Hydrogen Production from Ethanol catalysed by Group 8 Metal Complexes

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Different strategies for the catalytic thermal production of hydrogen from ethanol are discussed and demonstrated using various Group 8 metal catalysts, in the presence of added base. Where the metal has a low affinity for carbon monoxide, *e.g.* in $[PtH(PEt_3)_3]^+$, simple dehydrogenation of ethanol to ethanal and its aldol condensation products is observed. When the metal has a high affinity for CO, CO abstraction from the formed ethanol occurs and, as in reactions catalysed by $[RhCl(PPh_3)_3]$ or $[RhH(PPr^i_3)_3]$, can poison the reaction. In some cases, the CO abstraction reaction can be used to promote the thermodynamically favourable reaction of formation of hydrogen, methane, and carbon monoxide; although irradiation with visible light is often required to release the carbon monoxide from the metal centre {*e.g.* $[RhH(CO)(PPr^i_3)_2]$ in the absence of base}. Finally, in catalytic reactions carried out in the presence of base, water–gas shift type chemistry is observed in reactions catalysed by $[Rh(bipy)_2]Cl$, so that ethanol can be converted into $2H_2$, CH_4, and CO_2. In the cases of $[Rh(bipy)_2]Cl$ and $[RuH_2(N_2)(PPh_3)_3]$, rates of hydrogen production of >100 catalyst turnovers h^{-1}, corresponding to >1 l per litre of catalyst solution per hour can readily be sustained over long periods. The role of base in, and the mechanisms of, these interesting reactions are discussed; as are synergistic effects and reasons for the success of $[Rh(bipy)_2]Cl$ and $[RuH_2(N_2)(PPh_3)_3]$ as catalysts for hydrogen production.

A number of recent studies has demonstrated that a high grade fuel oil can be produced from biomass.[1] However, the need for an external supply of hydrogen, which is required for catalytic biomass hydrogenation, means that these reactions are not generally commercially viable. We have, therefore, attempted to identify processes which allow the production of hydrogen either from biomass or from a fermentation product that is readily available from biomass. To this end, we have been carrying out studies aimed at the production of hydrogen from alkanols, as these are readily available from fermentation of biomass, but also because they model reactions which may be possible for the direct production of hydrogen from the alcoholic moieties of, for example, cellulose.

In addition to the importance that these reactions have for biomass conversion, they may also provide viable routes to: (*a*) the production of hydrogen from waste alkanols; (*b*) the production of alkanals and other down-stream products; and (*c*) the storage of energy, since the decomposition of alkanols to hydrogen and alkanals [equation (1)] is a thermodynamically uphill process. Product hydrogen can then find use in general hydrogenation, hydrogenation of N_2 or CO to NH_3 or MeOH, and, on a more limited scale, as a fuel.

$$RCH_2OH \rightleftharpoons RCHO + H_2; \Delta G^{\circ} = 30\text{—}40 \text{ kJ mol}^{-1} \quad (1)$$

Strategy

The simplest approach to the production of hydrogen from primary alkanols involves the direct dehydrogenation to alkanal [equation (1)]. Although these reactions are invariably thermodynamically uphill ($\Delta G^{\circ} \simeq$ 30—40 kJ mol^{-1}), various systems have been reported that allow the dehydrogenation to occur thermally under relatively mild conditions.

Since the principle of microscopic reversibility ensures that any complex that is active for hydrogenation of an alkanal will be active for dehydrogenation of an alkanol, it is logical to start any investigation aimed at the dehydrogenation of alkanols by studying the possible use of known hydrogenation catalysts. Immediately, a major problem arises because many of these co-ordinatively unsaturated (or potentially co-ordinatively unsaturated) complexes also decarbonylate alkanals and this reaction is seldom catalytic.[2,3] Indeed, this reaction has been used for the synthesis of hydrido and/or carbonyl complexes of several different metals.[2]

Table 1. Thermodynamics for reaction (2) for different primary alkanols

Alkanol	ΔG°/kJ mol^{-1}
MeOH	29.1
EtOH	−13.5
Pr^iOH	0.8
BuOH	8.4
$C_5H_{11}OH$	10.5

However, this type of decarbonylation reaction can possibly be used to advantage since, if the CO can be released from the metal, the overall decomposition of alkanols will be as in equation (2). Table 1 shows that the thermodynamics for this

$$RCH_2OH \longrightarrow RH + CO + H_2 \quad (2)$$

reaction are considerably more favourable than for the simple alcohol dehydrogenation and indeed, for ethanol, the reaction is exergonic at room temperature. In cases where the carbon monoxide is not readily released from the metal, it may perhaps be released photochemically thus leading to a light-driven catalytic reaction. Alternatively, it may be possible to make some improvement in reaction rates and yields if another complex, which allows rapid catalytic alkanal decarbonylation, is added to the system, and released CO then escapes into the reactor atmosphere or is removed chemically, *e.g.* by reaction with base.

Finally, a second strategy may be possible for the removal of CO from the metal. This involves attack of OH^- on co-ordinated CO to give CO_2 and a metal hydride, which on protonation releases hydrogen. These reactions are similar to those observed in the synthesis of metal–carbonyl–hydrides and in the water–gas shift reaction. In this case the overall reaction

Table 2. Rates of production of gases from ethanol in the presence of Group 8 metal complexes[a]

Catalyst	10^4 Concentration/mol dm^{-3}	T/°C	Rates of gas production[b]/turnover h^{-1}	
			H_2	CH_4
$[RhCl(PPh_3)_3]$	4.12	150	2.7[c]	0.15
$[RhH(PPr^i_3)_3]$	5.80	150	0.9[c]	*d*
$[Rh(bipy)_2]Cl$	3.04	120	1.2	0.11
$[RuH_2(N_2)(PPh_3)_3]$	3.70	150	5.1	0.32
$[RuH_2(PPh_3)_4]$	3.16	150	3.8	0.28

[a] All reactions were carried out for 2 h. Rates are expressed as mols of gas per mol of catalyst per h (turnover h^{-1}). [b] No other gaseous products were formed. [c] No further hydrogen was produced in an additional 2 h period. [d] Not measured.

Table 3. Rates of photochemical gas evolution from ethanol containing Group 8 metal complexes

Catalyst	10^4 Concentration/mol dm^{-3}	T/°C	Rates of gas production/turnover h^{-1}		
			H_2	CH_4	CO
$[RhCl(PPh_3)_3]$	3.04	150	2.1	0.31	
$[RhH(PPr^i_3)_3]$	3.10	150	6.2	0.48	*a*
$[RuH_2(N_2)(PPh_3)_3]$	3.48	150	14.5	0.39	*a*
$[RuH_2(PPh_3)_4]$	3.68	150	8.2	0.48	*a*

[a] Small quantities (<0.5 turnovers h^{-1}) were detected.

Table 4. Rates of production of gases from ethanol in the presence of Group 8 complexes *and* $[Rh(dppp)_2]Cl$ (3.32×10^{-4} mol dm^{-3})

Catalyst	10^4 Concentration/mol dm^{-3}	T/°C	Rates of gas production/turnover h^{-1}		
			H_2	CH_4	CO
$[RhCl(PPh_3)_3]$	2.82	150	1.06	*a*	*a*
$[RuH_2(N_2)(PPh_3)_3]$	3.04	150	8.32	0.59	*a*
$[RuH_2(PPh_3)_4]$	3.50[b]	150	4.25	0.34	*a*

[a] Small quantities (<0.5 turnovers h^{-1}) were detected. [b] $[Rh(dppp)_2]Cl$ at 3.76×10^{-4} mol dm^{-3}.

for alkanol decomposition is as shown in equation (3) and this

$$RCH_2OH + H_2O \longrightarrow RH + 2H_2 + CO_2 \qquad (3)$$

strategy has the added advantages that the reaction is thermodynamically favourable for all R groups (R = alkyl) ($\Delta G^{\circ} \simeq -30$ kJ mol^{-1}) and that two molar equivalents of hydrogen can be produced per mole of alcohol. We now report a number of systems in which these various strategies are realised using ethanol as the substrate, for which some preliminary results have been communicated.[4,5]

Results

Dobson and Robinson[6] have reported that hydrogen can be produced from a wide range of alcohols, including ethanol, at their boiling points in reactions catalysed by $[Ru(CF_3CO_2)_2(CO)(PPh_3)_2]$ and related complexes. However, there is some doubt as to the longevity of the catalyst since other workers have found that decarbonylation of the alkanal formed gives a catalytically inactive complex.[7]

Hydrogen is produced at a slow rate on heating ethanolic solutions of the ruthenium and rhodium complexes shown in Table 2. In all cases, methane is also observed as a gaseous product, demonstrating that decarbonylation of product ethanal occurs. In some cases, notably those involving $[RhCl(PPh_3)_3]$ or $[RhH(PPr^i_3)_3]$ this decarbonylation leads to a catalytically inactive carbonyl complex and sustained hydrogen production is not observed.*

In most cases, improvements in the rates and yields of hydrogen are observed if the reaction is carried out with illumination by a focused 500-W tungsten-halogen lamp (Table 3), but this is not effective for $[RhCl(PPh_3)_3]$.

Addition of $[Rh(dppp)_2]Cl$ [dppp = 1,3-bis(diphenylphosphino)propane], which itself does not dehydrogenate ethanol, but which is an alkanal decarbonylation catalyst[8] causes small increases in the rate of hydrogen production in most cases (Table 4) and, even for $[RhCl(PPh_3)_3]$, makes the reaction mildly catalytic, CO being observed as a gas-phase product.

Much more dramatic improvements are observed if the reactions are carried out in the presence of base (Table 5), particularly efficient reactions being observed with $[RuH_2(N_2)(PPh_3)_3]$ or $[Rh(bipy)_2]Cl$ (bipy = 2,2′-bipyridyl) as catalysts. In these cases, 100—150 turnovers per hour are observed and hydrogen production is sustained for many hours at an only slightly reduced rate. Analysis of the solution phase shows the presence of ethanal, and its aldol condensation products together with other higher molecular weight organic products.† It should be noted that the activity of $[Rh(bipy)_2]Cl$ is higher than that of $[RuH_2(N_2)(PPh_3)_3]$, comparable rates being obtained at 30 °C lower for the rhodium complex.

We have studied reactions catalysed by $[Rh(bipy)_2]Cl$ in

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* The amount of methane produced generally corresponds to less than one catalyst turnover so it may be that some other poisoning process also operates.

† Identical products are obtained on heating small amounts of ethanal in basic ethanol.

Table 5. Rates of evolution from ethanol containing Group 8 metal complexes and NaOH (1.0 mol dm^{-3})

Catalyst	10^4 Concentration/mol dm^{-3}	T/°C	Rates of gas production/turnover h^{-1} H_2	CH_4	CO_2[a]
$[RhCl(PPh_3)_3]$	2.82	150	7.5	0.17	
$[RhH(PPr^i_3)_3]$	5.16	150	5.6	0.55	
$[Rh(bipy)_2]Cl$	10.0	120	95.5[b]	10.5	9.5
$[RuH_2(N_2)(PPh_3)_3]$	2.6	150	148.1[c]	*d*	
$[RuH_2(CO)(PPh_3)_3]$	2.82	150	62	*d*	
$[RuH_2(PPh_3)_4]$	2.98	150	23.8	0.4	

[a] After neutralisation. [b] 64 h^{-1} after 24 h. [c] 97.6 h^{-1} after 19 h. [d] Not measured.

Table 6. Synergistic effects of additives on the rates of production of gases from ethanol containing Group 8 metal complexes in the presence of NaOH (1.0 mol dm^{-3})

Catalyst	10^4 Concentration/mol dm^{-3}	Additive	10^4 Concentration/mol dm^{-3}	Rates of gas production/turnover h^{-1} H_2	CH_4[a]
$[RhCl(PPh_3)_3]$	4.56	$h\nu$		11.4	*b*
	3.26	$[Rh(dppp)_2]Cl$	2.70	21.4[c]	0.22
$[RhH(PPr^i_3)_3]$	4.14	$h\nu$		23.1	1.85
	4.48	$[Rh(dppp)_2]Cl$	2.70	17.1	*b*
$[Rh(bipy)_2]Cl$	4.78	$[Rh(dppp)_2]Cl$	3.36	90.8	*b*
$[RuH_2(N_2)(PPh_3)_3]$	3.48	$h\nu$		210.2	*b*
	3.04	$[Ru(dppp)_2]Cl$	3.12	82.4	0.35
$[RuH_2(PPh_3)_4]$	2.10	$h\nu$		138.4	0.90
	3.68	$[Ru(dppp)_2]Cl$	4.38	53.3	*b*

[a] CO was not detected in any of these experiments. [b] Detected but not quantified. [c] 17.8 h^{-1} after a further 22 h.

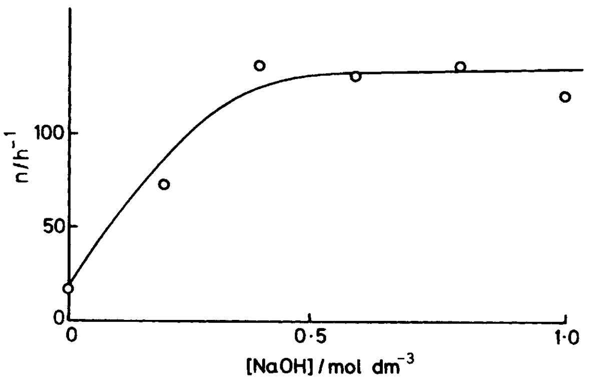

Figure 1. Dependence of the rate of hydrogen production [mol of hydrogen (mol of catalyst)$^{-1}$ h^{-1}] upon [NaOH] in reactions catalysed by $[Rh(bipy)_2]Cl$

some detail and find that although base is required for the reaction, saturation kinetics are observed and little or no rate enhancement occurs above *ca.* 0.25 mol dm^{-3} of NaOH (see Figure 1). Variable-temperature studies give an activation enthalpy of 62.5 kJ mol^{-1}.

In all the reactions carried out in the presence of base, methane is also a product and, for $[Rh(bipy)_2]Cl$, neutralisation of the solution after a given reaction time produces CO_2.

The amounts of methane and CO_2 produced are generally much less (up to 10%) than the amount of hydrogen produced, but for $[Rh(bipy)_2]Cl$ they generally correspond to one another. Addition of water simply retards the rate of the reaction without changing the relative proportion of methane, CO_2, or H_2 formed.

In some cases synergistic reactions are observed (Table 6). Thus, the most successful reactions catalysed by $[RhCl(PPh_3)_3]$ are those in which both base and $[Rh(dppp)_2]Cl$ are added.

In other cases, use of both light and base give the most efficient systems for catalytic hydrogen production and the effect of light is particularly pronounced in the case of $[RuH_2(PPh_3)_4]$ and $[RuH_2(N_2)(PPh_3)_3]$.

Discussion

It is not surprising that hydrogen production from ethanol can be catalysed by the complexes shown in Table 2 since they are all known to be active for hydrogenation of alkenes and/or alkanals.[9–13] The rates of these dehydrogenation reactions are, however, low and in the cases where rhodium–phosphine complexes are used as catalysts, catalytic hydrogen production is not observed because decarbonylation of the alkanal formed effectively poisons the catalyst. For reactions catalysed by $[PtH(PEt_3)_3]^+$, there is no evidence for carbonyl-containing species being formed, presumably on account of the low affinity of platinum for CO.

Effect of Irradiation with Visible Light.—It is well known that many metal–carbonyl complexes can release CO upon irradiation with visible or u.v. light. Irradiation of catalytic solutions clearly enhances the rate and yield of hydrogen production for many of the complexes by removing the poisoning effect of co-ordinated CO, which is formed by the alkanal decarbonylation. The overall reaction is then as shown in equation (2). Only in the case of $[RhCl(PPh_3)_3]$ is this strategy not effective. This is to be expected since, although flash photolysis studies have shown[14] that CO is released on photolysis of $[RhCl(CO)(PPh_3)_2]$, the back reaction is very rapid and it is known that continuous photolysis does not lead to CO evolution.[15] In addition, since the rate-determining step for alcohol dehydrogenation is loss of H_2, light probably increases the rate of this reaction by the well known photo-enhanced reductive elimination of H_2 from di- and poly-hydride complexes.[16]

Effect of $[Rh(dppp)_2]Cl$.—Detailed studies of the stoicheiometric dehydrocarbonylation of alkanols has provided strong evidence that the alkanal is released from the co-ordination sphere of the metal before it undergoes further oxidative addition of the C–H bond and decarbonylation.[3] Since $[Rh(dppp)_2]Cl$ is an efficient catalyst for alkanal decarbonylation,[8] the released ethanal may be catalytically decarbonylated and hence not available for decarbonylation by the primary catalyst in the solution. Carbon monoxide is then released into the gas phase of the reactor, where it can be detected. This accounts for the modest improvements in the rates and yields for hydrogen production in the presence of $[Rh(dppp)_2]Cl$, but poisoning will still occur because of competitive decarbonylation of product ethanal by the primary catalyst, and direct carbonylation by released CO.

Effect of Sodium Hydroxide.—In the presence of sodium hydroxide, much of the ethanal formed undergoes aldol condensation reactions. This has the effect not only of removing the ethanal, hence preventing the back reaction shown in equation (1), but also of reducing the amount of decarbonylation. We have evidence that decarbonylation of long-chain alkanals is considerably less facile than for ethanal.[17] In addition, the observation of significant amounts of methane and CO_2 as reaction products indicates that the base is capable of removing CO from the carbonyl complexes formed by decarbonylation of ethanal, presumably *via* nucleophilic attack of OH^- on co-ordinated CO; as is observed in the water-gas shift reaction, for which, at least, $[RhH(PPr^i_3)_3]$[18] and $[Rh(bipy)_2]Cl$[19] are known to be catalytically active.

In addition, at least in the case of reactions catalysed by $[PtH(PEt_3)_3]^+$, $[RhCl(PPh_3)_3]$, and $[Rh(bipy)_2]Cl$, the presence of sodium hydroxide will allow the formation of ethoxide ion * which readily metathesises with the chloride ion or binds to the cation to give co-ordinated ethoxide [equations (4) and (5)].

$$\text{M–Cl} + \text{OEt}^- \rightleftharpoons \text{M–OEt} + \text{Cl}^- \quad (4)$$

$$\text{M}^+ + \text{OEt}^- \rightleftharpoons \text{M–OEt} \quad (5)$$

The equilibrium constants for these reactions are likely to be much larger than for the direct oxidative addition of ethanol to the metal centre [equations (6) and (7)].

$$\text{M–Cl} + \text{HOEt} \rightleftharpoons \text{MOEt} + \text{HCl} \quad (6)$$

$$\text{M}^+ + \text{HOEt} \rightleftharpoons \text{MOEt} + \text{H}^+ \quad (7)$$

Support for this suggestion comes from observation of reactions catalysed by $[Rh(bipy)_2]Cl$. In the absence of base, the reaction solution retains the purple colour of the starting catalyst and little hydrogen is produced. In contrast, in the presence of base, the reaction solution rapidly becomes pale grey and hydrogen is produced at high rate.

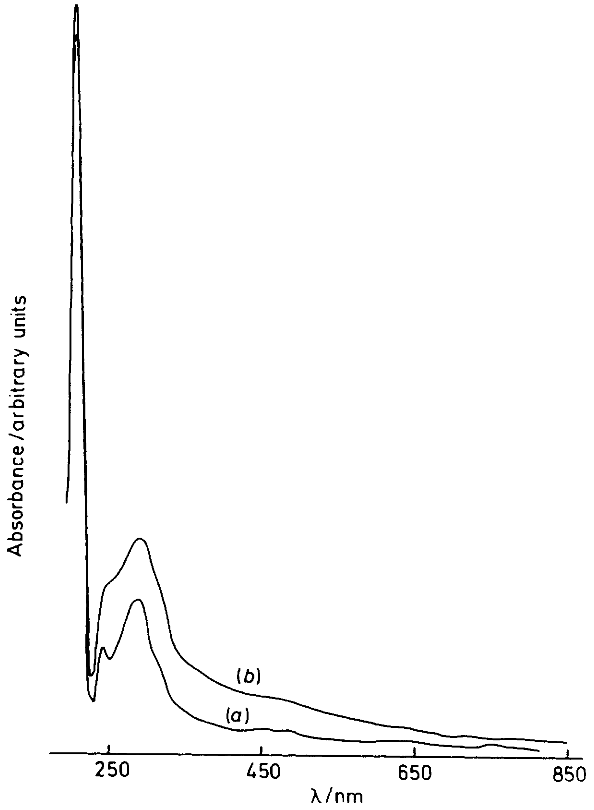

Figure 2. U.v.–visible spectra of (*a*) reaction solution after 2 h reaction at 120 °C, containing $[Rh(bipy)_2]Cl$, NaOH (1 mol dm^{-3}), and ethanol (5 cm^3); (*b*) solution obtained by addition of H_2 to $[Rh(bipy)_2]Cl$ in ethanol (5 cm^3) containing NaOH (1 mol dm^{-3}) at room temperature

Reaction of $[Rh(bipy)_2]Cl$ with hydrogen in ethanol produces a colourless solution but this rapidly returns to purple as the hydrogen is removed. In contrast, when the same reaction is carried out in ethanol containing NaOH, at the same concentrations that are used in the catalytic studies, a very pale grey solution is formed irreversibly. The u.v. spectrum of this solution is very similar to that of the solutions recovered after catalytic runs (see Figure 2). It has been reported[20] that the colourless product obtained from $[Rh(bipy)_2]Cl$ and H_2 in ethanol is $[RhH_2(bipy)_2]^+$, although little is known about its pK_a. We conclude that in basic ethanol $[RhH(bipy)_2]$ is the product and that this is also the major species in solution during ethanol dehydrogenation reactions catalysed by $[Rh(bipy)_2]Cl$.

In the reactions catalysed by $[RuH_2(X)(PPh_3)_3]$ ($X = N_2$ or PPh_3), the marked increase in rates of ethanol dehydrogenation in the presence of base may also arise in part from attack of ethoxide ion to give $[RuH_2(OEt)(PPh_3)_3]^-$ which would give the known $[RuH_3(PPh_3)_3]^-$ ion on loss of ethanal. This mechanism would be consistent with very recent studies which have shown[21] that this complex is an active hydrogenation catalyst precursor for ketones and that it can be protonated by alkanols to give $[RuH_4(PPh_3)_3]$ (see Scheme 1), which is known to contain co-ordinated molecular hydrogen[22] and very readily loses hydrogen in the presence of donors.[23] The situation is however complicated by decarbonylation of the product alkanal to give $[RuH_2(CO)(PPh_3)_3]$ which fortunately is itself an active ethanol dehydrogenation catalyst (62 turnovers per hour under similar conditions to those of Table 6). More detailed studies of this interesting system will be reported separately.

Synergistic Effects.—It is noteworthy that whereas base, $[Rh(dppp)_2]Cl$, or illumination individually do little to promote the production of hydrogen from ethanol catalysed by $[RhCl(PPh_3)_3]$, combinations of NaOH and either light or

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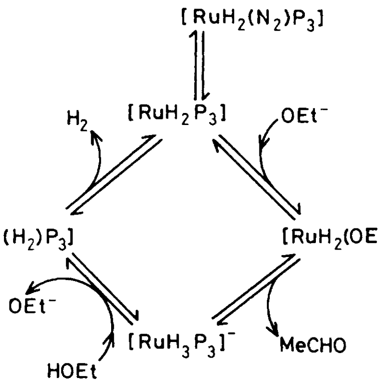
* Under the conditions of the catalytic reactions, *ca.* 96% of the base will be ethoxide, and ethanol is a slightly stronger acid than water (J. Hine and M. Hine, *J. Am. Chem. Soc.*, 1952, **74**, 5266; E. F. Caldin and G. Long, *J. Chem. Soc.*, 1954, 3737).

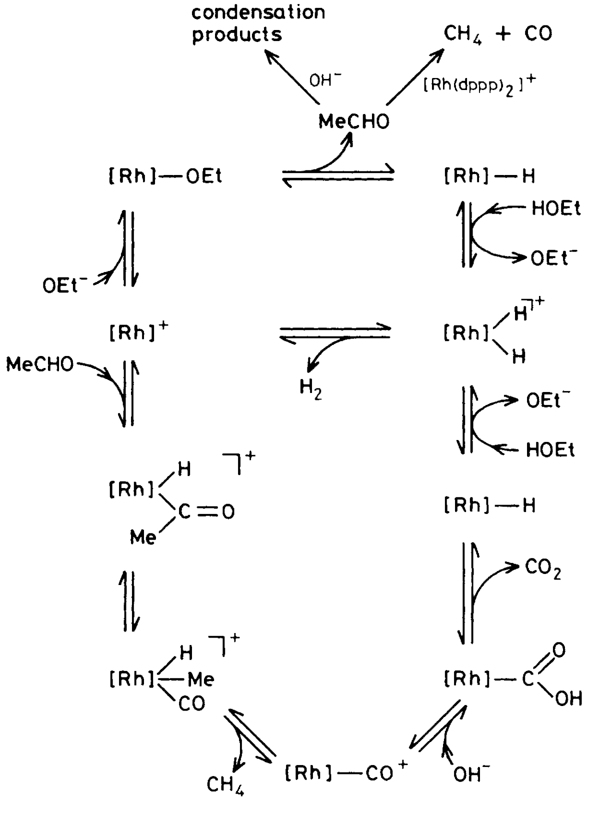


Scheme 1. Proposed mechanism for the production of hydrogen from ethanol catalysed by $[RuH_2(N_2)(PPh_3)_3]$; P = PPh_3

$[Rh(dppp)_2]Cl$ render the reaction genuinely catalytic. This can be attributed to the formation of free CO, either by decarbonylation of formed ethanal by $[Rh(dppp)_2]Cl$ or by photochemical loss of CO from $[RhCl(CO)(PPh_3)_2]$. The free CO is then scavenged by the base present in the known reaction to give sodium formate, and hence removed from the system. Consistent with this explanation, CO is not observed as a gas-phase product.

Reaction Mechanisms.—We have already identified that the role of base, which is essential in many cases for the successful dehydrogenation of ethanol, may be to promote aldol condensation, to allow attack of OH^- on co-ordinated CO, to scavenge free CO formed by ethanal decarbonylation and released thermally or photochemically from the metal, and to provide a source of ethoxide ion.

The exact mechanism of these reactions is likely to be highly complex, with many steps occurring simultaneously on the same, or different, metal atoms. However, a plausible mechanism for reactions catalysed by $[Rh(bipy)_2]Cl$, starting from the ethoxy complex generated by equations (4)—(7), is shown in Scheme 2. This is based on observations outlined in this paper as well as on mechanistic studies that have been carried out on, for example, catalytic hydrogenation, decarbonylation and water–gas shift reactions, as well as on stoicheiometric alcohol dehydrocarbonylation. The observation that $[RhH(bipy)_2]$ is the main species present during reactions catalysed by $[Rh(bipy)_2]Cl$ and that the hydride is in rapid equilibrium with $[RhH_2(bipy)_2]^+$, suggests that the rate-determining step is loss of H_2 from $[RhH_2(bipy)_2]^+$ but that, at the high pH involved in this study, protonation of $[RhH(bipy)_2]$ by ethanol is the dominant pre-equilibrium.* At lower $[OH^-]$, the first-order dependence on $[OH^-]$ presumably indicates that attack of ethoxide ion on $[Rh(bipy)_2]^+$ becomes the dominant pre-equilibrium.



Scheme 2. Proposed mechanism for the production of hydrogen from ethanol catalysed by $[Rh(bipy)_2]Cl$; [Rh] = $[Rh(bipy)_2]$

The relationships between studies reported in this paper and those that have been reported[19] on the use of $[Rh(bipy)_2]Cl$ to catalyse the water–gas shift reaction are worthy of comment. The water–gas shift studies show a marked pH dependence of the reaction, with maximum rates being observed at pH 3 and little or no activity above pH 5. This contrasts with our observation that CO_2 is produced from ethanol in reactions carried out at high pH. The loss of activity for water–gas shift catalysis at high pH has been attributed to a much lower rate of attack of OH^- on $[Rh(CO)(bipy)_2]^+$ than on $[RhH(CO)(bipy)_2]^{2+}$ (deprotonation occurring above pH 3) as well as to the formation of a dimeric, catalytically inactive complex, possibly of formula $[\{Rh(CO)(bipy)_2\}_2(CO)]^{2+}$ in the presence of excess CO. In the ethanol decomposition reaction, the absence of excess CO precludes the formation of the catalytically inactive complex. At the high pH values employed in these studies, the rate of attack of OH^- on $[Rh(bipy)_2(CO)]^+$ is then, apparently, rapid enough to allow formation of CO_2.

Finally, the reasons for the success of $[Rh(bipy)_2]Cl$ and $[RuH_2(N_2)(PPh_3)_3]$ as catalysts for hydrogen production from ethanol are noteworthy. First, as highly efficient catalysts for the hydrogenation of alkanals, it is expected that these complexes will also be efficient for dehydrogenation of primary alkanols. This, however, is not a sufficient criterion for ensuring rapid ethanol dehydrogenation. It is also important that the decarbonylation of product alkanal should be slow and/or that there is a process for the rapid removal of CO from the metal to prevent catalyst poisoning. In the case of $[Rh(bipy)_2]Cl$ it appears that CO abstraction is slow (*ca.* 10% the rate of H_2 formation), probably because the crucial intermediate, in decarbonylation, $[RhH(CO)(CH_3)(bipy)_2]^+$, must either be seven-co-ordinate or must contain a monodentate bipy ligand, both of which are high-energy intermediates. Finally, it appears that attack of OH^- on $[Rh(CO)(bipy)_2]^+$, once it is formed is rapid at high pH, presumably because of the positive charge on the complex. Together, these properties make for a highly efficient catalyst for alcohol dehydrogenation.

In the case of $[RuH_2(N_2)(PPh_3)_3]$, the efficiency of the catalyst may possibly be attributed to: (*i*) facile attack of OEt^- into a site on ruthenium made vacant by loss of N_2; (*ii*) facile protonation of $[RuH_3(PPh_3)_3]^-$ by alcohols; and (*iii*) the fact that hydrogen is lost from a *molecular* hydrogen complex.[22]

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* A decrease of rate at high $[OH^-]$ would be expected in this case, and, although our data do suggest a slight decrease, the accuracy is not sufficiently good to confirm that this occurs.

This means that assembly of the H–H bond occurs within the co-ordination sphere of the metal and the product of protonation contains H_2 already well down the reaction pathway to molecular H_2. We believe this to be a particularly important feature of this catalytic system, although further studies aimed at testing this hypothesis are currently being carried out.

Experimental

I.r. spectra were measured as Nujol mulls between CsI plates on a Perkin-Elmer 1310 spectrometer and n.m.r. spectra on Bruker associates WM 250 or WP 80 spectrometers operating in the Fourier transform mode with (for ^{31}P) proton-noise decoupling. For preparations of the catalysts all solvents were dried over sodium (C_6H_6) or by refluxing over sodium diphenylketyl [thf (tetrahydrofuran) and light petroleum, b.p. range 40—60 °C]. All reactions were carried out under dry, deoxygenated nitrogen.

The ethanol and sodium hydroxide were standard reagent grade and were used without further purification. $[RhCl(PPh_3)_3]$,[24] $[Rh(bipy)_2]Cl$,[20] $[RuH_2(PPh_3)_4]$,[25] and $[PtH(PEt_3)_3]OH$ [26,27] were prepared by standard literature methods.

Preparation of $[RuH_2(N_2)(PPh_3)_3]$.—$[RuCl_2(PPh_3)_3]$ (0.5 g, 0.435 mmol) was dissolved in a mixture of benzene (30 cm^3) and methanol (50 cm^3) under N_2. Dry, finely ground sodium borohydride (0.75 g, 0.02 mol) was added with rapid stirring. After 30 min the complex was precipitated as off-white microcrystals. Degassed methanol was added (50 cm^3) and the product filtered off and dried under vacuum. It was identified as $[RuH_2(N_2)(PPh_3)_3]$ by its i.r. spectrum. $\lambda_{max.}$ (cm^{-1}) 2 140 vs (lit.[28] 2 147 vs), $\nu(N{\equiv}N)$, 1 935 wbr (lit.[28] 1 947 br), 1 920 wbr (lit.[28] 1 917 br), ν(Ru–H).

Preparation of $[RhH(PPr^i_3)_3]$.—$RhCl_3{\cdot}3H_2O$ (0.75 g) was stirred for 18 h with PPr^i_3 (1.8 cm^3) in thf (35 cm^3) containing water (5 cm^3) and a few drops of concentrated HCl, after which the solvent was removed under vacuum at 45 °C. Thf (35 cm^3) was added to the solid which was reduced using Na/Hg amalgam (0.3 g, 6 cm^3) in the presence of PPr^i_3 (1 cm^3) for 18 h.

When the mixture had been allowed to settle, the solution was filtered. The amalgam was washed with thf (2 × 5 cm^3) and the washings added to the filtrate. The solvent was removed under vacuum and the resulting tar was extracted into light petroleum (3 × 15 cm^3). The volume was reduced to 10 cm^3 and PPr^i_3 (10 drops) added prior to crystallisation at −30 °C.

Yellow-orange crystals grew after 5 d which were collected by filtration and dried *in vacuo*. These were identified as $[RhH(PPr^i_3)_3]$ by their ^{31}P n.m.r. and i.r. spectra. ^{31}P; $\delta - 58.8$ [d, $J_{Rh-P} = 157$ Hz (lit.[29] 157 Hz)]. I.r. 1 970wbr cm^{-1} (lit.[29] 1 975 cm^{-1}), ν(Rh–H).

Catalytic Reactions.—All reactions were carried out in glass tubes of approximately 120 cm^3 capacity fitted with a screw on cap, tap adaptor for connection to a vacuum line, and septum for gas sampling.

Degassed ethanol (5 cm^3) containing the catalyst (10^{-4}—10^{-3} mol dm^{-3}) and sodium hydroxide (0—1 mol dm^{-3}) were placed in the vessel described above, which had previously been filled with nitrogen. The vessel was then closed and the portion of the vessel containing the liquid was placed in an oil bath at the required reaction temperature. The mixture was stirred magnetically at this temperature for the given reaction time (usually 2 h) and then cooled in air. Photochemical reactions were carried out in the same reactors, with light from a 500 W tungsten halogen lamp being focused onto the solution.

The gas was sampled (0.5 cm^3) with a gas-tight syringe and analysed by g.l.c. (gas–liquid chromatography) for H_2, CH_4, and CO. For reactions carried out in the presence of base, concentrated HCl (2 cm^3) was added by injection through the septum and, after all gas evolution was complete, the gases were reanalysed for CO_2 by g.l.c. All reactions were carried out in duplicate and reproducibility of $\pm 5\%$ was observed.

In some cases the volumes of evolved gases were measured with a gas burette and were found to correspond to the volumes obtained by g.l.c.

Peak heights from g.l.c. were converted to percentages of gas in the vessel by calibration with standards of known composition, due account being taken for non-linearities in the response of the detector at different concentrations. These percentages were converted into volumes of gas evolved, knowing the volume of the reaction vessel.

In some reactions, particularly those involving long reaction times, significant increases in pressure within the reaction vessel were observed. In all cases, the reactions were sampled at the pressure within the cell as 0.5 cm^3 samples at that pressure. It can readily be shown that peak heights obtained in this way relate directly to the volume of hydrogen produced, corrected to 1 atm (10^5 Pa).

All gases were analysed as 0.5 cm^3 samples by g.l.c. using Philips Scientific Series 104 or 204 gas–liquid chromatographs and a thermal conductivity detector. Columns were molecular series 4A (H_2 using N_2 as carrier gas), Chromosorb 102 (CO, CO_2 using He as carrier gas), or Carbosieve 100/120S [CH_4, using N_2 as carrier gas and a f.i.d. (flame ionisation detector)].

Test for Homogeneity.—A reaction catalysed by $[Rh(bipy)_2]Cl$ was tested for homogeneity by stirring with liquid mercury which is known to inhibit colloidal catalysis. After heating for 30 min the cell was analysed for H_2 (57.7 turnovers) and then cooled. Mercury was added and the reaction stirred for 10 min. The solution was filtered away from the mercury and the reaction re-run for 30 min. Hydrogen corresponding to 55.2 turnovers was detected in the gas phase, suggesting that the reaction was genuinely homogeneous.

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References

1 See, for example, E. M. Goodger, 'Alternative Fuels, Chemical Energy Resources,' Macmillan, London, 1980.
2 See, C. A. McAuliffe, 'Transition Metal Complexes of Phosphorus, Arsenic and Antimony Ligands,' Macmillan, London, 1973 and refs. therein.
3 B. N. Chaudret, D. J. Cole-Hamilton, R. S. Nohr, and G. Wilkinson, *J. Chem. Soc., Dalton Trans.*, 1977, 1546 and refs. therein.
4 E. Delgado-Lieta, M. A. Luke, R. F. Jones, and D. J. Cole-Hamilton, *Polyhedron*, 1982, **1**, 839.
5 D. Morton and D. J. Cole-Hamilton, *J. Chem. Soc., Chem. Commun.*, 1987, 248.
6 A. Dobson and S. D. Robinson, *Inorg. Chem.*, 1977, **16**, 137.
7 C. W. Jung and P. E. Garrou, *Organometallics*, 1982, **1**, 658.
8 L. H. Pignolet and D. H. Doughty, *J. Am. Chem. Soc.*, 1978, **100**, 7083.
9 G. Mestroni, R. Spogliarich, A. Camus, F. Martinelli, and G. Zassinovich, *J. Organomet. Chem.*, 1978, **157**, 345.
10 J. F. Young, J. A. Osborn, F. H. Jardine, and G. Wilkinson, *Chem. Commun.*, 1965, 31.
11 T. Yoshida, T. Okano, and S. Otsuka, *J. Chem. Soc., Chem. Commun.*, 1979, 870.
12 R. A. Sanchez-Delgado, A. Andriollo, O. L. de Ochoa, T. Suarez, and N. Valencia, *J. Organomet. Chem.*, 1981, **209**, 77.

13 F. Pennella, *J. Organomet. Chem.*, 1974, **65**, C17.

14 D. A. Wink and P. C. Ford, *J. Am. Chem. Soc.*, 1987, **109**, 436.

15 G. L. Geoffroy, D. A. Denton, M. E. Keeney, and R. R. Bucks, *Inorg. Chem.*, 1976, **15**, 2382.

16 G. L. Geoffroy, *Prog. Inorg. Chem.*, 1980, **27**, 123.

17 D. Morton and D. J. Cole-Hamilton, *J. Chem. Soc., Dalton Trans.*, submitted for publication.

18 T. Yoshida, T. Okano, Y. Ueda, and S. Otsuka, *J. Am. Chem. Soc.*, 1981, **103**, 3411.

19 D. Mahajan, C. Creutz, and N. Sutin, *Inorg. Chem.*, 1985, **24**, 2063.

20 M. Chou, C. Creutz, D. Mahajan, N. Sutin, and A. P. Zipp, *Inorg. Chem.*, 1982, **21**, 3989.

21 D. E. Linn and J. Halpern, *J. Am. Chem. Soc.*, 1987, **109**, 2969.

22 R. H. Crabtree and D. G. Hamilton, *J. Am. Chem. Soc.*, 1986, **108**, 3124.

23 D. J. Cole-Hamilton and G. Wilkinson, *Nouv. J. Chim.*, 1977, **1**, 141.

24 J. A. Osborn, F. H. Jardine, J. F. Young, and G. Wilkinson, *J. Chem. Soc. A*, 1966, 1711.

25 R. Young and G. Wilkinson, *Inorg. Synth.*, 1977, **XVII**, 75.

26 R. A. Schunn, *Inorg. Chem.*, 1976, **15**, 208.

27 D. H. Gerlach, A. R. Kane, G. W. Parshall, J. P. Jesson, and E. L. Muetterties, *J. Am. Chem. Soc.*, 1971, **93**, 3543.

28 W. H. Knoth, *Inorg. Synth.*, 1974, **XV**, 31.

29 T. Yoshida, T. Okano, D. L. Thorn, T. H. Tulip, S. Otsuka, and J. A. Ibers, *J. Organomet. Chem.*, 1979, **181**, 183.

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