Homogeneous hydrogenation of aqueous hydrogen carbonate to formate under exceedingly mild conditions—a novel possibility of carbon dioxide activation†

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Received (in Cambridge, UK) 24th March 1999, Accepted 26th April 1999

Water soluble ruthenium(II)– and rhodium(I)–phosphine complexes catalyze the hydrogenation of aqueous HCO_3^- to HCO_2^- under mild conditions with turnover frequencies up to 262 TO h^{-1}.

Reduction of carbon dioxide into useful starting materials of organic synthesis is an aim of paramount importance both for economic and environmental reasons.[1] It is intriguing that while in the dark reactions of photosynthesis carbon dioxide reacts in an aqueous medium under very mild conditions, efficient synthetic systems usually require elevated temperatures and pressures to achieve reasonable reaction rates. In homogeneous systems, both in the liquid and in the supercritical state, several ruthenium complexes, such as $[RuCl_2(PMe_3)_4]$ **1** and $[RuCl_2(dppe)_2]$ **2** showed impressive catalytic activity in the reaction of CO_2, H_2 and $HNMe_2$ yielding dimethyl formamide.[2,3] Leitner *et al.*[4] investigated the hydrogenation of CO_2 in *aqueous solutions* with $[RhCl(tppts)_3]$ **3** as catalyst [tppts = tris(3-sulfonatophenyl)phosphine] which gave formate with initial reaction rates of 7260 h^{-1} at 81 °C and 1365 h^{-1} at 23 °C in the presence of $HNMe_2$ under 40 atm total pressure ($CO_2/H_2 = 1$). It is of interest that under identical conditions $[RuCl_2(tppts)_3]$ **4** showed[4] a TOF of only 6 h^{-1} (23 °C), and no formic acid was detected in aqueous solutions with **3** without an amine.

Water soluble phosphine complexes of platinum metals were introduced into the homogeneous catalysis scene by Joó and Beck[5] who also noted the interaction of CO_2 with $[HRuCl(tppms)_3]$ **5** (tppms = 3-sulfonatophenyldiphenylphosphine) in aqueous solution.[6] Recently it was established that formation of the water soluble hydrides of ruthenium(II), such as **5** $[H_2Ru(tppms)_4]$ **6** and $[HRuCl(tppms)_2]_2$ **7** from $[RuCl_2(tppms)_2]_2$, **8**, tppms and H_2, and their distribution in aqueous solution is strongly pH-dependent which leads to opposite selectivities in acidic and basic solutions during the biphasic hydrogenation of unsaturated aldehydes.[7] This prompted us to reinvestigate the hydrogenation of carbon dioxide and its derivatives in aqueous solutions catalyzed by water soluble platinum group metals phosphine complexes *as a function of pH*. In addition to $[RuCl_2(tppms)_2]_2$, $[RhCl(tppms)_3]$ **9** [HRu(ac)(tppms)$_3$] **10**, *trans*-[IrCl(CO)(tppms)$_2$] **11**, $[PdCl_2(tppms)_2]$ **12**, and complexes of 1,3,7-triaza-7-phosphaadamantane (pta), such as $[RuCl_2(pta)_4]$ **13** and $[RhCl(pta)_3]$ **14** were also studied.[8] Here we report that **8–10** and **13** catalyze the hydrogenation of CO_2 in aqueous solutions under mild conditions without the need of an amine additive.

When solutions of **8**, **9** and **13** were agitated under a CO_2–H_2 atmosphere (up to 80 atm total pressure) at 24 °C, small amounts of formic acid were detected by $^1H/^{13}C$ NMR with TOFs not exceeding 1.5 h^{-1} (Table 1). However, when the solvent was changed for 0.2–1.0 M $NaHCO_3$ a substantial increase in the catalytic activity was observed and TOFs reached 262 h^{-1} with **9** at 24 °C. Further increase of the pH decreased the rate of hydrogenation (entry 7). These data represent a significant improvement over previous results in that the turnover frequencies for Ru-based catalysts are among the highest obtained so far in aqueous solutions, moreover, the reductions do not require addition of an organic co-solvent or an amine or alcohol to stabilize the product. In contrast, no formate production took place with **11**, **12** and **14** under the conditions of entry 13. Instead, **12** yielded a dark brown precipitate while the originally yellow solutions of **11** and **14** became colorless; these reactions were not investigated in further detail. We note, however, that Pruchnik *et al.*[9] observed catalysis of the reverse water gas shift reaction in aqueous solution by $[Rh_2(ac)_4(H_2O)_2]$ + pta (Rh : pta = 1 : 3); no sign of CO formation in our system with **14** was detected.

Most of the experiments were done on the hydrogenation of aqueous $NaHCO_3$ solutions; the results are summarized in Table 1. No carbon containing products other than formate were

Table 1 Reduction of CO_2 in aqueous systems at various pH catalyzed by water soluble Ru- and Rh-phosphine complexes‡

Entry	Catalyst	[P]/[M][a]	Base/solvent	$p(CO_2)$/atm	$p(H_2)$/atm	T/°C	t/h	TON	TOF/h^{-1} average
1	**8**	5	H_2O	20	60	24	14.5	21.6	1.49
2	**9**	6	H_2O	20	60	24	14.5	1.6	0.11
3	**13**	4	H_2O	20	60	24	13.5	3.2	0.24
4	**8**	4	1 M $NaHCO_3$	—	60	54	209	289	1.4 (47)[b]
5	**13**	4	1 M $NaHCO_3$	—	60	54	456	358	0.78 (4.5)[b]
6	**13**	4	1 M $NaHCO_3$	—	60	103	22.5	358	16 (49)[b]
7	**13**	4	0.2M $NaHCO_3$+0.8 M Na_2CO_3	—	60	54	286	75	0.26
8	**10**	6	1 M $NaHCO_3$	—	10	50	18	284	16
9	**8**	5	200 mg $CaCO_3$/2 ml H_2O[c]	20	60	24	14	372[d]	26.6
10	**9**	6	200 mg $CaCO_3$/2 ml H_2O[c]	20	60	24	14	262	18.7
11	**13**	4	200 mg $CaCO_3$/2 ml H_2O[c]	20	60	24	14	35	2.5
12	**8**	2	0.2 M $NaHCO_3$	—	10	50	4	0.04	0.01
13	**8**	4	0.2 M $NaHCO_3$	—	10	50	4	60	15
14	**8**	6	0.2 M $NaHCO_3$	—	10	50	4	60	15
15	**8**	4	0.2 M $NaHCO_3$ + 0.2 M KI	—	10	50	4	55	14
16	**9**	7	1 M $NaHCO_3$	5	35	24	2	524	262

[a] Total phosphorus to metal ratio; [M] = 2.0–2.5 mM. [b] Initial turnover frequencies in parentheses. [c] Suspensions. [d] 0.93 M HCO_2^- final solution.

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† Dedicated to Prof. Mihály T. Beck on the occasion of his 70th birthday.

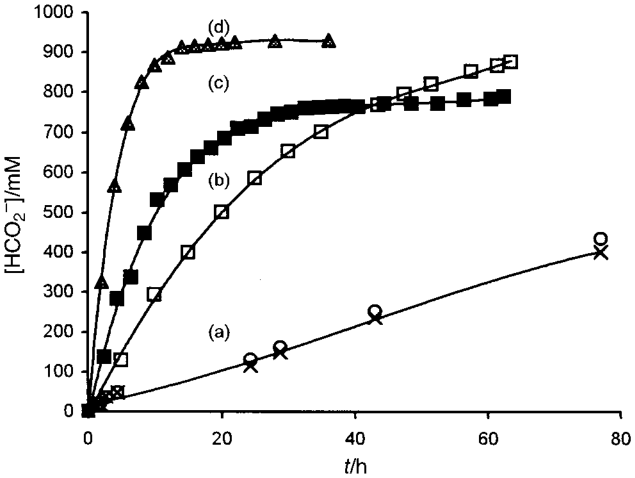

Fig. 1 Time course of formate production in reaction of HCO_3^- with H_2 catalyzed by $[RuCl_2(pta)_4]$ [(a), (b), (d)] and by ½$[RuCl_2(tppms)_2]_2$ + 2 tppms (c) at 50 (c), 54 (a), 90 (b) and 103 °C (d) followed by ^1H [(a), –**x**–] or ^{13}C NMR (all other cases).

detected. With any of **8**–**10** and **13** the reactions started with no appreciable induction period (Fig. 1). Increase of the temperature from 54 to 103 °C caused an 11-fold increase of the initial rate of formate production with **13** (entries 5, 6). Despite the similarity[10] of pta to PMe_3, **13** proved considerably less active than **8**. However, the anionic ligand of the catalyst (precursor) had no significant influence: either **8** in the presence of NaI or **10** gave approximately the same rate as the unmodified **8** (entries 8, 13, 15). Both with **8** and **9** some excess of tppms proved beneficial for activity and catalyst stability—in fact **8** was almost completely inactive without added tppms; however, its catalytic activity was no further increased when the total tppms/Ru ratio exceeded 4 (entries 12–14). As expected, increase of the hydrogen pressure increased the rate of reduction with all catalysts. Conversely, while CO_2 in the gas phase was detrimental with **8** and **13**, it was essential for high reaction rates with **9** (although a much slower reaction still proceeded in its absence). The substrate bicarbonate can be produced *in situ* in the reaction of carbonates and CO_2. When a 2 ml aqueous suspension of 200 mg $CaCO_3$ was pressurized with CO_2 (20 atm) and H_2 (60 atm) and shaken in an NMR tube overnight at 24 °C with **8**, calcium formate was produced with TOF = 26.6 h^{-1}, the total TON reaching 372. Similar experiments with **9** and **13** yielded formate with TOF 18.7 and 2.5 h^{-1}, respectively (see also Table 1). The presence of $CaCO_3$ in these systems is highly beneficial, since under the same conditions CO_2 alone is reduced with TOF 1.49 (**8**), 0.11 (**9**), and 0.24 h^{-1} (**13**); the rate increase with **9** is more than 160-fold!

It is premature to speculate on detailed mechanisms of the hydrogenation of bicarbonate in these systems. It is known[7] that in aqueous KCl solutions, at the pH (8.3) corresponding to that of 1 M of $NaHCO_3$ solutions used in the present experiments, **8** + tppms + H_2 rapidly yields **6** in which the total P/Ru ratio is 4, found optimal for reductions here (entry 13). However, pH-static titrations (similar to those described in ref. 7) of **8** under H_2 in $NaHCO_3$ solutions containing an excess of tppms showed formation of only 0.4–0.6 mol H^+ for 1 mol Ru during the early phase of the reaction (instead of 2 mol required for **6**). This suggests a monohydride, possibly $[HRu(HCO_3)(tppms)_4]$ as a more likely intermediate. Both of these catalysts would account for the observed independence of the rate from the starting composition of the catalyst precursor. Assuming a constant catalyst composition in the pH range from 8.3 (1 M $NaHCO_3$) to 10.8 (0.2 M $NaHCO_3$ + 0.8 M Na_2CO_3) the lower reactivity of CO_3^{2-} (entry 7) is consistent with its known inferior tendency of oxygen exchange with H_2O compared to HCO_3^-.[11]

So far homogeneous catalytic hydrogenation of HCO_3^- in aqueous solutions has not been reported in the literature. Stalder *et al.*[12] used various heterogeneous Pd catalysts with a maximum TOF of 35 h^{-1} (Pd/C, 25 °C). Kudo *et al.*[13] studied in detail the reduction of CO_2 (40 atm) catalyzed by $PdCl_2$ in aqueous KOH at forcing conditions (106 atm H_2, 240 °C). In our opinion, based on the $CO_3^{2-}/HCO_3^-/H_2O$ equilibrium, all similar reactions using *aqueous* solutions or mixture of amines or carbonates under CO_2 pressure, in fact, may have utilized HCO_3^- as the real substrate in the catalytic cycle. This could also explain the beneficial effect of a small amount of H_2O on CO_2 reductions often observed[4*b*,14] in organic solvent systems.

This work was supported by the Hungarian National Research Foundation (OTKA T023997 and F 023159) and by the Office Fédéral de l'Education et de la Science, Suisse (OFES C98.0011 to G.L.). L. N. is grateful for an OFES fellowship, 1998/99. The loan of $RuCl_3.xH_2O$ by Johnson-Matthey PLC is gratefully acknowledged. This research is part of the collaboration within the COST Action D10 /0001 Working Group.

Notes and references

‡ Non-SI units: *p*/atm = 101.325 kPa; *T*/K = T/°C + 273.15. Ligands tppms, pta and their Rh, Ru and Ir complexes were prepared as described in refs 8–10. Hydrogenation experiments were carried out in well stirred, heavy walled glass tubes with 10 atm H_2 or in high pressure sapphire NMR tubes with 60 atm H_2 (pressures at room temperature) intensively shaken (300 min^{-1}) on top of a laboratory shaker. Formate concentration was determined by HPLC or the reaction mixture was analyzed *in situ* by ^1H and/or ^{13}C NMR spectroscopy (Bruker AC 200, AM 360, DRX 400) using ^{13}C-enriched (99%) $NaHCO_3$.

1 Most recent reviews: D. Walther, M. Ruben and S. Rau, *Coord. Chem. Rev.*, 1999, **182**, 67; X. Yin and J. R. Moss, *Coord. Chem. Rev.*, 1999, **181**, 27.
2 P. G. Jessop, T. Ikariya and R. Noyori, *Nature*, 1994, **368**, 231.
3 O. Kröcher, R. A Köppel and A. Baiker, *Chem. Commun.*, 1997, 453.
4 (*a*) W. Leitner, *Angew. Chem.*, 1995, **107**, 2391; *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 2207; (*b*) W. Leitner, E. Dinjus and F. Gassner, in *Aqueous-Phase Organometallic Catalysis*, ed. B. Cornils and W. A. Herrmann, Wiley-VCH, Weinheim, 1998, p. 486.
5 F. Joó and M. T. Beck, *Magy. Kém. Foly.*, 1973, **79**, 189; F. Joó, *Proc. 15th ICCC* (*Moscow, USSR, 1973*), p. 556.
6 F. Joó and M. T. Beck, *React. Kinet. Catal. Lett.*, 1975, **2**, 257.
7 F. Joó, J. Kovács, A. Cs. Bényei and Á. Kathó, *Catal. Today*, 1998, **42**, 441.
8 (**8**, **10**): Z. Tóth, F. Joó and M. T. Beck, *Inorg. Chim. Acta.*, 1980, **42**, 153; (**9**, **11**): F. Joó, J. Kovács, Á. Kathó, A. C. Bényei, T. Decuir and D. J. Darensbourg, *Inorg. Synth.*, 1998, **32**, 1; (**12**): K.-C. Tin, N.-B. Wang, R.-X. Li, Y.-Z. Li and X.-J. Li, *J. Mol. Catal. A: Chem.*, 1998, **137**, 113; (**13**): D. J. Darensbourg, F. Joó, M. Kannisto and Á. Kathó, *Organometallics*, 1992, **11**, 1990; (**14**): F. Joó, L. Nádasdi, A. Cs. Bényei and D. J. Darensbourg, *J. Organomet. Chem.*, 1996, **512**, 45.
9 F. P. Pruchnik, P. Smolenski and I. Raksa, *Pol. J. Chem.*, 1995, **69**, 5.
10 J. R. Delerno, L. M. Trefonas, M. Y. Darensbourg and R. J. Majeste, *Inorg. Chem.*, 1976, **15**, 816.
11 H. Gamsjäger and R. K. Murmann, in *Adv. Inorg. Bioinorg. Mech.*, 1983, **2**, 343.
12 C. J. Stalder, S. Chao, D. P. Summers and M. S. Wrighton, *J. Am. Chem. Soc.*, 1983, **105**, 6318.
13 K. Kudo, N. Sugita and Y. Takezaki, *Nippon Kagaku Kaishi*, 1997, 302; *Chem. Abstr.*, 1977, **86**, 178068s.
14 Y. Inoue, H. Izumida, Y. Sasaki and H. Hashimoto, *Chem. Lett.*, 1976, 863.

Communication 9/02368B