Characterization and Recycle Experiments on the Dicarbonyl Triiodide Iridium(II) Intermediate in the Carbonylation of Ethanol to Propionic Acid

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Iridium complex catalysts have not received as much attention as the rhodium catalysts for the catalytic carbonylation of alcohols [1, 2] although their performance is shown to be comparable to that of Rh catalysts in terms of activity and selectivity [3–7]. Hieber *et al.* [8] were probably the first to study the products of carbonylation of methanol using solid iridium halides. Complexes of the type IrCl(cod)L (where $L = C_5H_5N$, 3-Cl-C_5H_5N or 2-Me-C_5H_4N) and $Ir(cod)L'^+$ (where L' = phen or bipy) have been used as precursors with various iodide promoters [5]. The cationic complexes were found to possess higher activities. It was further shown that under these reaction conditions, anionic iodocarbonyl complexes of iridium are also formed. The kinetics and mechanism of Ir-catalyzed carbonylation of methanol were studied by Matsumoto *et al.* [3] and by Forster [6], who revealed that the mechanism with the Ir catalyst is much more complex. These studies have shown that catalytically active species of Ir can involve either neutral or anionic complexes depending on the reaction conditions, especially on the acidity and on the iodide concentration. The complexes $IrI_2(CO)_2^-$ and $IrI_3(CO)_3$ were isolated from the reaction mixture by addition of iodide or iodine respectively. This suggests that the complex $IrI(CO)_3$ may be present in the solution. Ir(II) species have also been postulated as intermediates in the catalytic cycle proposed by Forster [6], although these have not been isolated or characterized. The nature of the active species in the carbonylation reactions of alcohols using Ir catalysts thus remains speculative.

In the present communication we report, probably for the first time, the isolation and characterization of an intermediate Ir(II) species stabilized as its isoquinoline salt during the carbonylation of ethanol using $IrCl_3 \cdot 3H_2O$ as a catalyst precursor with HI as a promoter.

The carbonylation experiments were carried out in a 300-ml high pressure stirred autoclave (Parr Instrument Co., U.S.A.) charged with $IrCl_3 \cdot 3H_2O$ (5.68×10^{-6} mol/cm^3), hydroiodic acid (7.50×10^{-4} mol/cm^3), ethanol (3.47×10^{-3} mol/cm^3), propionic acid (9.39×10^{-3} mol/cm^3) and isoquinoline (1.14×10^{-5} mol/cm^3) as described in ref. 9. The autoclave was flushed twice with carbon monoxide and heated to 200 °C. The reactor was then pressurised to 55 atm pressure and the reaction started. The reaction was continued until there was no absorption of carbon monoxide and the progress of the reaction was monitored by observing the pressure drop in the reservoir vessel. On completion of the reaction, the autoclave was cooled to room temperature and carbon monoxide was flushed out. The reaction mixture yielded a microcrystalline orange product on cooling at 0 °C which analyzes for $(C_9H_8N)(Ir(CO)_2I_3(COC_2H_5))$ after recrystallization from dichloromethane. *Anal.* Calc. for $IrC_{14}H_{13}NI_3O_3$: C, 20.69; H, 1.60; I, 46.65; Ir, 23.55. Found: C, 19.87; H, 1.52; I, 46.02; Ir, 23.55%. The ESCA analysis [10] on the compound also confirmed the presence of the above elements (Supplementary Material, Fig. 1).

The conductivity measurements in methanol (100 Ω) and acetonitrile (130 Ω) as solvents indicate it to be an anionic iridium species, suggested as a possible intermediate in the catalytic cycle of methanol carbonylation by Forster [6]. The IR

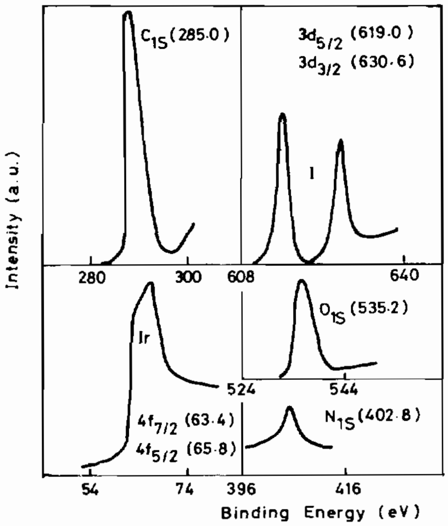

Fig. 1. ESCA spectra of the iridium intermediate, dicarbonyl triodide iridium(II) propionate anion (see Supplementary Material).

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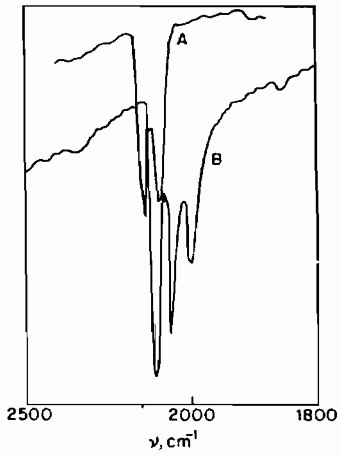

Fig. 2. IR spectra of the iridium intermediate isolated from the reaction mixture at various HI concentrations: (A) HI concentration = 7.5×10^{-4} mol/cm^3; (B) HI concentration = 3.75×10^{-4} mol/cm^3.

spectrum of the isolated compled (Fig. 2A) shows a doublet at 2060 and 2105 cm^{-1}, indicating the presence of two *cis*-carbonyl groups [6]. Similar absorptions have been observed for an anionic iridium(II) complex stabilized by the tetraphenylarsonium cation [11]. No absorption corresponding to an Ir–H linkage is seen around 2150–2200 cm^{-1} [12], which rules out the possibility of a hydrido derivative. The isolated complex also does not exhibit strong bands at 1996 and 2067 cm^{-1} which are characteristic of the $M(CO)_2I_2^-$ ion [6, 11, 13]. At a lower HI concentration (Fig. 2B), an additional infrared band is observed in the region of the carbonyl absorption, indicating the generation of a tricarbonyl derivative [11]. All these features taken together suggest the presence of a dicarbonyl triiodide iridium anion associated with the protonated isoquinoline cation in the isolated complex. Besides the carbonyl absorption, the compound exhibits yet another strong absorption at 1645 cm^{-1}, which can be assigned to the coordinated propionyl group which has undergone a downward shift of *ca.* 100 cm^{-1} on complexation [14]. The least coupled Ir–O stretching mode can be located at 555 cm^{-1} in the present complex.

Indication of the presence of Ir(II) species comes from the room temperature magnetic moment of the isolated complex (1.33 B.M.) since the other common oxidation states for this metal ion are diamagnetic [15]. A slight lowering of the magnetic moment is of common occurrence amongst the iridium complexes through metal–metal interactions. The examples of stable, mononuclear Ir(II) complexes have become available in the literature only after 1974 [16], although their existence as the transient species had been suggested in some oxidative addition reactions of Ir(I) complexes [17].

In marked contrast to cobalt(II) ions which are isoelectronic with Ir(II), the complex compounds of the latter exhibit electronic spectra characterized by a very intense metal-to-ligand charge-transfer band [15, 18]. Such a CT transition is observed for the present complex at 326 nm ($C = 9.24 \times 10^3$ mol^{-1} cm^{-1}), which perhaps contributes significantly to its orange–red colour.

Finally, the cyclic voltamogram profile of the compound (Fig. 3) in DMSO shows a number of oxidation and reduction peaks, most of which are irreversible. Thus of the four reduction peaks at +0.250, –0.375, –0.550 and –1.025 V *versus* SCE, the first three represent irreversible processes while the last one probably corresponds to a reversible one-electron reduction process of Ir(I) ro Ir(0).

The role of the isoquinoline cation on the stability of the Ir complex was examined through the

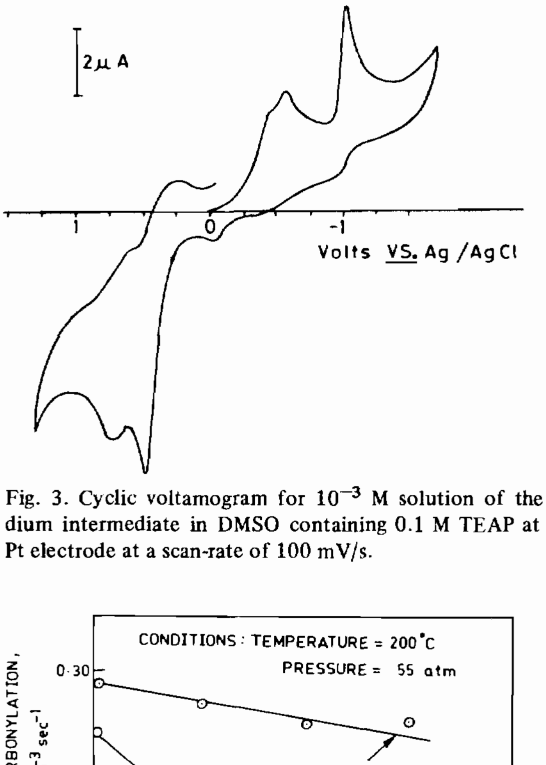

Fig. 3. Cyclic voltamogram for 10^{-3} M solution of the iridium intermediate in DMSO containing 0.1 M TEAP at the Pt electrode at a scan-rate of 100 mV/s.

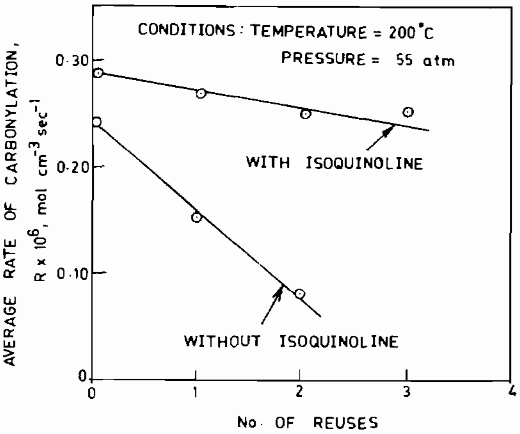

Fig. 4. Comparison of reaction rates during the recycle experiments with and without isoquinoline (for experimental details, see text).

recycle experiments with and without isoquinoline. In these experiments the reaction product, *viz.* propionic acid, was separated out by distillation and the residual solution was charged to the reactor along with the fresh ethanol and the lighter fraction containing ethyl iodide. It can be observed (Fig. 4) that the average rate of the reaction decreased with each recycle when isoquinoline was not used. On the other hand, in the presence of isoquinoline the activity was found to be nearly constant even after recycles. This indicates that isoquinoline indeed stabilizes the active catalytic species without loss of activity and selectivity.

Supplementary Material

ESCA spectra of the isolated complex (Fig. 1) are available from the authors upon request.

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