Visible-light-photoinduced Hydrogenation and Hydroformylation by Use of Water-soluble Rhodium Triphenylphosphine Complexes

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Chlorotris-(3-diphenylphosphinobenzenesulphonate)rhodium $[Rh^ICl(dpm)_3]^{3-}$, acts as a homogeneous catalyst in the photosensitized hydrogenation of ethylene or acetylene and for the hydroformylation of ethylene in the presence of CO.

Considerable efforts are being directed towards the development of light-induced H_2-evolution processes using heterogeneous[1,2] and homogeneous[3] catalysts. Hydrogen atoms photogenerated *in situ* and bound to heterogeneous catalysts have been applied in the hydrogenation of unsaturated substrates[4] and of hydrogencarbonate.[5] Photogenerated hydrido transition metal complexes could provide homogeneous catalysts for a variety of hydrogen-transfer reactions.[6]

Recently, photoinduced H_2-evolution by use of a water-soluble Rh triphenylphosphine complex has been reported.[7] Here we report the photosensitized hydrogenation and hydroformylation of unsaturated substrates in aqueous media by use of chlorotris-(3-diphenylphosphinobenzenesulphonate)rhodium $[Rh^ICl(dpm)_3]^{3-}$ (1),[8] as catalyst.

The hydrogenation system was composed of aqueous phthalate buffer (pH 4.5; 3 ml) containing trisbipyridineruthenium(II) $[Ru(bpy)_3]^{2+}$ (1.4×10^{-4} M), as photosensitizer, the rhodium catalyst (1) (1.0×10^{-4} M), and ascorbate as sacrificial electron donor (5×10^{-2} M). To the deaerated system was added ethylene or acetylene (0.2 ml), and the solution was illuminated ($\lambda >400$ nm) with a 150 W Xenon arc. In the presence of ethylene, photohydrogenation proceeded to form ethane with concomitant evolution of H_2. Photohydrogenation of acetylene yielded ethylene and ethane together with evolved H_2. In the absence of the unsaturated substrates only H_2 evolution was observed. The rates of the photoinduced hydrogenations of ethylene or acetylene and the H_2-evolution rates in the presence and absence of the substrates are displayed in Figure 1(A).† It is evident that ethylene is hydrogenated to ethane, and that the hydrogenation products of acetylene are ethylene and ethane. It is also evident from Figure 1(A) that the sum of the amounts of hydrogenation products and concomitant hydrogen evolved with ethylene as substrate correspond to the total amount of H_2 evolved in the absence of the unsaturated substrate. These results imply that a portion of the photogenerated hydrogen is utilized for the hydrogenation of ethylene or acetylene. Control experiments where the amount of photogenerated hydrogen was injected into an aqueous solution (pH 4.5) that included the catalyst (1) and the unsaturated substrate ethylene or acetylene revealed that no hydrogenation of the substrates occurs in the dark within 24 h. Thus, photohydrogenation of ethylene and acetylene involves an *in-situ* photogenerated hydridorhodium intermediate rather than photogenerated molecular hydrogen. It should be noted that hydrogenation of unsaturated substrates proceeds in the dark[8] in the presence of (1) at H_2 pressure corresponding to 3 atm. However, in the photochemical experiments the partial photogenerated hydrogen pressure corresponds to *ca.* 0.1 atm.; consequently the dark process is prohibited. The quantum yields (ϕ) for photohydrogenation of ethylene and acetylene are 1.8 and 0.61%, respectively. The estimated

turnover numbers of the catalyst (1) are 40 and 13 in the corresponding two systems.

Introduction of carbon monoxide (1 ml) and ethylene (0.2 ml) to an aqueous solution (pH 4.5) of $[Ru(bpy)_3]^{2+}$, the catalyst (1), and ascorbate as electron donor, and illumination ($\lambda >400$ nm), results in the hydroformylation of ethylene to form propionaldehyde,‡ with concomitant evolution of H_2. Under these conditions, no hydrogenation of ethylene to ethane occurs. The rate of propionaldehyde formation as a function of illumination time is displayed in Figure 1(B). The quantum yield for propionaldehyde formation (ϕ) is 0.1% and the turnover number of $[Rh^ICl(dpm)_3]^{3-}$ (1) is 3.5. A control dark experiment where the photogenerated amount of H_2 was injected into the aqueous system containing ethylene and CO revealed that no hydroformylation product was formed. Thus, propionaldehyde originates from a hydridorhodium complex rather than from photogenerated molecular hydrogen. It is well established[10] that under hydroformylation conditions, $[Rh^ICl(PPh_3)_3]$ is transformed into hydridocarbonyltris(triphenylphosphine)rhodium(I) $[RhH(CO)(PPh_3)_3]$. Indeed, substitution of (1) by [hydridocarbonyltris(3-diphenylphosphinobenzenesulphonate)]rhodium(I) $[RhH(CO)(dpm)_3]^{3-}$ (2) in the photochemical system results in the hydroformylation of ethylene at a rate similar to that observed with (1). This suggests that $[RhH(CO)(dpm)_3]^{3-}$ is the actual hydroformylation catalyst, with (1) as precursor.
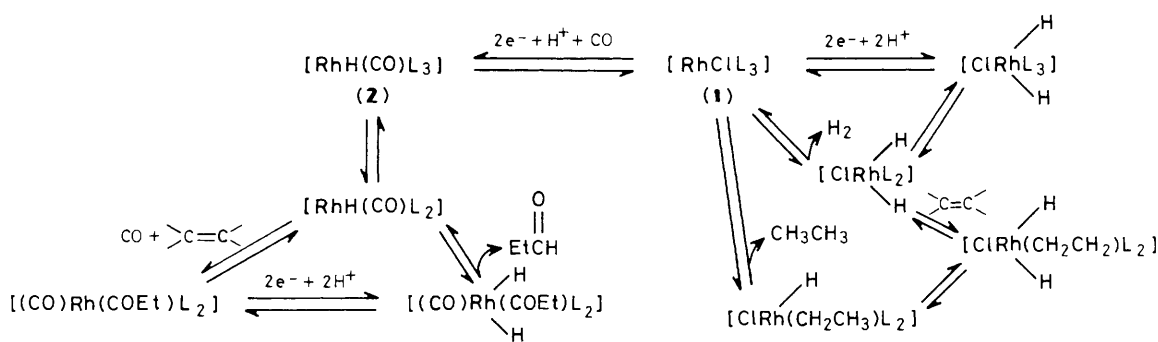
The photosensitized transformation that leads to the reduction of $[Rh^ICl(dpm)_3]^{3-}$ (1) has been elucidated by laser flash photolysis. The primary step involves the reductive quenching of excited $[Ru(bpy)_3]^{2+}$ by ascorbate (HA^-) [equation (1)].[3a] The resulting $[Ru(bpy)_3]^+$, $E^0 = -1.28$ V vs. normal hydrogen electrode (n.h.e.),[11] reduces $[Rh^ICl(dpm)_3]^{3-}$ [equation (2)].

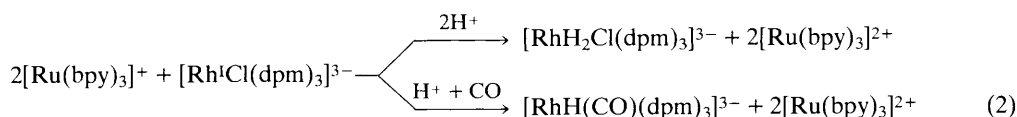$$2[Ru(bpy)_3]^{2+} + HA^- \xrightarrow{h\nu} 2[Ru(bpy)_3]^+ + A^{2-} + H^+ \quad (1)$$
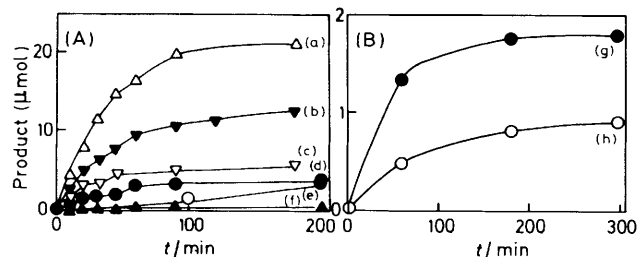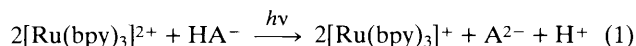
Figure 1. Rates of photoinduced formation of: (A) hydrogenation products and (B) hydroformylation products; (a) H_2 evolution in the absence of unsaturated substrate; (b) ethane formation from ethylene; (c) H_2 evolution concomitant with ethylene hydrogenation; (d) ethylene formation from acetylene; (e) H_2 evolution concomitant with acetylene hydrogenation; (f) ethane formation from acetylene; (g) H_2 evolution concomitant with ethylene hydroformylation; (h) propionaldehyde formation from ethylene and CO.

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† The gaseous products were analysed by g.l.c. (MS 5A column for hydrogen; Spherosil XOB 075 column for hydrocarbons).

‡ Propionaldehyde concentration was determined by h.p.l.c. analysis of the dinitrophenylhydrazone.[9]

$$[RhH(CO)L_3] \xrightleftharpoons{2e^- + H^+ + CO} [RhClL_3] \xrightleftharpoons{2e^- + 2H^+} [ClRhL_3]\begin{smallmatrix}H\\H\end{smallmatrix}$$
$$(2) \qquad\qquad (1)$$

$$[RhH(CO)L_2]$$

$$CO + {>}C{=}C{<} \rightleftharpoons [(CO)Rh(COEt)L_2] \xrightleftharpoons{2e^- + 2H^+} [(CO)Rh(COEt)L_2]{\begin{smallmatrix}H\end{smallmatrix}}$$

$$\overset{O}{\underset{\parallel}{}} \; EtCH$$

$$H_2 \quad [ClRhL_2] \quad {>}C{=}C{<}$$

$$CH_3CH_3 \qquad [ClRh(CH_2CH_2)L_2]$$

$$[ClRh(CH_2CH_3)L_2]$$

Scheme 1. L = dpm

$$2[Ru(bpy)_3]^+ + [Rh^ICl(dpm)_3]^{3-} \Big\langle \begin{array}{l} \xrightarrow{2H^+} [RhH_2Cl(dpm)_3]^{3-} + 2[Ru(bpy)_3]^{2+} \\[1ex] \xrightarrow{H^+ + CO} [RhH(CO)(dpm)_3]^{3-} + 2[Ru(bpy)_3]^{2+} \end{array} \qquad (2)$$

The subsequent hydrogenation[12] and hydroformylation[10] reactions by hydridorhodium complexes have been the subject of numerous studies. Scheme 1 represents a possible route that utilizes the photogenerated hydridorhodium product in subsequent H_2 evolution, hydrogenation, and hydroformylation processes.

In conclusion, we have demonstrated that photohydrogenation and photohydroformylation of unsaturated substrates proceed with a water-soluble Rh^I homogeneous catalyst. The stability of these systems is limited. Spectroscopic studies reveal that the photosensitizer $[Ru(bpy)_3]^{2+}$ is degraded, peresumably through photoinduced ligand dissociation to form $[Ru(bpy)_2(dpm)]^+$, and thus a search for other sensitizers and catalysts is desirable. Preliminary studies indicate that ruthenium, rhenium, and palladium dpm complexes are also active H_2-evolution, hydrogenation, and hydroformylation catalysts.

This research was supported by the Berman Foundation Grant.

Received, 26th November 1987; Com. 1721

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