

Liquid-Phase Dehydrogenation of Methanol with Homogeneous Ruthenium Complex Catalysts

Hiroaki ITAGAKI, Sumio SHINODA,[†] and Yasukazu SAITO*

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

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Catalytic dehydrogenation of methanol proceeded with homogeneous ruthenium(II) complexes, yielding formaldehyde and dihydrogen as primary products under refluxing conditions of the solution. The effects of additives on the initial reaction rate were examined for lithium chloride, lithium acetate, acetic acid and ethyldiphenylphosphine. A catalyst complex, $[\text{Ru}(\text{OAc})\text{Cl}(\text{PEtPh}_2)_3]$, was deactivated gradually by the displacement of the bidentate OAc ligand with H and CO ligands during the reaction. These cis-disposed sites would be used for splitting the C–H bonds. A catalytic reaction cycle is proposed, in which such processes are included as solvolysis of the catalyst complex, β -H elimination from the OCH_3 ligand and attack of acetic acid on the hydride intermediate to generate dihydrogen.

Dehydrogenation of methanol, yielding formaldehyde and dihydrogen, is thermodynamically less favorable ($\Delta G^\circ = 64.0 \text{ kJ mol}^{-1}$) than oxidative dehydrogenation ($\Delta G^\circ = -173.2 \text{ kJ mol}^{-1}$). The endothermic reaction ($\Delta H^\circ = 130.4 \text{ kJ mol}^{-1}$) of Eq. 1 proceeds, however, in the liquid phase under very mild conditions, since most of the product dihydrogen is removed from the reaction medium owing to its limited solubility.¹⁾



Homogeneous catalysts for alcohol dehydrogenation evolving dihydrogen have been extensively studied both thermally²⁾ and photochemically³⁾ except for methanol. Dobson and Robinson proposed a reaction mechanism for (trifluoroacetato)ruthenium(II) complexes, $[\text{Ru}(\text{OAcF})_2\text{CO}(\text{PPh}_3)_2]$,^{2c)} the catalytic activity of which was compared later among a series of (trifluoroacetato)ruthenium(II) complexes.^{2e)}

As for the methanol photocatalytic dehydrogenation was explored to give not only carbon monoxide^{3d)} but also ethylene glycol,^{4a–c)} dimethoxymethane,^{4b,c)} and products related to its reaction counterpart. Homogeneous catalytic dehydrogenation of methanol to yield organic products without photoirradiation has never been reported until some ruthenium(II) complexes were revealed to be active. Formaldehyde was formed under refluxing conditions (65 °C) with $[\text{Ru}_2(\text{OAc})_4\text{Cl}]$ mixed with tertiary phosphine, or with $[\text{Ru}(\text{OAc})\text{Cl}(\text{PEtPh}_2)_3]$.⁵⁾ Independently, the catalytic activity of $[\text{RuCl}_2(\text{PPh}_3)_3]$ was shown by Smith et al. to form methyl formate as the main product together with dimethoxymethane at 150 °C in good stoichiometric correlation with dihydrogen.⁶⁾

In the present work, a reaction scheme is given for the acetato and phosphine-coordinated ruthenium(II) complexes based on the experimental details concern-

ing the time course of the product distribution, the effect of additives on the initial rates and the structural change of a catalyst complex during deactivation.

Experimental

Procedure. All the operations of catalyst syntheses and dehydrogenation reactions were conducted under argon or nitrogen atmosphere. Degassing by repeated freeze-pump-thaw cycles was necessary for methanol, as the catalyst complexes were air sensitive in solution. The gas evolution reaction from the solution of $[\text{Ru}_2(\text{OAc})_4\text{Cl}]$ (0.0474 g, 0.1 mmol) admixed with triphenylphosphine (0.1836 g, 0.7 mmol) (designated as 'composite-type' hereafter) or of $[\text{Ru}(\text{OAc})\text{Cl}(\text{PEtPh}_2)_3]$ (0.1677 g, 0.2 mmol) in methanol (200 ml) was performed under refluxing conditions in a flask (500 ml) connected to a gas buret (50 ml) through a condenser. All the products, other than dihydrogen, were condensed by using an ethylene glycol/water mixture cooled to -15 – -20 °C with a circulating cooler (Taiyo Kagaku Kogyo Ltd., Type CML-III). The volume increase due to the gas evolution was started to plot against the elapsed time after thermal equilibrium had been attained in the closed reaction system at atmospheric pressure. After the reaction, the solution was chilled with ice in order to perform GC analysis of the liquid components without loss by evaporation of dehydrogenated products.

Spectra. Infrared spectra using pressed potassium bromide pellets were taken on a Hitachi 260-10 spectrophotometer from 650 to 4000 cm^{-1} with polystyrene reference. Proton, $^{31}\text{P}\{^1\text{H}\}$ and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were recorded on a Jeol JNM-FX60Q spectrometer operating in the FT mode at 59.80, 24.21, and 15.04 MHz, respectively. ^{31}P chemical shifts were referenced to an external standard of 85% H_3PO_4 , with the downfield chemical shifts taken to be positive, whereas ^1H and ^{13}C NMR spectra were referenced internally to the CH_2Cl_2 solvent and converted to the TMS scale by using the CH_2Cl_2 chemical shifts of +5.3 and +54.2 ppm, respectively. GC analysis was performed on a Yanagimoto G-3800 gas chromatograph using GP-54 and active carbon columns. The sensitivity of formaldehyde detection was enhanced by adopting a methane converter with the $\text{Ru}/\text{Al}_2\text{O}_3$ catalyst, which was added to a Porapak-T column in the Ohkura Rikagaku GC 103 gas chromatograph.

[†] Present address: Department of Industrial Chemistry, Faculty of Engineering, Seikei University, 3-1 Kichijyoji-Kitamachi 3 Chome, Musashino-Shi, Tokyo 180.

Syntheses. $[\text{Ru}_2(\text{OAc})_4\text{Cl}]$ was prepared by the literature method.⁷ Ruthenium(III) trichloride trihydrate and tertiary phosphine from commercial sources were used without further purification.

$[\text{Ru}(\text{OAc})\text{Cl}(\text{PPh}_3)_3]$ was synthesized from $[\text{Ru}_2(\text{OAc})_4\text{Cl}]$ and PPh_3 . A methanol (500 ml) solution of $[\text{Ru}_2(\text{OAc})_4\text{Cl}]$ (0.437 g, 1.00 mmol) and PPh_3 (1.836 g, 7.00 mmol) was refluxed for 1 h, after which part of the solvent methanol was removed by evacuation. When the solution was allowed to stand at -20°C overnight, an orange crystal was precipitated. Its isolation was performed by decantation, washing with methanol, and drying in vacuo. Yield 0.81 g, 82%. Found: C, 70.61; H, 4.94; P, 9.20%. Calcd for $\text{C}_{56}\text{H}_{48}\text{P}_3\text{O}_2\text{ClRu}$: C, 68.46; H, 4.92; P, 9.46%. ^{31}P NMR: $\delta=43.8(2\text{P})$ and $77.7(1\text{P})$, $J(\text{PP})$ 27.3 Hz; $^{13}\text{C}(\text{OAc})$: $\delta=182.2$ and 24.3 .

$[\text{Ru}(\text{OAc})\text{Cl}(\text{PEtPh}_2)_3]$ was synthesized in a similar manner. Yield 0.58 g, 69%. Found: C, 63.03; H, 5.62; P, 10.81%. Calcd for $\text{C}_{44}\text{H}_{48}\text{P}_3\text{O}_2\text{ClRu}$: C, 63.04; H, 5.77; P, 10.84%. ^{31}P NMR: $\delta=40.0$; $^{13}\text{C}(\text{OAc})$: $\delta=187.1$ and 25.8 .

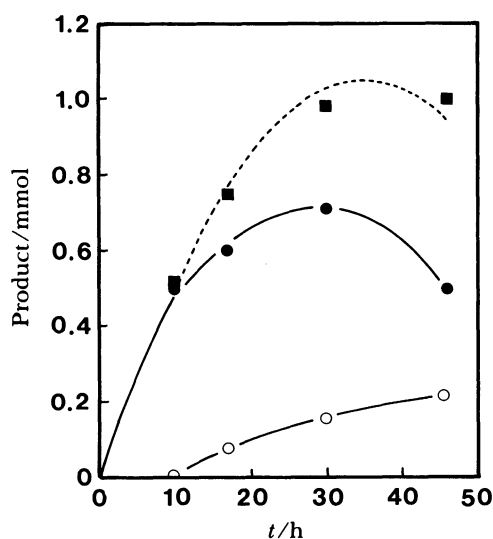


Fig. 1. Time-course plot of product distribution for methanol dehydrogenation with $[\text{Ru}_2(\text{OAc})_4\text{Cl}]/\text{PPh}_3$ catalyst. $[\text{Ru}_2(\text{OAc})_4\text{Cl}]$ 0.5 mmol dm^{-3} , $[\text{PPh}_3]$ 3.5 mmol dm^{-3} , methanol 200 ml , 65°C (refluxing), (●) HCHO , (○) HCOOCH_3 , (■) H_2 . (-----) amount of H_2 equivalence calculated from the dehydrogenated products ($[\text{HCHO}] + [\text{HCOOCH}_3] \times 2$).

Results and Discussion

Product Distribution. The change of product distribution in the composite-type ($[\text{Ru}_2(\text{OAc})_4\text{Cl}]/\text{PPh}_3$; $[\text{PPh}_3]/[\text{Ru}_2]=7.0$) catalyst solution during the reaction was shown in Fig. 1. The reaction product in the initial 10 h period was only formaldehyde (5.2 turnovers), whereas methyl formate was formed as the secondary product, without accompanying dimethoxymethane in this catalyst solution. Neither carbon monoxide nor methane was detected in the evolved gas.

Excellent stoichiometry between dihydrogen and the sum of the dehydrogenated products was ascertained throughout the reaction.

Products during the 17 h reaction in the catalyst solutions of both the composite-type, $[\text{Ru}_2(\text{OAc})_4\text{Cl}]/\text{PR}_3$ ($\text{PR}_3=\text{PPh}_3$, PEtPh_2 , and PET_2Ph ; $[\text{PR}_3]/[\text{Ru}_2]=7.0$), and the mononuclear type, $[\text{Ru}(\text{OAc})\text{Cl}(\text{PEtPh}_2)_3]$ are summarized in Table 1. Formaldehyde was found for all the catalysts. Methyl formate was found as the main product for the ruthenium complex coordinated with PEtPh_2 or PET_2Ph . Some dimethoxymethane was detected in these catalyst solutions after the 17 h reaction.

Excellent stoichiometric coincidence of dihydrogen toward the sum of the dehydrogenated products was observed throughout the catalysts.

Initial Reaction Rate Dependence on Catalyst Concentration. The reaction rates at the refluxing temperature (65°C) for the methanol solution of $[\text{Ru}(\text{OAc})\text{Cl}(\text{PEtPh}_2)_3]$ were almost time-independent over a concentration range from 0.5 mmol dm^{-3} to 5.0 mmol dm^{-3} during the initial 17 h period (Fig. 2).

The dependence of the initial rate on catalyst concentration was linear below 0.5 mmol dm^{-3} and deviated to decrease from linearity at higher concentration ($>1.0 \text{ mmol dm}^{-3}$). A similar rate dependence on the catalyst concentration was noted for the $[\text{RuCl}_2(\text{PPh}_3)_3]$ complex previously in the dehydrogenation of alcohol to evolve dihydrogen⁹ and hydrogen transfer processes.⁹

Catalyst Deactivation Due to Structural Change.

The catalytic activity of $[\text{Ru}(\text{OAc})\text{Cl}(\text{PEtPh}_2)_3]$ for

Table 1. Product Distribution in Catalytic Methanol Dehydrogenation with Ruthenium Complexes

Catalyst	Gas phase H_2	Product/mmol			
		HCHO 1	Liquid phase $\text{CH}_2(\text{OCH}_3)_2$ 2	HCOOCH_3 3	$1+2+3 \times 2$
$[\text{Ru}_2(\text{OAc})_4\text{Cl}]/\text{PPh}_3^a$	0.75	0.60	Trace	0.08	0.76
$[\text{Ru}_2(\text{OAc})_4\text{Cl}]/\text{PEtPh}_2^b$	3.65	0.40	0.04	1.67	3.78
$[\text{Ru}(\text{OAc})\text{Cl}(\text{PEtPh}_2)_3]^c$	2.49	0.26	0.18	0.99	2.42
$[\text{Ru}_2(\text{OAc})_4\text{Cl}]/\text{PET}_2\text{Ph}^d$	3.20	0.24	0.09	1.56	3.45

a) $[\text{Ru}_2(\text{OAc})_4\text{Cl}]$ 0.5 mmol dm^{-3} , PPh_3 3.5 mmol dm^{-3} . b) $[\text{Ru}_2(\text{OAc})_4\text{Cl}]$ 2.5 mmol dm^{-3} , PEtPh_2 $17.5 \text{ mmol dm}^{-3}$. c) $[\text{Ru}(\text{OAc})\text{Cl}(\text{PEtPh}_2)_3]$ 2.5 mmol dm^{-3} . d) $[\text{Ru}_2(\text{OAc})_4\text{Cl}]$ 2.5 mmol dm^{-3} , PET_2Ph $17.5 \text{ mmol dm}^{-3}$. Methanol 200 ml , reaction period 17 h, 65°C (refluxing).

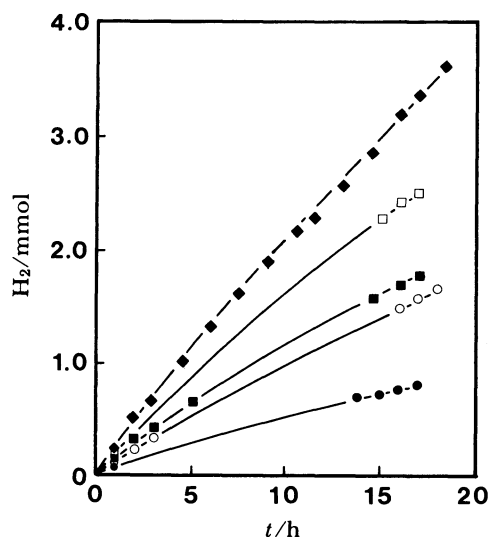
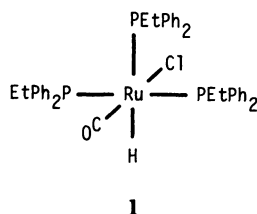


Fig. 2. Time-course plot of dihydrogen evolution from methanol with $[\text{Ru}(\text{OAc})\text{Cl}(\text{PEtPh}_2)_3]$ catalyst. $[\text{Ru}(\text{OAc})\text{Cl}(\text{PEtPh}_2)_3]$: (●) $0.50 \text{ mmol dm}^{-3}$, (○) 1.0 mmol dm^{-3} , (■) 1.5 mmol dm^{-3} , (□) 2.5 mmol dm^{-3} , (◆) 5.0 mmol dm^{-3} . Methanol 200 ml , 65°C (refluxing).

methanol dehydrogenation decreased gradually and disappeared finally (88 h). From the deactivated solution, a white complex was isolated and identified as $[\text{RuClH}(\text{CO})(\text{PEtPh}_2)_3]$ on the basis of NMR, IR and elemental analyses. Found: C, 63.92; H, 5.79%. Calcd for $\text{C}_{43}\text{H}_{46}\text{P}_3\text{OClRu}$: C, 63.90; H, 5.74%. ^{31}P NMR: $\delta=36.9(2\text{P})$ and $12.8(1\text{P})$. $^2J(\text{PP})=15.1 \text{ Hz}$, $^2J(\text{PH})_{\text{cis}}=22.9 \text{ Hz}$, and $^2J(\text{PH})_{\text{trans}}=103.9 \text{ Hz}$. ^1H NMR: $\delta=-7.1$. IR (KBr): $\nu(\text{CO})$ at $1924 (\text{s})$, $\nu(\text{RuH})$ at $1819 (\text{w}) \text{ cm}^{-1}$. Since one of the phosphine and hydride ligands are trans-disposed to each other ($^2J(\text{PH})_{\text{trans}}=103.9 \text{ Hz}$) and the other two and hydride are cis-disposed ($^2J(\text{PH})_{\text{cis}}=22.9 \text{ Hz}$), the remaining two ligands of Cl and CO are required to be coaxial. Based on these chemical analyses and spectroscopic characteristics, the coordination structure of the hydride carbonyl complex **1** in the solution is described as shown below.



After the 20 h reaction, the ^{31}P NMR spectrum of the catalyst solution (5.0 mmol dm^{-3}) consisted of only the hydride carbonyl complex **1** besides the original complex, suggesting its exclusive change into **1** during the reaction. The addition of paraformaldehyde accelerated the rate decrease, supporting the view that the product formaldehyde supplied the H

Table 2. Effect of Additives on the Initial Rate of Dihydrogen Evolution from Methanol with $[\text{Ru}(\text{OAc})\text{Cl}(\text{PEtPh}_2)_3]$ Catalyst^{a)}

Additive	Amount/ mmol dm^{-3}	H_2/mmol
None	—	0.54
LiCl	1.0	0.58
$\text{LiOAc} \cdot 2\text{H}_2\text{O}$	1.0	0.55
PEtPh_2	3.0	0.55

a) $[\text{Ru}(\text{OAc})\text{Cl}(\text{PEtPh}_2)_3]$ 1.0 mmol dm^{-3} , methanol 200 ml , reaction period 5 h, 65°C (refluxing).

Table 3. Effect of Added CH_3COOH on the Rate of Dihydrogen Evolution from Methanol with $[\text{Ru}(\text{OAc})\text{Cl}(\text{PEtPh}_2)_3]$ Catalyst^{a)}

$[\text{CH}_3\text{COOH}]/[\text{Ru}]$ ratio	Turnover number	
	17 h	42 h
0.0	10.20	18.59
0.5	14.11	21.81
1.0	16.15	24.52
2.0	16.32	26.87
5.1	15.30	26.97
20.0	14.28	29.67

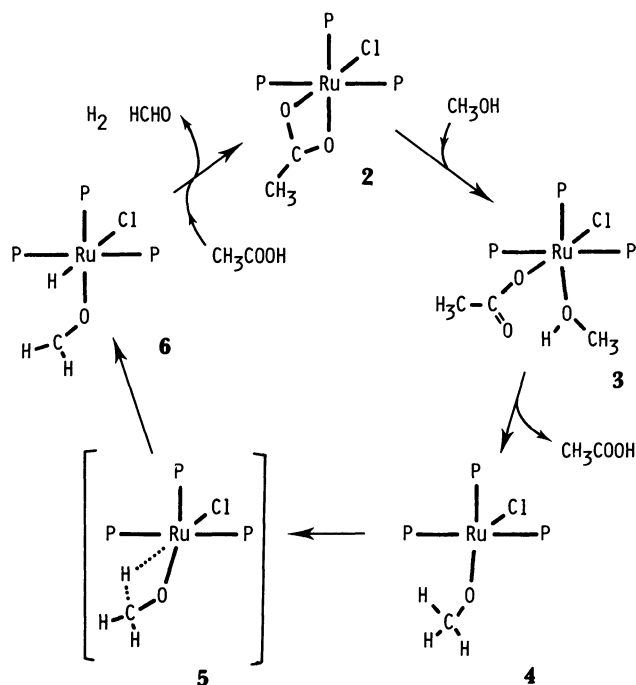
a) $[\text{Ru}(\text{OAc})\text{Cl}(\text{PEtPh}_2)_3]$ $0.25 \text{ mmol dm}^{-3}$, methanol 400 ml , 65°C (refluxing).

and CO ligands of this deactivated complex **1**. Provided that these ligands replaced the bidentate OAc ligand of the original complex, these cis-disposed sites were usable for splitting the methoxyl C—H bond to give a hydride complex.¹⁰⁾

Effect of Additives on Reaction Rate. As shown in Table 2, initial reaction rate of the $[\text{Ru}(\text{OAc})\text{Cl}(\text{PEtPh}_2)_3]$ complex was unchanged by adding either an equimolar amount of lithium acetate or lithium chloride. Even at a three-fold excess, free PEtPh_2 gave a negligible effect. Consequently, spontaneous dissociation of the acetato, chlorido and phosphine ligands would be unlikely in the methanol solution.

Rate enhancement was observed, however, on the addition of acetic acid (Table 3). During the initial reaction period (17 h), the rate increased up to an optimum ratio of catalyst to acid of 2.0 mol mol^{-1} , accompanied by progressive inhibition at higher concentrations. Monotonous rate enhancement was observed after the reaction period of 42 h. As is well-known, some kinds of hydride complexes react with protonic compounds, yielding dihydrogen.¹¹⁾ It is therefore reasonable that acetic acid accelerates the dihydrogen evolution, as far as a hydride complex is incorporated as the reaction intermediate in the catalytic dehydrogenation cycle. In the presence of excess free acid, this accelerating effect would be depressed by another reaction process such as solvolysis of the catalyst.^{2a)}

Postulated Reaction Scheme for Dehydrogenation of Methanol. A reaction mechanism of alcohol de-



Scheme 1. Reaction scheme postulated for methanol dehydrogenation.

hydrogenation was proposed previously by Dobson and Robinson. This consisted of three essential processes: (1) substitution of a bidentate carboxylato ligand (Ac_2O) with alcohol (ROH) to generate free acid (Ac_2OH), an alkoxyl ligand (RO) and a vacant site, (2) splitting of the C-H bond at the β position of the alkoxyl ligand to give an intermediate coordinated with a hydride ligand, leaving the dehydrogenated product, and (3) dihydrogen evolution by protonating this hydride ligand with free acid (Ac_2OH) to regenerate the carboxylato ligand (Ac_2O).^{2c)} On the basis of this reaction mechanism in addition to our experimental results concerning the structure of deactivated complex 1 and the effect of additives on the initial reaction rate, the following reaction scheme is postulated for the catalytic methanol dehydrogenation with $[\text{Ru}(\text{OAc})\text{Cl}(\text{PEtPh}_2)_3]$ (Scheme 1).

The bidentate acetato ligand of the original complex 2 is changed into a monodentate one by methanol coordination 3. By a proton transfer from the coordinated methanol to the monodentate acetato ligand, acetic acid is liberated from the complex, leaving a vacant site cis-disposed to the methoxyl ligand 4. The C-H splitting at the β -position of the

methoxyl ligand would be facilitated by an agostic interaction^{12,13)} between the ruthenium and hydrogen atoms 5.¹⁰⁾ The hydride intermediate complex 6 thus formed is attacked by free acetic acid to yield the products H_2 and HCHO , regenerating the original complex 2.

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