Rapid Thermal Hydrogen Production from Alcohols catalysed by [Rh(2,2′-bipyridyl)$_2$]Cl

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Turnover numbers of up to 100 h^{-1} are observed for hydrogen production from alcohols catalysed by [Rh(2,2′-bipyridyl)$_2$]Cl.

The catalytic production of hydrogen from alcohols has been the subject of substantial research interest in recent years since it offers a means of obtaining a useful fuel from industrial waste alcohol, or of producing hydrogen from biomass-derived materials. Hydrogen so produced can then be used directly as a fuel, or for the hydrogenation of biomass to a high grade liquid fuel.[1]

Most reported alcohol dehydrogenations involve the direct formation of hydrogen and alkanals (or ketones) but the unfavourable thermodynamic nature of this reaction (equilibrium 1) means that yields of hydrogen in a closed system will be low, and the increasing rate of the back reaction as [alkanal] increases will mean that the rate of hydrogen production will also be low. In general, hydrogen is produced at a rate corresponding to ~1—20 catalyst turnovers h^{-1}.[2,3]

$$C_2H_5OH \rightleftharpoons CH_3CHO + H_2;\ \Delta G^\circ + 41.2\ \text{kJ mol}^{-1} \quad (1)$$

Some improvements may be gained by working in an open system but more dramatic increases in rates and yields for hydrogen production may require initiation of a different decomposition reaction such as (2), in which not only are 3 moles of usable fuel ($2H_2 + CH_4$) formed per mole of alcohol but also the thermodynamics for the forward reaction are highly favourable.

$$C_2H_5OH + H_2O \rightleftharpoons CH_4 + 2H_2 + CO_2;\ \Delta G^\circ\ -33.3\ \text{kJ mol}^{-1} \quad (2)$$

For a catalyst or series of catalysts to promote reaction (2) it is necessary to catalyse (i) the dehydrogenation of the alcohol, (ii) the decarbonylation of the alkanal, and (iii) the water-gas shift reaction.

We now report the first example of a homogeneous catalyst, [Rh(bipy)$_2$]Cl (bipy = 2,2′-bipyridyl), which is capable of thermally catalysing all these reactions and we demonstrate that the rates of hydrogen production using this catalyst are dramatically higher than has previously been observed. $[PtH(PEt_3)_3]^+$ catalyses similar reactions for 2-hydroxypropanoic acid,[4] although it is not capable of decarbonylating ethanol.[3]

A reaction similar to (2) has been observed[5] in the photochemical production of H_2 and CO_2 from methanol catalysed by Pt/TiO$_2$, whilst we have previously reported[6] the photochemical decomposition of ethanol to CH_4, H_2, and CO catalysed by [RhH(CO)(PPr$^i_3$)$_2$].

The reaction of ethanol (5 cm^3) containing water (5% v/v) and NaOH (5×10^{-3} mol) with [Rh(bipy)$_2$]Cl (5×10^{-6} mol) at 120 °C in a closed system for 3 h produces 34.4 cm^3 of hydrogen. This corresponds to ~100 catalyst turnovers h^{-1}.† Methane (3.8 cm^3) is also produced and addition of acid to the spent reaction solution produces CO_2 (3.4 cm^3) suggesting

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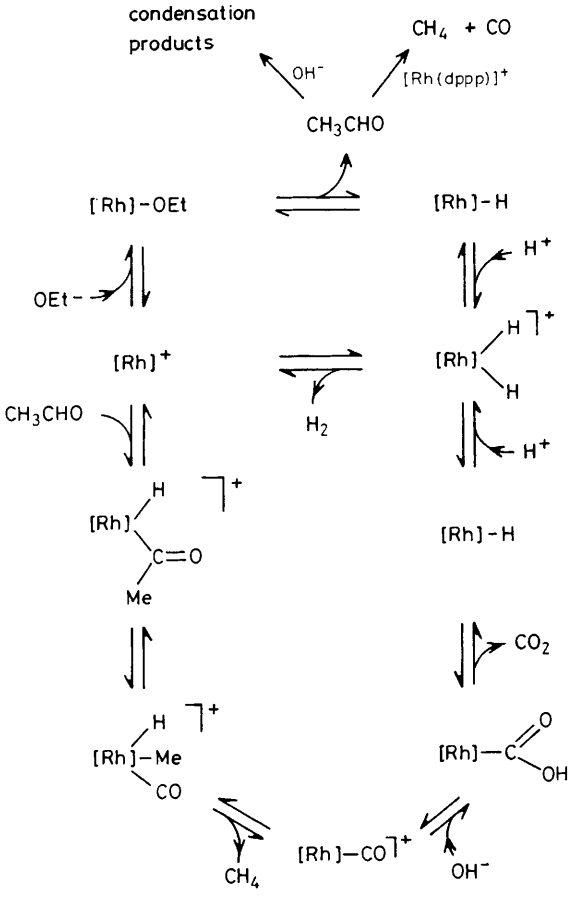
† The catalyst, [Rh(bipy)$_2$]Cl, has considerable longevity; 1546 turnovers were observed in 24 h (average 64 h^{-1}). The slight drop in rate with time can be attributed to a build-up of reaction products in the closed reaction system.



Scheme 1. Proposed mechanism for the decomposition of ethanol catalysed by $[Rh(bipy)_2]Cl$; [Rh] = $Rh(bipy)_2$.

that methane and CO_2 are formed in the same stoicheiometry but at a rate only 10% of that for hydrogen production.

Analysis of the liquid phase products from an experiment before the addition of acid to release CO_2 shows that ethanal and its condensation products, 3-hydroxybutanal and but-3-enal, are formed. In the presence of $[Rh(dppp)_2]Cl$ (5×10^{-6} mol dm^{-3}) [dppp = 1,3-bis-(diphenylphosphino)propane], a known alkanal decarbonylation catalyst,[7] CO is also formed as a product of the catalytic reaction. The rates of hydrogen and CO_2 production are unaffected.

Preliminary studies suggest that the reaction occurs with a minimal induction period although the initially purple solution of $[Rh(bipy)_2]Cl$ rapidly becomes colourless and remains clear and colourless throughout the reaction. We are currently attempting to identify the species present during the catalytic reaction but note that species such as $[Rh(bipy)_2H_2]^+$ are colourless.[8]

The production of the various products can be rationalised in terms of the processes in Scheme 1, with an initial dehydrogenation of ethanol. The ethanal so produced can then undergo base-catalysed aldol condensation, decarbonylation catalysed by $[Rh(dppp)_2]Cl$, or decarbonylation by $[Rh(bipy)_2]Cl$. In the last case, it appears that CO is not released from the metal thermally but, instead, nucleophilic attack of hydroxide ion on co-ordinated CO is followed by loss of CO_2, protonation, and loss of hydrogen.

Table 1. Hydrogen production from various alcohols (5 cm^3) catalysed by $[Rh(bipy)_2]Cl$ (10^{-3} mol dm^{-3}).

Substrate	[NaOH] /mol dm^{-3}	T/°C	Rate of H_2 production /mol [mol cat]$^{-1}$ h^{-1}
Methanol	1.0	120	7
Ethanol	1.0	120	96
Propan-2-ol	0.25	120	115
Butane-2,3-diol	1.0	140	115

The similarity of the last series of reactions to those of the water-gas shift reaction make it pertinent to compare the results obtained in this work with those obtained for the water-gas shift reaction catalysed by $[Rh(bipy)_2]Cl$. Detailed studies[9] of the water-gas shift reaction suggest that H_2 and CO_2 should not be formed under the highly alkaline conditions employed in this work.

The failure to observe water-gas shift chemistry under alkaline conditions has been attributed[9] to the low rate of attack of hydroxide ion on $[Rh(CO)(bipy)_2]^+$, compared with $[RhH(CO)(bipy)_2]^{2+}$, which is only present at significantly acid pH, and to the formation of a catalytically inactive species, possibly $[\{Rh(bipy)(CO)\}_2(CO)]^{2+}$, in alkaline solution under CO.

In the ethanol decomposition reactions reported here, formation of the inactive species will not occur since there is insufficient carbon monoxide present, and the rate of attack of hydroxide ion on $[Rh(CO)(bipy)_2]^+$ will be higher because of the high concentration of hydroxide ion present in solution. Fortunately, the high basicity of $[Rh(bipy)_2H]$ will ensure[8] that it is significantly protonated even under the basic conditions employed in this study. It is interesting to note that the rate of CO_2 production from ethanol is comparable with the highest rates observed[9] for the water-gas shift reaction under any conditions of pH, when allowance is made for the rather higher temperatures used in the ethanol decomposition reactions.

$[Rh(bipy)_2]Cl$ is also an efficient catalyst for thermal hydrogen production from propanol and butane-2,3-diol, but much less so from methanol (see Table 1).

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