyl iodide concentration would be expected to increase the reaction rate provided that there is sufficient methanol present to act as a ' sink ' for the HI. Continued increases in the methyl iodide level will eventually lead to appreciable levels of HI being produced if the methanol level is not raised simultaneously. The reaction rate will not then increase with increasing HI level but will start to decrease as the sequential reaction of the hydride with HI to give $[Ir(CO)_2I_4]^-$ starts to become appreciable. As noted earlier, in the carbonylation experiments at the highest MeI : Ir ratio examined, the $[Ir(CO)_2I_4]^-$ ion was clearly observed in the reacting solutions.

A scheme which summarizes the observations on the catalytic reaction is given below. It is apparent that both hydriodic acid and ionic iodide concentrations can play very significant roles in controlling not only the catalytic cycle in which the iridium complexes operate but the actual reaction which predominates, *i.e.* methanol carbonylation ***versus*** water–gas shift ***versus*** methanol to methane. The hydriodic acid and ionic iodide levels are affected by methyl iodide, water, methanol, and methyl acetate concentrations all of which are not only influenced by the initial charge to the catalytic reaction but also vary markedly during a batch reaction. Thus, a



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detailed mechanistic interpretation of this system will require a considerably sharper definition of the reaction parameters than is required for the rhodium system.

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