APPLIED ORGANOMETALLIC CHEMISTRY
Appl. Organometal. Chem. **14**, 857–859 (2000)

NOTE

Homogeneous hydrogenation of aqueous hydrogen carbonate to formate under mild conditions with water soluble rhodium(I)– and ruthenium(II)–phosphine catalysts†

Ferenc Joó,[1,2]* Gábor Laurenczy,[3] Péter Karády,[1] János Elek,[2] Levente Nádasdi[2,3] and Raymond Roulet[3]

[1]Institute of Physical Chemistry, University of Debrecen, H-4010 Debrecen, PO Box 7, Hungary
[2]Research Group of Homogeneous Catalysis of the Hungarian Academy of Sciences, H-4010 Debrecen, PO Box 7, Hungary
[3]Université de Lausanne, Institut de Chimie Minérale et Analytique, CH-1015 Lausanne-Dorigny, Switzerland

Water-soluble rhodium(I)- and ruthenium(II)–tertiary phosphine complexes with *meta*-monosulphonated triphenylphosphine (TPPMS) and 1,3,5-triaza-7-phosphaadamantane (PTA) as ligands catalyze the hydrogenation of aqueous HCO_3^- to HCO_2^- under mild conditions. No amine additive is needed for good turnovers. CO_2 accelerates the reactions with [RhCl(TPPMS)$_3$] catalyst; however, it slightly inhibits the reductions catalyzed by [RuCl$_2$(TPPMS)$_2$]. Bicarbonate formed in the reaction of limestone with aqueous CO_2 can also be used as starting material for formate production. Copyright © 2000 John Wiley & Sons, Ltd.

Keywords: carbon dioxide; hydrogenation; rhodium; ruthenium; homogeneous catalysis; aqueous organometallic catalysis

INTRODUCTION

Reduction of CO_2 to formic acid in *aqueous solution* is catalyzed by the water-soluble rhodium-(I)–tertiary phosphine complex: [RhCl(TPPTS)$_3$] (TPPTS = tris(3-sulfonatophenyl)phosphine), as described by Gassner and Leitner.[1] An efficient hydrogenation requires the presence of a base. For this purpose usually alkyl- or hydroxyalkylamines are used. In one of the most active systems the highly water-soluble dimethylamine serves as a component of the catalytically active rhodium complex. This way an *initial* turnover frequency (TOF) of 7260 h^{-1} could be achieved at 81°C under 40 atm total pressure (CO_2:H_2 = 1:1).[2]

Ruthenium complexes are less frequently applied in studies of CO_2 activation. Use of [RuCl$_2$ (TPPTS)$_2$], as catalyst resulted in a slow production of formic acid with a TOF of only 6 h^{-1} (23 °C); addition of an amine was again required.[2] This is in sharp contrast to the outstandingly high activity of ruthenium(II) complexes either with monodentate[3] or with bidentate[4] phosphine ligands in reduction of $CO_2 + Me_2NH$ into dimethylformamide in supercritical solutions.

Recently, we have communicated that water-soluble rhodium(I)- and ruthenium(II)–phosphine complexes with TPPMS (*meta*-monosulphonated triphenylphosphine) and PTA (1,3,5-triaza-7-phosphaadamantane) ligands catalyzed the hydrogenation of aqueous HCO_3^- to HCO_2^- under mild conditions.[5] Our results show that in aqueous solutions amines could be replaced by sodium

---

* Correspondence to: Ferenc Joó, Institute of Physical Chemistry, University of Debrecen, H-4010 Debrecen, PO Box 7, Hungary.
E-mail: jooferenc@tigris.klte.hu

Contract/grant sponsor: Hungarian National Research Foundation; Contract/grant number: OTKA T029934; Contract/grant number: OTKA F023159.
Contract/grant sponsor: Office Fédéral de l'Education et de la Science, Suisse; Contract/grant number: OFES C98.0011.

† This note is based on work presented at the Fifth International Conference on Carbon Dioxide Utilization (ICCDU V), held on 5–10 September 1999 at Karlsruhe, Germany.

hydroxide or other bases. Here we report some interesting kinetic features of these reactions.

EXPERIMENTAL

TPPMS,[6] PTA,[6] $[RhCl(TPPMS)_3]$,[6] $[RuCl_2(TPPMS)_2]_2$,[6] $[RuCl_2(PTA)_4]$[7] and $[RhCl(PTA)_3]$[7] were prepared following published procedures. Hydrogenations were run in well–stirred heavy–walled glass reactors (≤12 bar), medium pressure UV–VIS spectrophotometric cells (≤40 bar) or in high-pressure sapphire NMR tubes (≤100 bar) intensively shaken on top of a laboratory shaker placed inside a thermostatically controlled cabinet. Reaction mixtures were analyzed by high performance liquid chromatography (HPLC) or monitored by ^1H and ^{13}C NMR spectroscopy (Bruker AC 200, AM 300, DRX 400) using ^{13}C-enriched (99%) $NaHCO_3$.

RESULTS AND DISCUSSION

When an aqueous solution of 2.5 mM $[RhCl(TPPMS)_3]$ was stirred at 24 °C under 10 bar CO_2 and 10 bar hydrogen very slow formation of formic acid was detected by HPLC with a turnover frequency of 0.12 h^{-1}. Using 0.5 M dimethylamine solutions and 40 bar total pressure (CO_2:H_2 = 1:1) the same catalyst afforded formic acid with a TOF 6 h^{-1} together with a small amount of dimethylformamide (TOF 0.13 h^{-1}). Although the absolute reaction rate is smaller than that reported in the literature, it is seen that the amine additive is as effective as in the case of the analogous $[RhCl(TPPTS)_3]$ catalyst. By way of contrast, when the aqueous phase was changed for 1 M Na_2CO_3 under otherwise identical conditions, 1.25 mM $[RhCl(TPPMS)_3]$ produced 0.29 M $HCOO^-$ in 2 h, corresponding to a TOF of 116 h^{-1} without any amine additive. It was obvious that Na_2CO_3 reacted with CO_2 to form $NaHCO_3$, and indeed, when using 1 M $NaHCO_3$ solutions the same TOF, i.e. 116 h^{-1}, was determined. Further reactions were typically run with 1 M, aqueous $NaHCO_3$, 1.25M catalyst, 24 °C, 20 bar CO_2 and 20 bar hydrogen.

The reaction is of first order in the catalyst concentration; however, the rate goes through a maximum with increasing [TPPMS]/[Rh] ratio, the highest rate (TOF 136 h^{-1}) being observed in the presence of four equivalents of excess phosphine ($[P]_{total}/[Rh] = 7$). At constant CO_2 pressure (20 bar) the rate varies according to a saturation curve with increasing hydrogen pressure. Conversely, at constant hydrogen pressure (10 bar) a small amount of CO_2 increased the rate abruptly, but no further effect was seen on further increase of CO_2 pressure (Fig. 1).

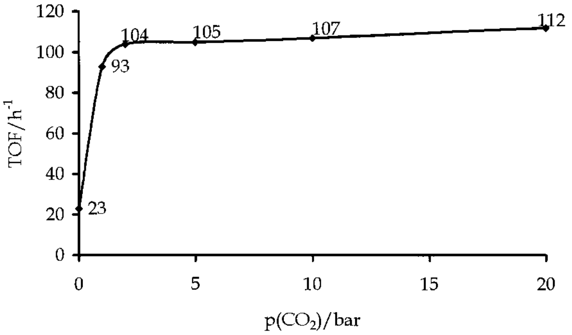

Figure 1 The effect of CO_2 pressure on the activity of the catalyst in hydrogenation of aqueous $NaHCO_3$ catalyzed by $[RhCl(TPPMS)_3]$. [Rh] = 1.25 mM, $[P]_{total}/[Rh] = 7$, $[NaHCO_3]$ = 1 M, $p(H_2)$ = 10 bar, T = 24 °C, reaction time 2 h.

Under optimized conditions (3 bar CO_2, 37 bar hydrogen otherwise as above) 0.51M formate was produced in 2 h yielding an average TOF of 204 h^{-1}.

Surprisingly, CO_2 had a slight negative effect on the rate of hydrogenation of bicarbonate with $[RuCl_2(TPPMS)_2]_2$ as catalyst, whereas with $[RuCl_2(PTA)_4]$ an increase of the rate was observed with increasing CO_2 pressure.

Since with neither catalyst was a strongly detrimental effect of CO_2 pressure observed, bicarbonate solutions obtained in the reaction of $CaCO_3$ and aqueous CO_2 could also be used[5] for formate production with TOF of 26.6 h^{-1} ($[RuCl_2(TPPMS)_2]_2$), 18.7 h^{-1} ($[RhCl(TPPMS)_3]$) and 2.5 h^{-1} ($[RuCl_2(PTA)_4]$).

CONCLUSION

It is rather hard to rationalize such diverse effects of CO_2 on the rate of bicarbonate hydrogenation with the three different catalysts. It is important to mention that in our reactions formate was never produced in excess to the initial bicarbonate, i.e. addition of CO_2 did not increase the total turnover. Furthermore, CO_2 effects the pH of the solutions and it is known from our earlier studies[8,9] that the formation and the distribution of the catalytically important hydrido species, $[HRuCl(TPPMS)_3]$, $[H_2Ru(TPPMS)_4]$, $[H_2RhCl(TPPMS)_3]$ and $[HRh(TPPMS)_4]$, is markedly influenced by the pH of the solutions. Similar pH effects are observed with the hydrides formed from $[RuCl_2(PTA)_4]$.[10] Basic solutions such as 1 M $NaHCO_3$ facilitate the formation of $[H_2Ru(TPPMS)_4]$ and of $[HRh(TPPMS)_4]$, and the effect of excess TPPMS, both in the case of the ruthenium[5] and the rhodium catalyst, is consistent with the catalytic role of higher phosphine-coordinated complexes. Further studies are under way in our laboratories in order to obtain a more detailed picture of the mechanism of bicarbonate hydrogenation with water-soluble platinum metal posphine complexes.

Acknowledgements This work was supported by the Hungarian National Research Foundation (OTKA T029934 and F 023159) and by the Office Fédéral de l'Education et de la Science, Suisse (OFES C98.0011 to G.L.). N.L. is grateful for an OFES fellowship, 1998–99. The loan of $RuCl_3$(aq) by Johnson-Matthey p.l.c. is gratefully acknowledged. This research is part of the collaboration within the COST Action D10/0001 Working Group.

REFERENCES

1. Gassner F, Leitner W. *J. Chem. Soc. Chem. Commun.* **1993**; 1465.
2. Leitner W, Dinjus E, Gassner F. In *Aqueous-Phase Organometallic Catalysis*, Cornils B, Herrmann WA (eds.). Wiley-VCH: Weinheim, **1998**; 486.
3. Jessop PG, Ikariya T, Noyori R. *Nature* 1994; **368**: 231.
4. Kröcher O, Köppel RA, Baiker A. *J. Chem. Soc. Chem. Commun.* 1997; 453.
5. Joó F, Laurenczy G, Nádasdi L, Elek J. *J. Chem. Soc. Chem. Commun.* 1999; 971.
6. Joó F, Kovács J, Kathó Á, Bényei AC, Decuir T, Darensbourg DJ. *Inorganic Synthesis*, vol. 32 Darensbourg MY, (ed.). Wiley: New York, 1998; 1.
7. Darensbourg DJ, Joó F, Kannisto M, Kathó Á, *Organometallics* 1992; **11**: 1990.
8. Joó F, Kovács J, Bényei AC, Kathó Á. *Angew. Chem.* 1998; **110**: 1024.
9. Joó F, Csiba P, Bényei A. *J. Chem. Soc. Chem. Commun.* 1993; 1602.
10. Laurenczy G, Nádasdi L, Joó F. *Inorg. Chem.*, submitted for publication.