# Dehydrogenation of Methanol in the Liquid Phase with a Homogeneous Ruthenium Complex Catalyst

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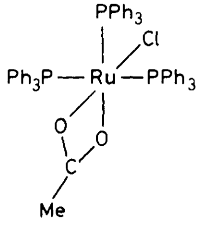
Catalytic dehydrogenation of methanol occurs in solution by use of a homogeneous ruthenium complex, $[Ru_2(OAc)_4Cl]$–t-phosphine, or mononuclear ruthenium(II) complexes, which can be isolated from the reaction solution as catalysts.

Dehydrogenation of methanol [equation (1)] has attracted considerable interest, because the product is free from water (in contrast to oxidative dehydrogenation with $O_2$), and thus giving a solution stable against gelation. If this endothermic reaction is conducted in solution it can proceed under very mild conditions, with dihydrogen separating as a gas. Although several homogeneous catalysts which dehydrogenate secondary or primary alcohols with high carbon chain length ($\geq C_2$) are known,[1—3] methanol is dehydrogenated efficiently only under photocatalytic conditions.[4] We report here the first example of thermal dehydrogenation of methanol in solution with a homogeneous complex catalyst, $[Ru_2(OAc)_4Cl]$–t-phosphine.[†]

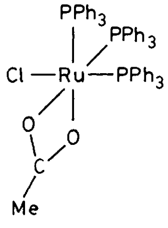
$$MeOH \longrightarrow HCHO + H_2 \qquad (1)$$

On heating the reaction solution of $[Ru_2(OAc)_4Cl]$ and t-phosphine, $PR_3$, dissolved in anhydrous methanol, the colour changes from brown to orange-yellow, indicating the formation of mononuclear complexes. From the orange-yellow solution, a mononuclear diamagnetic ruthenium(II) complex was isolated, $[Ru(OAc)Cl(PR_3)_3]$, $PR_3 = PPh_3$ and $PEtPh_2$, 60% yield.[‡]

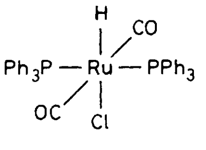
The magnitude of $^2J(PP)$ in the $^{31}P$ n.m.r. spectrum indicates that two phosphines (A and X in an $A_2X$ spin system) are in the *cis* configuration.[5] The $^{13}C$ n.m.r. spectrum is consistent with the existence of an acetate ligand. Based on these spectroscopic characteristics together with analysis data, the structure of the isolated complexes is formulated as (**1**) or (**2**) (shown for the $PPh_3$ complex).



(**1**)



(**2**)



(**3**)

The catalytic activity of the composite catalysts, $[Ru_2(OAc)_4Cl]$–$PR_3$, and the isolated complexes are summarized in Table 1. Consistent with the observed colour change of the reaction solution, the electronic spectrum indicated that cleavage of the binuclear complex occurred almost immediately upon heating. Thus the mononuclear complexes were the active catalytic species.

As Table 1 shows, the mononuclear $PEtPh_2$ complex is the most active; the difference betweeen it and the composite system is small. Contrastingly the mononuclear $PPh_3$ complex is the least active but the difference between it and the corresponding composite system is large. Therefore the more active unidentified catalyst species is probably contained in the supernatant solution.

As the reaction proceeds, the initial product formaldehyde (and its dimethyl acetal) was gradually converted into secondary products including methyl formate, as detected by gas chromatography.

Addition of free acid (AcOH) enhanced the catalytic activity of $[Ru(OAc)Cl(PEtPh_2)_3]$, but with progressive inhibition at higher concentrations (Table 2).The observed acceleration may be explained in terms of the protonation of a metal-hydride intermediate[2] to generate $H_2$. In the presence

**Table 1.** Rates of dihydrogen evolution for the liquid phase dehydrogenation of methanol with ruthenium complex catalysts.[a]

| Catalyst | Turnover frequency/$h^{-1}$ [b] |
|---|---|
| $[Ru_2(OAc)_4Cl]$–$PPh_3$ | 0.20 |
| $[Ru(OAc)Cl(PPh_3)_3]$ | 0.05 |
| $[Ru_2(OAc)_4Cl]$–$PEtPh_2$ | 0.59 |
| $[Ru(OAc)Cl(PEtPh_2)_3]$ | 0.58 |
| $[Ru_2(OAc)_4Cl]$–$PEt_2Ph$ | 0.47 |

[a] At 339 K under reflux. Ruthenium complex 0.1 mmol, methanol 500 $dm^3$. $[PR_3]/[Ru_2] = 7$ for composite systems. [b] Based on the total amount of ruthenium. The time–conversion curve was linear within *ca.* 17 h of the start of the volumetric analysis.

**Table 2.** Effect of the addition of acetic acid on the rate of dihydrogen evolution for the liquid phase dehydrogenation of methanol with $[Ru(OAc)Cl(PEtPh_2)_3]$ catalyst.[a]

| [AcOH]/[Ru] ratio | Initial turnover frequency/$h^{-1}$ [b] | Reaction time/h | Total turnover number |
|---|---|---|---|
| 0.0 | 0.60 | 65.5 | 22.6 |
| 0.5 | 0.83 | 64.5 | 24.5 |
| 1.0 | 0.95 | 68.5 | 29.0 |
| 2.0 | 0.96 | 90.0 | 34.0 |
| 5.1 | 0.90 | 70.5 | 32.2 |
| 20.0 | 0.84 | 42.0 | 29.7 |

[a] At 339 K under reflux. Ruthenium complex 0.1 mmol, methanol 400 $dm^3$. [b] Based on the total amount of ruthenium. The time–conversion curve was linear within *ca.* 17 h of the start of the volumetric analysis.

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[†] All operations were carried out in an inert atmosphere.

[‡] *Selected spectroscopic data:* n.m.r. $^{31}P$ (relative to 85% $H_3PO_4$) $PR_3 = PPh_3$: δ 43.8 (2P) and 77.7 p.p.m. (1P), $J$(PP) 27.3 Hz; $PR_3 = PEtPh_2$: δ 39.0 (2P) and 69.0 p.p.m. (1P), $J$(PP) 29.2 Hz; $^{13}C$ (OAc) $PR_3 = PPh_3$: δ 182.2 and 24.3; $PR_3 = PEtPh_2$: δ 187.1 and 25.8. Satisfactory elemental analyses were obtained.

of an excess of free acid this process would be replaced by a preceding one as the rate determining step.

Deactivation of the catalyst appears to occur, at least in part, by its reaction with formaldehyde product (decarbonylation), since (**3**) was isolated as white crystals after loss of activity.§

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§ *Data for* (**3**): $\nu_{max.}$ 1926s and 1976w (CO) and 2042 (RuH) cm$^{-1}$; n.m.r. $^1$H ($CD_2Cl_2$) δ −16.5, *J*(PH) 19.7 Hz; $^{31}$P ($CD_2Cl_2$) δ 45.2 p.p.m.

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