

Journal of Organometallic Chemistry, 430 (1992) 111–116
Elsevier Sequoia S.A., Lausanne
JOM 22485

Carbonylation of methanol to acetic acid using homogeneous Ru complex catalyst *

Ashutosh A. Kelkar, Devidas S. Kolhe and Raghunath V. Chaudhari

Chemical Engineering Division, National Chemical Laboratory, Pune, 411008 (India)

(Received August 28, 1991)

Abstract

Carbonylation of methanol to give acetic acid catalysed by Ru complexes such as *trans*-Ru(CO)₂Cl₂(PPh₃)₂, *cis*-Ru(CO)₂Cl₂(PPh₃)₂ and H₂Ru(CO)(PPh₃)₃ is reported. The highest activity and selectivity were obtained with H₂Ru(CO)(PPh₃)₃ as the catalyst precursor. Hydrogen increases the activity and selectivity of catalysts such as *trans*-Ru(CO)₂Cl₂(PPh₃)₂, *cis*-Ru(CO)₂Cl₂(PPh₃)₂, but has no influence on the activity and selectivity in the case of H₂Ru(CO)(PPh₃)₃.

Introduction

Carbonylation of alcohols to give carboxylic acids is of commercial importance, as evidenced by the Monsanto process for acetic acid [1]. In this process, a combination of Rh complex catalysts and iodide promoters has been found to be most suitable, though Ir, Co and Ni complex catalysts are also known to be selective [2–4]. Ruthenium is used as a catalyst in the preparation of acetic acid by isomerisation of methyl formate [5]. Ruthenium is considered to be a poor catalyst for the carbonylation of alcohols in general and methanol in particular, and its use requires very high pressure conditions. Jenner [6,7] reported that the ruthenium catalysts such as RuCl₃ · 3H₂O or Ru(acac)₃ give very poor rates and selectivity for methanol carbonylation even at 400 atm pressure and 200°C. We report below our observations of highly active and selective homogeneous ruthenium complex catalysts for carbonylation of methanol to acetic acid.

Experimental

Carbonylation experiments were carried out in a 50 cm³ capacity stirred Hastelloy C-276 reactor supplied by Autoclave Engineers, USA. Liquid reactants

Correspondence to: Professor R.V. Chaudhari, Chemical Engineering Division, National Chemical Laboratory, Pune, 411008, India.

* NCL Communication No. 4913.

Table 1

Effect of solvents on the activity and selectivity ^a

Run	Solvent	Time (min)	Conversion of methanol (%(mmol)) ^b	Selectivity (%(mmol)) ^c			
				AcOH	MeOAc	methane	DME
1	Acetic acid	335	93.50 (91.16)	90.21 (82.24)	02.39 (1.09)	06.20 (5.65)	01.51 (0.69)
2	Propionic acid	305	94.35 (91.99)	89.36 (82.20)	02.39 (1.10)	06.04 (5.56)	01.50 (0.69)
3	Nonanoic acid	280	94.50 (92.14)	90.50 (83.39)	02.50 (1.15)	06.04 (5.57)	00.21 (0.10)
4	Toluene	350	40.35 (39.34)	05.36 (02.11)	35.38 (06.96)	23.36 (9.19)	30.22 (5.94)
5	Methanol	300	35.62 (34.73)	04.38 (01.52)	30.29 (05.26)	24.53 (8.52)	38.44 (6.67)
6	Water	320	45.54 (44.40)	03.56 (01.58)	26.35 (05.85)	28.53 (12.67)	40.54 (9.00)

^a Reaction conditions: *cis*-Ru(CO)₂Cl₂(PPh₃)₂ 1.354 × 10⁻⁴, PPh₃ 2.70 × 10⁻⁴, MeI 1.606 × 10⁻², MeOH 9.75 × 10⁻² mol; Temperature 240°C; Total pressure 6.89 MPa; Agitation speed 800 rpm; H₂ partial pressure 2.07 MPa. ^b Conversion = [MeOH_{initial}] - [MeOH_{final} + methyl propionate_{final}] / [MeOH_{initial}]. ^c Selectivity = Acetic acid formed / [MeOH_{initial}] - [MeOH_{final} + methyl propionate_{final}].

and products were analysed with Hewlett Packard gas chromatograph (Model no. 5840) filled with a 5 m column packed with 5% OV-17 on Chromosorb WAW. Gaseous products were analysed with a 3 m Porapak Q column. Ruthenium complexes H₂Ru(CO)(PPh₃)₃ [8], *trans*-Ru(CO)₂Cl₂(PPh₃)₂ [9], *cis*-Ru(CO)₂Cl₂(PPh₃)₂ [9] and RuCl₂(PPh₃)₃ [9] were prepared by published procedures from RuCl₃ · hydrate (Arrora-Mathey, India). Elemental analytical data for these complexes were within 2% of the expected values.

Results

In preliminary experiments carried out with *cis*-Ru(CO)₂Cl₂(PPh₃)₂ as a catalyst it was observed that the activity of the catalyst was very poor when solvents such as toluene, water, or methanol were used. There was poor selectivity towards carbonylation products, mainly because of formation of methane and dimethyl ether. Only carboxylic acids such as acetic acid and propionic acid were found to be satisfactory solvents for carbonylation of methanol (see Table 1). In these solvents almost all the methanol was converted into methyl acetate or methyl propionate. (Esterification prevents the dehydration of the methanol to dimethyl ether, and Lutgendorf *et al.* [10] have also found that alkyl esters are better substrates than the alcohols.) Thus in the main study carbonylation of methanol was carried out with propionic acid as solvent, and the results obtained with various catalysts are presented in Table 2. The complex RuCl₃ · 3H₂O was the least active catalyst and rather similar activity was observed when RuCl₂(PPh₃)₃, *trans*-Ru(CO)₂Cl₂(PPh₃)₂, NBu₄⁺[Ru(CO)₃I₃]⁻, and *cis*-Ru(CO)₂Cl₂(PPh₃)₂ were used as catalyst precursors. However, when the dihydrido Ru complex H₂Ru(CO)(PPh₃)₃ was used, both the activity and selectivity were substantially enhanced (run

Table 2

Effect of feed gas on carbonylation of methanol to acetic acid ^a

Run	Catalyst system	Feed gas	Total time (min)	Conversion of methanol (%(mmol)) ^b	Selectivity (%(mmol)) ^c			
					AcOH	MeOAc	methane	dimethyl ether
1	RuCl ₃ ·3H ₂ O ^b	Pure CO	320	44.1 (42.99)	23.35 (10.04)	53.12 (11.42)	6.91 (2.97)	15.91 (3.42)
2	<i>cis</i> -Ru(CO) ₂ Cl ₂ (PPh ₃) ₂	Pure CO	325	42.15 (41.40)	21.33 (08.77)	56.79 (11.67)	6.59 (2.71)	14.31 (2.94)
3	<i>trans</i> -Ru(CO) ₂ Cl ₂ (PPh ₃) ₂	Pure CO	319	44.21 (43.10)	26.31 (11.34)	50.91 (10.97)	6.40 (2.76)	16.10 (3.47)
4	RuCl ₂ (PPh ₃) ₃	Pure CO	310	45.3 (44.17)	25.42 (11.23)	51.71 (11.42)	6.72 (2.97)	15.40 (3.40)
5	[Ru(CO) ₃ I ₃] ⁻ [NBu ₄] ⁺ ^b	Pure CO	345	43.45 (42.36)	23.84 (10.10)	52.69 (11.16)	7.25 (3.07)	15.34 (3.25)
6	H ₂ Ru(CO)(PPh ₃) ₃	Pure CO	330	96.65 (94.23)	90.35 (85.14)	02.14 (01.01)	6.32 (5.96)	00.76 (0.36)
7	RuCl ₃ ·3H ₂ O ^b	CO/H ₂ ^c	345	55.47 (54.08)	30.34 (16.41)	50.18 (13.57)	6.34 (3.43)	12.13 (3.28)
8	<i>cis</i> -Ru(CO) ₂ Cl ₂ (PPh ₃) ₂	CO/H ₂ ^c	305	94.35 (92.00)	89.36 (82.21)	2.39 (01.10)	6.04 (5.56)	01.50 (0.69)
9	<i>trans</i> -Ru(CO) ₂ Cl ₂ (PPh ₃) ₂	CO/H ₂ ^c	298	94.55 (92.19)	89.15 (82.19)	01.17 (00.54)	6.84 (6.31)	02.10 (0.97)
10	RuCl ₂ (PPh ₃) ₃	CO/H ₂ ^c	325	95.92 (93.52)	90.32 (84.47)	01.56 (00.73)	6.64 (6.21)	00.96 (0.45)
11	[Ru(CO) ₃ I ₃] ⁻ [NBu ₄] ⁺ ^b	CO/H ₂ ^c	365	91.75 (89.46)	88.75 (79.40)	03.23 (01.45)	6.49 (5.81)	00.85 (0.38)
12	H ₂ Ru(CO)(PPh ₃) ₃	CO/H ₂ ^c	334	97.88 (95.43)	91.50 (87.32)	02.05 (00.98)	5.90 (5.63)	00.21 (0.10)

^a Reaction conditions: Catalyst 1.354 × 10⁻⁴, PPh₃ 2.70 × 10⁻⁴, MeI 1.606 × 10⁻², MeOH 9.75 × 10⁻² mol; Solvent propionic acid (0.2 mol); Temperature 240°C; Total pressure 6.89 MPa; Agitation speed 800 rpm. ^b In these experiments PPh₃ was not used as a ligand. ^c H₂ partial pressure 2.07 MPa.

Table 3

Effect of iodide promoters on the activity and selectivity ^a

Run	Iodide promoter	Time (min)	Conversion of methanol (%(mmol))	Selectivity (%(mmol))			
				AcOH	MeOAc	methane	DME
1	CH ₃ I	315	93.95 (91.60)	90.21 (82.63)	2.38 (1.09)	6.20 (5.68)	1.51 (0.69)
2	HI	325	94.05 (91.70)	89.36 (81.94)	2.44 (1.12)	6.02 (5.52)	1.48 (0.68)
3	LiI	280	—	—	—	—	—
4	NaI	350	—	—	—	—	—

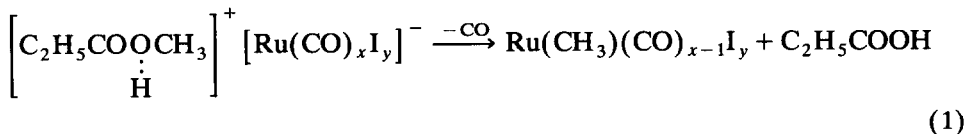
^a Reaction conditions: *cis*-Ru(CO)₂Cl₂(PPh₃)₂ 1.354 × 10⁻⁴, PPh₃ 2.70 × 10⁻⁴, iodide used 1.606 × 10⁻², MeOH 9.75 × 10⁻² mol; Solvent propionic acid (0.2 mol); Temperature 240°C; Total pressure 6.89 MPa; Agitation speed 800 rpm; H₂ partial pressure 2.07 MPa.

no. 6, Table 2). Complete conversion of methanol into acetic acid with a selectivity > 90% was achieved. In other experiments (runs 7–11, Table 2) 2.07 MPa of H₂ was introduced into the reactor initially and the reactions were carried out as usual with RuCl₃ · 3H₂O, *trans*-Ru(CO)₂Cl₂(PPh₃)₂, *cis*-Ru(CO)₂Cl₂(PPh₃)₂, NBu₄⁺[Ru(CO)₃I₃]⁻ and RuCl₂(PPh₃)₃ as catalyst precursors. In all cases except RuCl₃ · 3H₂O there was a dramatic increase in the activity and selectivity (see Table 2). It is noteworthy that the effectiveness of H₂Ru(CO)(PPh₃)₃ with pure CO as a feed gas and that of RuCl₂(PPh₃)₃, *trans*-Ru(CO)₂Cl₂(PPh₃)₂ and *cis*-Ru(CO)₂Cl₂(PPh₃)₂ with H₂ in the feed gas were comparable, indicating that the hydrido carbonyl ruthenium complex may be the key intermediate in the catalytic cycle and that the presence of H₂ in the gas phase may assist in the formation of such complexes. Interestingly, the activity of H₂Ru(CO)(PPh₃)₃ was not further increased by the presence of H₂. In order to check the role of iodide promoters, experiments were carried out with various iodine-containing species such as aq. HI, CH₃I, LiI and NaI. It was observed that the activities of the catalyst with aq. HI or CH₃I as a promoter were comparable, but no activity was observed with LiI or NaI as a promoter. The results are presented in Table 3. Analysis of the gas phase was carried out in all the experiments, and the formation of methane and dimethyl ether in varying quantities was observed in all cases.

Discussion

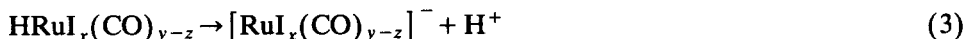
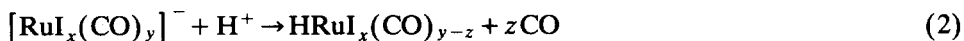
The effect of hydrogen was previously observed by Braca *et al.* [11,12] in the homologation/carbonylation of methyl acetate and dimethyl ether at 200°C and 200 atm. The present report is the first on the carbonylation of methanol to acetic acid with high selectivity involving a ruthenium catalyst system. There has been no previous detailed discussion of the mechanism of carbonylation of methanol to acetic acid with Ru catalysts, but the need to have a carboxylic acid as solvent and the enhancement in the activity of the catalyst by hydrogen suggest that the catalytically active species may have the form of a species in which a protonated methyl propionate cation is the counterion of a ruthenium iodocarbonyl derivative of the type [Ru(CO)_xI_y]⁻. The IR spectrum of the catalytic intermediate isolated

from the reaction mixture in which *cis*-Ru(CO)₂Cl₂(PPh₃)₂ was used as a catalyst (run 8, Table 2), clearly showed the $\nu(\text{CO})$ frequencies at 2105, 2030 and 1920 cm⁻¹. These characteristic peaks indicate that the anionic carbonyl iodide species of the type [Ru(CO)_xI_y]⁻ may be the active species [13]. The active catalytic intermediate may consist of a protonated methyl propionate cation associated with the ruthenium iodocarbonyl anion derivative [Ru(CO)₃I₃]⁻, which could form alkylruthenium complex similar to that suggested by Mizoroki and Nakayama [3] and Wender [14] for cobalt-catalysed methanol carbonylation and homologation, respectively.



The need for a carboxylic acid solvent and the strong promoting effect of hydrogen suggest that ruthenium complex HRu(CO)₃I₃ may play an important role in the catalytic cycle. It has been reported [15] that the complex HRu(CO)₃I₃ can directly protonate the substrate, as depicted in eq. 1. It is necessary to have an I/Ru ratio of 2 for formation of HRu(CO)₃I₃; at higher I/Ru ratios, [Ru(CO)₂I₄]⁻ is formed [16]. In our work the I/Ru ratio was around 200, and at such high iodide concentrations, the dominant presence of HRu(CO)₃I₃ is unlikely. At present it is very difficult to define the role of HRu(CO)₃I₃ in the catalytic cycle, but the possibility of reaction 1 indicates that oxidative addition of methyl iodide to give metal-alkyl complexes may not be an important step in the cycle. The results in Table 3 show that use of aq. HI and CH₃I as promoters resulted in comparable activities, whereas LiI and NaI were ineffective in the carbonylation of methanol. Similar observations were made in carbonylation of methanol catalysed by rhodium complexes [17]. Thus, it would not be justifiable at this stage to pursue the above speculation further and discard the well established mechanism in which it is oxidative addition of methyl iodide that leads to formation of metal-alkyl complex [18]. It is quite likely that the protonation step proposed and the oxidative addition of methyl iodide may compete under certain conditions.

An alternative explanation for H₂ effect could be that H₂ induces dissociation of CO from the catalytic species, perhaps by oxidising the ruthenium species to a higher valence state and so generating the active catalyst [19].



However, further work is needed to provide understanding of the role of hydrogen in the catalytic cycle and to define the mechanism for carbonylation of methanol with ruthenium complex catalysts.

References

- 1 J.F. Roth, J.H. Craddock, A. Hershman and F.E. Paulik, CHEMTECH, (1971) 600.
- 2 D. Forster, in F.G.A. Stone and R. West (Eds.), Advances in Organometallic Chemistry, Vol. 17, Academic Press, London, 1979, p. 255.

- 3 T. Mizoroki and M. Nakayama, *Bull. Chem. Soc. Jpn.*, 41 (1968) 1628.
- 4 N. Rizkalla, in D. Fahey (Ed.), *Industrial Chemicals Via C₁ Processes*, ACS Symposium Series No. 328, Am. Chem. Soc., Washington DC, Ch. 5, 1987, p. 61.
- 5 Mitsubishi Gas Chemical Company Inc., *Jpn. Kokai Tokkyo Koho JP 81, 83, 439*, (1981).
- 6 G. Bitsi and G. Jenner, *Appl. Catal.*, 21 (1986) 201.
- 7 G. Jenner and G. Bitsi, *J. Mol. Catal.*, 40 (1987) 71.
- 8 N. Ahmad, J.J. Levison, S.D. Robinson and M.F. Uttley, in G.W. Parshall (Ed.), *Inorganic Synthesis*, Vol. 15, McGraw-Hill Book Co., New York, 1974, p. 48.
- 9 T.A. Stephenson and G. Wilkinson, *J. Inorg. Nucl. Chem.*, 28 (1965) 945.
- 10 M. Lutgendorf, E.O. Elvevoll and M. Roper, *J. Organomet. Chem.*, 289 (1985) 97.
- 11 G. Braca, G. Sbrana, G. Valentini, G. Andrich and G. Gregorio, *J. Am. Chem. Soc.*, 100 (1978) 6328.
- 12 G. Braca, L. Paladini, G. Sbrana, G. Andrich and G. Gregorio, *Ind. Eng. Chem. Prod. Res. Dev.*, 20 (1981) 115.
- 13 A.M. Raspollo Galletti, G. Braca, A. Sbrana and F. Marchetti, *J. Mol. Catal.*, 32 (1986) 291.
- 14 I. Wender, *Catal. Rev. Sci. Eng.*, 14 (1976) 97.
- 15 G. Braca, A.M. Raspollo Galletti and G. Sbrana, in D. Fahey (Ed.), *Industrial Chemicals Via C₁ Processes*, ACS Symposium Series No. 328, Am. Chem. Soc., Ch. 5, 1987, p. 221.
- 16 G. Braca and G. Sbrana, in R. Ugo (Ed.), *Aspects of Homogeneous Catalysis*, D. Reidel Publishing Co., Dordrecht, Netherlands, Vol. 5, 1984, p. 241.
- 17 R.T. Eby and T.C. Singleton, in B.E. Leach (Ed.), *Applied Industrial Catalysis*, Vol. 1, Academic Press, New York, Ch. 10, 1983, p. 275.
- 18 D. Forster, *J. Am. Chem. Soc.*, 98 (1976) 846.
- 19 T.W. Deklewa and D. Forster, *Adv. Catal.*, 34 (1986) 81.