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

Sumio Shinoda, Hiroaki Itagaki, and Yasukazu Saito*

Institute of Industrial Science, University of Tokyo, 22–1, Roppongi 7 Chome, Minato-ku, Tokyo 106, Japan

Catalytic dehydrogenation of methanol occurs in solution by use of a homogeneous ruthenium complex, $[Ru_2(OAc)_4CI]$ -t-phosphine, or mononuclear ruthenium(#) 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, [Ru₂(OAc)₄Cl]-t-phosphine.[†]

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

On heating the reaction solution of $[Ru_2(OAc)_4Cl]$ and t-phosphine, PR₃, dissolved in anhydrous methanol, the colour changes from brown to orange-yellow, indicating the formation of mononuclear complexes. From the orangeyellow solution, a mononuclear diamagnetic ruthenium(II) complex was isolated, $[Ru(OAc)Cl(PR_3)_3]$, PR₃ = PPh₃ and PEtPh₂, 60% yield.[‡]

The magnitude of ${}^{2}J(PP)$ in the ${}^{31}P$ n.m.r. spectrum indicates that two phosphines (A and X in an A₂X 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,



† All operations were carried out in an inert atmosphere.

‡ Selected spectroscopic data: n.m.r. ³¹P (relative to 85% H₃PO₄) PR₃ = PPh₃: δ 43.8 (2P) and 77.7 p.p.m. (1P), J(PP) 27.3 Hz; PR₃ = PEtPh₂: δ 39.0 (2P) and 69.0 p.p.m. (1P), J(PP) 29.2 Hz; ¹³C (OAc) PR₃ = PPh₃: δ 182.2 and 24.3; PR₃ = PEtPh₂: δ 187.1 and 25.8. Satisfactory elemental analyses were obtained. the structure of the isolated complexes is formulated as (1) or (2) (shown for the PPh₃ complex).

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 PEtPh₂ complex is the most active; the difference betweeen it and the composite system is small. Contrastingly the mononuclear PPh₃ 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 intermediate² to generate H₂. 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-1t
[Ru ₂ (OAc) ₄ Cl]-PPh ₃	0.20
[Ru(OAc)Cl(PPh ₃) ₃]	0.05
Ru ₂ (OAc) ₄ Cl]-PEtPh ₂	0.59
[Ru(OAc)Cl(PEtPh ₂) ₃]	0.58
[Ru ₂ (OAc) ₄ Cl]–PEt ₂ Ph	0.47

^a At 339 K under reflux. Ruthenium complex 0.1 mmol, methanol 500 dm³. [PR₃]/[Ru₂] = 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 ^{-1b}	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 dm³. ^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.

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. 1H (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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