Journal of Organometallic Chemistry, 335 (1987) C27–C31
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

Preliminary communication

1-Alkylbenzimidazoles as unique promoters for a homogeneous ruthenium catalyst for direct ethylene glycol formation from synthesis gas

Yoshihisa Kiso,* Kenji Saeki, Tetsuo Hayashi, Masahide Tanaka, Yuichi Matsunaga

Chemical Synthesis Laboratories, Mitsui Petrochemical Industries Ltd., Waki-cho, Kuga-gun, Yamaguchi-ken, 740 (Japan)

Masaru Ishino, Mitsuhisa Tamura, Takashi Deguchi, and Shuzo Nakamura

Takatsuki Research Laboratory, Sumitomo Chemistry Co., Ltd., Tsukahara, Takatsuki, Osaka, 569 (Japan)

(Received May 23rd, 1987; in revised form September 2nd, 1987)

Abstract

1-Alkylbenzimidazoles such as 1-methylbenzimidazole and 1,5,6-trimethylbenzimidazole have been found to be excellent promoters for direct ethylene glycol formation from hydrogen and carbon monoxide in the presence of a homogeneous ruthenium catalyst. High pressure IR analyses revealed that three Ru species, $[HRu_3(CO)_{11}]^-$ (I), $Ru(CO)_5$ (II) and $Ru(CO)_4$(1-alkylbenzimidazole) (III) had formed. An analysis of the relationship between activity and identity of Ru species showed that ruthenium species III plays an important role in ethylene glycol formation, and that the high coordination ability of benzimidazoles is essential to the promoting effect on ethylene glycol formation.

We report here a novel ruthenium catalyst which when combined with a large excess of 1-alkylbenzimidazole leads to direct ethylene glycol (EG) formation from synthesis gas, with good catalytic activity and selectivity.

Recently there has been considerable interest in the formation of EG from synthesis gas [1–14]. It is well known that group VIII metal complexes, especially rhodium carbonyls, are effective as homogeneous catalysts for this reaction. Low catalytic activities coupled with the severe reaction conditions required, limit their practical value [6]. Recently, some of us found an active Ru catalyst, which when combined with a large excess of unsubstituted imidazole or benzimidazole is effective in EG formation [15]. Promotion of catalytic activity by these imidazole compounds is more pronounced than by those of other *N*-containing bases. Unfortunately, catalysts containing unsubstituted imidazole or benzimidazole showed only a poor selectivity to EG formation, like most of the other Ru catalysts reported to

0022-328X/87/$03.50

Table 1

Hydrogenation of carbon monoxide by homogeneous ruthenium-"imidazoles" catalysts [a]

Run No.	"Imidazoles"	(pK_{BH^+}) [b]	Solvent [c]	Activity [d]		Selectivity [e] (%)
				N(EG)	N(MeOH)	
1	1-ethylimidazole	(7.30)	NMP	6.9	92.1	13.1
2	imidazole	(6.95)	NMP	5.7	179.4	6.0
3	1-methylimidazole	(6.95)	NMP	5.3	52.1	16.9
4	4-phenylimidazole	(6.00)	NMP	2.2	88.9	4.7
5	2-phenylimidazole	(6.40)	NMP	0.5	34.5	2.9
6	5,6-dimethylbenzimidazole	(5.96)	NMP	27.2	100.7	35.1
7	1,5,6-trimethylbenzimidazole	(–)	NMP	20.0	34.3	53.8
8	benzimidazole	(5.53)	NMP	19.6	67.5	36.8
9	1-methylbenzimidazole	(5.54)	NMP	16.7	22.4	59.9
10	1-ethylbenzimidazole	(5.59)	NMP	16.1	24.8	56.5
11	1-n-propylbenzimidazole	(5.44)	NMP	16.4	24.9	56.9
12	2-methylbenzimidazole	(6.19)	NMP	4.3	59.5	12.6
13	2-ethylbenzimidazole	(6.18)	NMP	1.7	43.0	7.4
14	2-i-propylbenzimidazole	(6.21)	NMP	0.3	10.5	4.9
15	1-methylbenzimidazole	(5.54)	TGM	20.1	12.6	76.1
16	1-methylbenzimidazole		THF	22.6	17.5	72.1
17	1-methylbenzimidazole		benzene	13.4	17.8	60.1
18 [f]	1-methylbenzimidazole		TGM	2.9	4.8	54.8
19 [f]	1-methylbenzimidazole		TGM	5.1	5.0	66.9
20 [f]	1-methylbenzimidazole		TGM	0	2.4	0
21 [f]	none		TGM	0	< 0.1	0

[a] Conditions were as follows, except where stated otherwise. Charge: $Ru_3(CO)_{12}$ 0.1 mg-atom as Ru, "imidazoles" 10.0 mmol, solvent 10 ml; run conditions: CO/H_2 (1 : 1) 50 MPa, 240 °C, 2h. [b] See ref. 16 (at 25 °C). [c] NMP = *N*-methyl-2-pyrrolidinone, TGM = tetraglyme, THF = tetrahydrofuran. [d] N(EG) = EG mol/Ru g-atom/h, N(MeOH) = MeOH mol/Ru g-atom/h. [e] Selectivity = $100 \times 2EG_{mol}/(2EG + MeOH)_{mol}$. [f] Charged: $Ru_3(CO)_{12}$ 0.4 mg-atom as Ru, solvent 20 ml and others (run no. 18: NMBI 20 mmol, run no. 19: NMBI 40 mmol, run no. 20: NMBI 20 mmol and bis(triphenylphosphine)iminium acetate 0.4 mmol, run no. 21: none); run conditions: CO/H_2 (1 : 1) 30 MPa, 200 °C, 2 h.

date [2,3,12], and a large amount of methanol (MeOH) is also formed. We have studied a series of Ru catalyst systems with different "imidazoles" in order to find a more effective catalyst system for EG formation (from here on the "imidazoles" refers to substituted imidazoles and benzimidazoles).

To this end we investigated the influence that different substituents, on imidazole and benzimidazole had upon catalytic performance. Both activity and selectivity were greatly affected by the nature of substituents, see Table 1, run no. 1–17.

(1) Activity for EG formation (N(EG) = EG mol/Ru g-atom/h) increased with increased basicity (pK_{BH^+}) [16] of imidazole or benzimidazole derivative, with the exception of 2-substituted derivatives, which caused a decrease in N(EG) with increase in bulkiness of the 2-alkyl substituent.

(2) The 1-alkyl derivatives gave higher selectivities for EG formation than 1-unsubstituted derivatives, because of a lower activity for MeOH formation (N(MeOH)). High selectivity was achieved especially with 1-alkylbenzimidazole promoters in tetraglyme solvent.

A Ru catalyst combined with 1-methylbenzimidazole (NMBI) in tetraglyme solvent produced EG as the main product with good catalytic activity, under

suitable conditions; a selectivity ($100 \times 2EG_{mol}/(2EG + MeOH)_{mol}$) of 67% and an N(EG) of 211 under a CO/H_2 (1 : 2) pressure of 50 MPa at 260 °C (molar ratio of NMBI/$Ru_3(CO)_{12}$ = 450). The activity of this catalyst for EG formation is about 10 times greater than that of the active rhodium catalysts under a similar CO/H_2 pressure, and the selectivity of this catalyst is almost the same as that of effective rhodium catalysts [2,3,9,10]. This catalyst showed a high activity for EG formation, not only in polar solvent (NMP), but also in nonpolar solvent (benzene, see Table 1). The solvent effects suggest that a neutral Ru species is important in this catalyst system, which is definitely different from the halide-promoted Ru catalysts in which ionic species are considered to be the active species [2,12].

In order to learn more about the function of "imidazoles" promoters, we subjected reaction mixtures containing the Ru species to IR spectroscopy. In reaction mixtures with the Ru-NMBI catalyst, under 1 atm of synthesis gas, $[HRu_3(CO)_{11}]^-$ (I) [17] was present as the sole Ru species. However, the high pressure IR spectra of these reaction mixtures under the conditions used for the synthesis gas reaction (Table 1, run no. 18, 19) revealed two neutral Ru species, $Ru(CO)_5$ (II) [17] and $Ru(CO)_4$(Imid) (III; Imid represents an "imidazoles" ligand)*, in addition to (I). Both the concentration of (III) and the N(EG) value increased with increasing concentration of NMBI (Run No 18: NMBI = 0.88 mol/l, (I) : (II) : (III) = 70 : 19 : 12 mol%; Run No 19: NMBI = 1.58 mol/l, (I) : (II) : (III) = 70 : 14 : 16 mol%). When bis(triphenylphosphine)iminium acetate was added to this system in an amount equivalent to that of Ru (Run No 20), only anionic species I was observed under these reaction conditions, but it showed only activity for MeOH formation. On the other hand, in the absence of "imidazoles" (run no. 21), only neutral species II was observed, and the catalyst produced only a small amount of MeOH as reported by Bradley [18].

We measured the equilibrium constants K of the reaction as shown in eq. 1 using benzimidazole derivatives to elucidate "imidazoles" effects.

$$\underset{\text{(II)}}{Ru(CO)_5} + Imid \overset{K}{\rightleftharpoons} \underset{\text{(III)}}{Ru(CO)_4(Imid)} + CO \qquad (1)$$

A good linear correlation between N(EG) and K was observed (Fig. 1). However the relation between N(MeOH) and K was not clear.

These studies show that coordination of "imidazoles" to Ru is important for EG formation, and that the neutral Ru species III plays an important role in catalysis. It is plausible that the hydrogenated Ru species of III, $H_2Ru(CO)_3$(Imid), is the active species for EG formation **. As described above, the other Ru species I and II

* This complex was identified by comparison of its IR spectrum with that of $Ru(CO)_4(Ph_3P)$ [17] ($Ru(CO)_4$(NMBI) in THF; ν(CO) 2048w, 1960sh, 1934s cm^{-1}). No other ruthenium complexes such as $Ru(CO)_{5-n}(Imid)_n$ ($n \geqq 2$) were observed. Details will be reported elsewhere.

** This species was not visible in the IR spectra of the reaction mixtures under the conditions used for the synthesis gas reaction. However, formation of this species was revealed by high pressure IR spectroscopy of the reaction mixture of III and H_2. Thus III (Imid = NMBI) was heated at 80 °C under a H_2 pressure of 19 MPa in THF. High pressure IR spectroscopy of this reaction mixture revealed the formation of a new species (ν(CO) 2065m, 2000s, 1980sh cm^{-1}) which was thought to be $H_2Ru(CO)_3$(Imid) from a comparison of its IR spectrum with that of $H_2Ru(CO)_3(Ph_3P)$ [17].

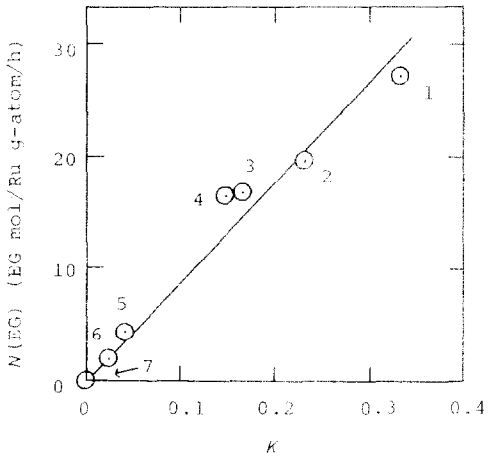

Fig. 1. Relation between activity (N(EG)) and equilibrium constant (K).
1: 5,6-dimethylbenzimidazole, 2: benzimidazole, 3: 1-methylbenzimidazole, 4: 1-n-propylbenzimidazole, 5: 2-methylbenzimidazole, 6: 2-ethylbenzimidazole, 7: 2-i-propylbenzimidazole. N(EG): see Table 1 (run no 6–14). The values of K were measured by IR analyses of equilibrium reactions with benzimidazole derivatives (eq. 1) at 20 °C in THF solvent.

themselves produce MeOH but not EG. The poor relation between N(MeOH) and K is due to MeOH formation activity by these Ru species.

Nitrogen bases other than "imidazoles", such as N-methylmorpholine, pyridine and pyrazole, were much less effective in EG formation [15]. These N-bases were found to have K values lower than those of the "imidazoles" (K at 20 °C in THF; N-methylmorpholine 5×10^{-3}, pyridine 1×10^{-2}, pyrazole 1×10^{-2}, NMBI 1.6×10^{-1}). Furthermore, I and II were the only detectable Ru species in the reaction system when N-methylmorpholine was used. The unique promoting effect of "imidazoles" on EG formation thus appears to be attributable to their high coordination ability to the Ru carbonyl complex [19 *].

This work is part of the "C_1 Chemistry Project", a National Research and Development Program of the Agency of Industrial Science and Technology, Ministry of International Trade and Industry, Japan.

Acknowledgment. The authors are grateful to the members of the Ethylene Glycol Groups of the Project for valuable discussions.

References

1 G. Henrici-Olivé and S. Olivé, The Chemistry of the Catalyzed Hydrogenation of Carbon Monoxide. Springer-Verlag, Berlin, 1984.
2 B.D. Dombek, Adv. Catal., 32 (1983) 325; J. Chem. Educ., 63 (1986) 210 and references therein.
3 L.C. Costa, Catal. Rev., 25 (1983) 325 and references therein.
4 K. Saeki and Y. Kiso, Kagaku (Kyoto), 40 (1985) 369.
5 W. Keim, Pure Appl. Chem., 58 (1986) 825.
6 J. Koller, Chemtech., 14 (1984) 504.

* Reference number marked with an asterisk indicates a note in the list of references.

7 a) J.F. Knifton, J. Chem. Soc., Chem. Commun., (1983) 729. b) R. Whyman, J. Chem. Soc., Chem. Commun., (1983) 1439. c) B.D. Dombek, Organometallics, 4 (1985) 1707.
8 M. Roper, M. Schieren and A. Fumagalli, J. Mol. Catal., 34 (1986) 173.
9 a) E. Watanabe, K. Murayama, Y. Hara, Y. Kobayashi, K. Wada and T. Onoda, J. Chem. Soc., Chem. Commun., (1986) 227. b) T. Masuda, K. Murata, T. Kobayashi and A. Matsuda, Bull. Chem. Soc. Jpn., 59 (1986) 2349. c) Y. Ohgomori, S. Mori, S. Yoshida and Y. Watanabe, Chem. Lett., (1986) 1935.
10 a) E. Watanabe, Y. Hara, K. Wada and T. Onoda, Chem. Lett., (1986) 285. b) H. Tanaka, Y. Hara, E. Watanabe, K. Wada and T. Onoda, J. Organomet. Chem., 312 (1986) C71. c) M. Tamura, M. Ishino, T. Deguchi and S. Nakamura, J. Organomet. Chem., 312 (1986) C75.
11 Y. Kiso and K. Saeki, J. Organomet. Chem., 303 (1986) C17; Idem, Bull. Chem. Soc. Jpn., 60 (1987) 617.
12 Y. Kiso, M. Tanaka, H. Nakamura, T. Yamasaki and K. Saeki, J. Organomet. Chem., 312 (1986) 357.
13 W. Keim, M. Anstock, M. Roper and J. Schlupp, C_1 Mol. Chem., 1 (1984) 21.
14 T. Takano, T. Deguchi, M. Ishino and S. Nakamura, J. Organomet. Chem., 309 (1986) 209.
15 Y. Kiso and K. Saeki, J. Organomet. Chem., 309 (1986) C26.
16 D.D. Perrin, Dissociation Constants of Organic Bases in Aqueous Solution, Butterworths, London, 1965.
17 E.A. Seddon and K.R. Seddon, The chemistry of Ruthenium, Elsevier, Amsterdam, 1984.
18 J.S. Bradley, J. Am. Chem. Soc., 101 (1979) 7419.
19 Similar high coordination ability of imidazole compounds have been reported. K.M. Kadish, D.J. Leggett and D. Chang, Inorg. Chem., 21 (1982) 3618.