Tetrahedron Letters 50 (2009) 1603–1606

Contents lists available at ScienceDirect

Tetrahedron Letters

journal homepage: www.elsevier.com/locate/tetlet

Improved hydrogen generation from formic acid

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ARTICLE INFO

Article history:
Received 24 November 2008
Revised 13 January 2009
Accepted 20 January 2009
Available online 23 January 2009

Keywords:
Catalysis
Formic acid
Hydrogen
Ruthenium

ABSTRACT

The ruthenium-catalyzed generation of hydrogen from formic acid was investigated in the presence of amines and halide additives. While amidines and halide additives increase the production of hydrogen with $[RuCl_2(p\text{-cymene})]_2$, >330 mL hydrogen/h is generated in the presence of $[RuCl_2(\text{benzene})]_2$/dppe and *N*,*N*-dimethyl-*n*-hexylamine.

A central challenge for the next decades is the sufficient and sustainable supply of energy. Due to ever-increasing energy demand, more efficient technologies for the production, distribution, storage, and conversion of energy are stringent necessary.[1] This has to go hand in hand with the growing exploitation of non-fossil, renewable energy resources. In this respect, a hydrogen economy would allow for the reduction of greenhouse gases.[2] The deployment of hydrogen as a carbon-free fuel source is dependent on its safe and efficient production and transport.[3] A key issue is also the current lack of safe and practical methods for onboard storage of hydrogen. In general, this problem might be solved by reversible hydrogenation and dehydrogenation reactions of organic compounds.[4,5] Unfortunately, the release of hydrogen from most potential substrates, for example, alcohols or cyclic and linear alkanes requires high temperatures.[6] Other potential inorganic molecules like ammonia, amino boranes, and metal hydrides lack either price, toxicity, handling or reactivity. Recently, we and the groups of Laurenczy and Fukuzumi demonstrated independently that formic acid can be used as efficient storage material for hydrogen.[7] This allows for a CO_2-neutral energy generation, if the used hydrogen is made without concomitant production of carbon dioxide. More specifically, it was shown that the catalytic hydrogen generation from formic acid is possible at ambient conditions from organic[8] as well as aqueous solutions.[9,10] In this Letter, we describe the influence of organic bases and of inorganic salt additives on the productivity and activity of the Ru-catalyzed hydrogen generation from formic acid (Scheme 1). Based on our previous work, formic acid was catalytically decomposed within 3 h at 40 °C applying $[RuCl_2(p\text{-cymene})]_2$ as pre-catalyst. Selected results indicating the influence of various organic bases (Fig. 1) are listed in Table 1. Besides the nature of the base, its ratio to formic acid controls the activity of the catalyst system. For the majority of bases, an increase in the base concentration improved the catalyst activity.

In general, tertiary alkyl amines such as triethylamine (NEt_3), *N*,*N*-dimethyl-*n*-hexylamine, and *N*,*N*-dimethyl-ethanolamine (Table 1, entries 1–6) allow for significantly higher catalyst activities compared to pyridine, piperidine, urea, *N*,*N*,*N*′,*N*′-tetramethylurea, *N*,*N*-dimethylglycine as well as diethanolamine, and ethanolamine (Table 1, entries 7–11, 13–15). However, the ethyl ester of *N*,*N*-dimethyl-glycine improved the activity (Table 1, entry 12). To our delight, in the presence of more basic amidines higher activities are achieved. Hence, with 1,5-diazabicyclo-[4.3.0]non-5-ene (DBN), the best catalyst performance for this ruthenium catalyst known to date is observed (Table 1, entries 18 and 19). It should be noted that the concentration of DBN cannot be increased (a 4:5 adduct is not possible) because of immiscibility. Other amidines and guanidines bearing an N=C–N motive are appropriate bases, too. Hence, 1,5,7-triazabicyclo-[4.4.0]dec-5-ene (TBD; Table 1, entry 20), 7-methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene (MTBD; Table 1, entry 21), and *N*′-*tert*-butyl-*N*,*N*-dimethylformamidine

$$HCO_2H \xrightarrow[\text{3 h, 40 °C}]{\text{Ru, ligand, base}} H_2 + CO_2$$

Scheme 1. Hydrogen from formic acid.

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0040-4039/$ - see front matter © 2009 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tetlet.2009.01.101

(Table 1, entry 22) allowed for fast hydrogen generation. However, imidazole and guanidine acetate caused lower activity (Table 1, entries 23 and 24). Noteworthy, the so-called Schwesinger base (P1–*t*Bu) with N=P–N unit resulted also in a highly active system (Table 1, entry 26).

In general, the rate of hydrogen is correlated with the pK_a of the corresponding R_3NH^+ ions of the respective base (Scheme 2). In all catalytic experiments, hydrogen, carbon dioxide, and argon (inert gas atmosphere) were detected as gaseous products. In addition, up to 56 ppm carbon monoxide was observed. Important for applications, in most cases the CO content is below our limit of detection (10 ppm), which allows for a direct use of the hydrogen in a H_2/O_2 fuel cell.

Next, we studied the effect of different additives on the rate of hydrogen generation. Comparison of entries 1 and 2 in Table 2 reveals that the presence of halide ions has also a significant influ-

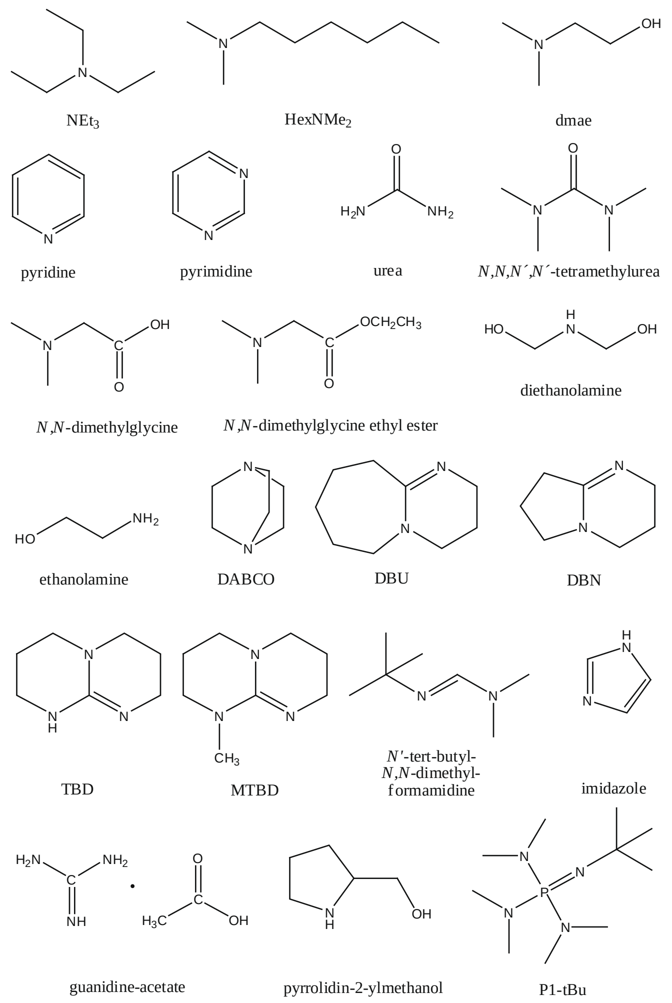
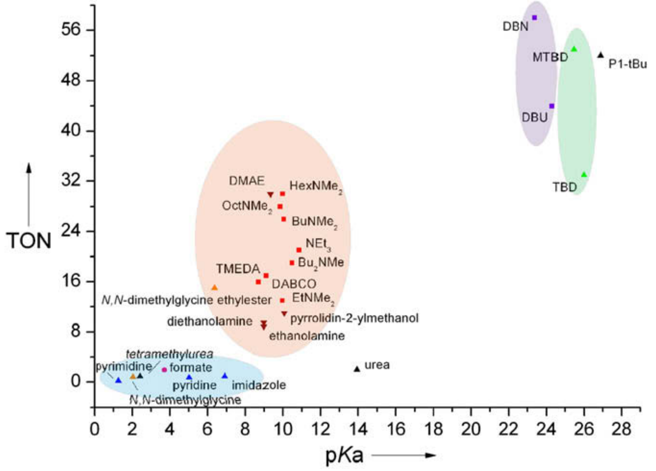


Figure 1. Nitrogen-containing organic compounds tested in the decomposition of formic acid.



Scheme 2. Relationship between the pK_a of the corresponding R_3NH^+ ions and TON values.

Table 1

Decomposition of formic acid amine adducts with $[RuCl_2(p\text{-cymene})]_2$

Entry	Amine	Ratio amine:HCO_2H	V_{gas} 2 h[a] (mL)	TON 2 h	V_{gas} 3 h[a] (mL)	TON 3 h	CO (ppm)
1	NEt$_3$	2:5	41	14	61	21	<10
2	**NEt$_3$**	**3:4**	**111**	**38**	**222**	**76**	**<10**
3	HexNMe$_2$	2:5	59	20	88	30	<10
4	**HexNMe$_2$**	**4:5**	**94**	**32**	**116**	**40**	**<10**
5	dmae	2:5	59	20	88	30	10
6	dmae	4:5	28	10	39	13	10
7	Pyridine	4:5	1.8	0.62	2.3	0.79	28
8	Pyrimidine	2:5	0.50	0.17	0.80	0.27	21
9	Urea	2:5	3.3	1.1	5.6	1.9	56
10	*N,N,N′,N′*-Tetramethylurea	2:5	1.4	0.48	3.0	1.0	33
11	*N,N*-Dimethylglycine	2:5	2.0	0.68	2.5	0.85	<10
12	*N,N*-Dimethylglycine ethyl ester	2:5	32	11	44	15	<10
13	Diethanolamine	2:5	18	6.3	26	8.9	<10
14	Diethanolamine	4:5	17	5.9	26	8.9	<10
15	Ethanolamine	4:5	18	6.3	26	8.9	<10
16	DABCO	2:5	35	12	46	16	<10
17	DBU	2:5	86	29	127	44	<10
18	**DBN**	**2:5**	**116**	**40**	**168**	**58**	**<10**
19	**DBN**	**3:5**	**222**	**76**	**263**	**90**	**<10**
20	TBD	2:5	65	22	97	33	<10
21	**MTBD**	**2:5**	**104**	**36**	**155**	**53**	**<10**
22	***N′-tert*-Butyl-*N,N*-dimethylformamidine**	**2:5**	**88**	**30**	**130**	**44**	**15**
23	Imidazole	2:5	2.5	0.85	3.4	1.2	<10
24	Guanidine acetate	2:5	18	6.3	28	9.5	10
25	Pyrrolidin-2-ylmethanol	2:5	23	7.9	32	11	<10
26	**P1-*t*Bu**	**2:5**	**95**	**33**	**151**	**52**	**<10**

Reaction conditions:[11] 5.0 mL HCOOH/amine, 29.75 μmol $[RuCl_2(p\text{-cymene})]_2$, 40 °C, 3 h.

[a] Measured by gas burette (H_2:CO_2 = 1:1).

Table 2
Decomposition of formic acid/NEt_3 adducts with $[RuX_2(arene)]_2$ (X = Cl, I) in the presence of additives

Entry	Ru precursor/ligand	Additive (MX_y)	Ratio X:Ru	V_{gas} 2 h[a] (mL)	TON 2 h	V_{gas} 3 h[a] (mL)	TON 3 h
1	$[RuCl_2(p\text{-Cymene})]_2$	—	0	41	14	61	21
2	$[RuI_2(p\text{-Cymene})]_2$	—	0	84	29	126	43
3	$[RuCl_2(p\text{-Cymene})]_2$	KBr	3	58	20	88	30
4	$[RuCl_2(p\text{-Cymene})]_2$	KBr	10	101	34	150	51
5	$[RuCl_2(p\text{-Cymene})]_2$	KBr	20	111	38	164	56
6	$[RuCl_2(p\text{-Cymene})]_2$	$MgBr_2$	10	78	27	120	41
7	$[RuCl_2(p\text{-Cymene})]_2$	KI	10	279	96	338	116
8[b]	$[RuCl_2(Benzene)]_2$/40 PPh_3	—	0	133	454	147	505
9[b]	$[RuCl_2(Benzene)]_2$/40 PPh_3	KBr	3	87	296	98	336
10[b,c]	$[RuCl_2(Benzene)]_2$/40 PPh_3	H_2O	100	92	314	102	350
11[b,d]	$[RuCl_2(Benzene)]_2$/40 PPh_3	H_2O	46607	4.4	15	6.7	23
12	$[RuCl_2(Benzene)]_2$/12 PPh_3	—	0	347	371	423	452
13	$[RuCl_2(Benzene)]_2$/12 PPh_3	$MgBr_2$	10	245	262	306	326
14	$[RuCl_2(Benzene)]_2$/12 PPh_3	KI	10	207	221	260	277

Reaction conditions:[11] 5.0 mL 5 HCO_2H/2 NEt_3, 29.75 µmol $[RuX_2(p\text{-cymene})]_2$ or 9.55 µmol $[RuCl_2(benzene)]_2$, 40 °C, 3 h.

[a] Measured by gas burette (H_2:CO_2 = 1:1).

[b] 2.975 µmol $[RuCl_2(benzene)]_2$.

[c] 11 µL water added to the substrate.

[d] 5 mL water added to the substrate.

Table 3
Hydrogen generation from formic acid/NEt_3 adducts with $[RuCl_2(benzene)]_2/PR_3$: combination of best conditions

Entry	Amine	Ratio amine:HCO_2H	Ligand	V_{gas} 2 h[a] (mL)	TON 2 h	V_{gas} 3 h[a] (mL)	TON 3 h
1[b]	NEt_3	2:5	PPh_3	347	371	423	452
2[b]	DBN	3:5	PPh_3	378	403	479	511
3	DBN	3:5	PPh_3	366	391	472	504
4[b]	NEt_3	2:5	dppe	238	254	1289	1376
5[b]	DBN	3:5	dppe	20	21	33	35
6	DBN	3:5	dppe	140	149	181	193
7	NEt_3	3:4	dppe	1387	1480[c]	1541	1644[c]
8	$HexNMe_2$	4:5	dppe	1336	1425[d]	1377	1469[d]

Reaction conditions:[11] 5.0 mL formic acid/amine, 9.55 µmol $[RuCl_2(benzene)]_2$, Ru/P = 1:6, 40 °C, 3 h.

[a] Measured by gas burette (H_2:CO_2 = 1:1).

[b] Pre-treatment of the catalyst 2 h in 1.0 mL DMF.

[c] Conversion: 69% after 2 h, 77% after 3 h

[d] Conversion: 86% after 2 h, 89% after 3 h.

ence. Thus, addition of 3 equiv KBr led to an increase in the catalyst activity by more than 40% after 3 h (Table 2, entry 3). In the presence of 10 and 20 equiv of KBr, hydrogen production rose to 240% and 260%, respectively (Table 2, entries 4 and 5). Also, the addition of $MgBr_2$ (Table 2, entry 6) increased the catalyst activity.

The best result with $[RuCl_2(p\text{-cymene})]_2$ as pre-catalyst is obtained by addition of 10 equiv of KI (Table 2, entry 7). Here, the catalyst activity increased by >450% with respect to $[RuCl_2(p\text{-cymene})]_2$. Next, we applied these optimized conditions to more sensitive phosphine-containing ruthenium catalysts. Here, a decrease of the catalyst activity is observed by addition of KBr (Table 2, entries 8 and 9). We thought that this is explained in part due to the water sensitivity of the phosphine-containing catalyst. Indeed, addition of 11 µL water caused a similar decrease in reactivity of the catalytic system as the addition of KBr, while in the presence of 5.0 mL only little activity is seen (Table 2, entry 11).

Finally, we tested the standard ruthenium phosphine and a recently optimized catalyst system consisting of $[RuCl_2(benzene)]_2$ and 12 equiv 1,2-bis-(diphenyl-phosphino)ethane (dppe) (Table 3). While applying $[RuCl_2(benzene)]_2/PPh_3$, no significant effect of the amine on hydrogen production is observed, with dppe a significant deactivation of the catalyst occurred in the presence of DBN (Table 3, entries 1–6). Noteworthy, applying the latter catalyst system with triethylamine (3:4; amine to HCO_2H) or *N*,*N*-dimethyl-*n*-hexylamine (4:5), a fast hydrogen generation is possible with conversion of more than 69% within 2 h (Table 3, entries 7 and 8).

In conclusion, we have shown that depending on the ruthenium pre-catalysts, amines and halide additives have a significant influence on the catalyst activity. For the first time it is shown that amidines increase the production of hydrogen from formic acid. Moreover, under optimized conditions, >330 mL hydrogen/h is generated from 5 mL formic acid/amine mixture, which allows for electrical applications.

Acknowledgments

This work has been supported by the State of Mecklenburg-Vorpommern, the BMBF, and the DFG (Leibniz-prize). We thank Dr. C. Fischer, Ms. S. Buchholz, Ms. C. Mewes (LIKAT), and Ms. A. Meißner for their excellent analytical and technical support.

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11. All catalytic experiments were carried out under an inert gas atmosphere (argon) with exclusion of air. Formic acid and amines were distilled in vacuum prior to use and stored under argon. The catalyst precursors and phosphine ligands have been purchased from commercial suppliers and stored under argon. All reactions were performed in a double-walled thermostated reaction vessel with a reflux condenser, which is connected to a setup of two manual or one automatic gas burette, where the gases are collected. In addition, a GC for analyzing gases is applied (gas chromatograph HP 6890N, permanent gases: Carboxen 1000, TCD, external calibration; amines: HP Plot Q, 30 m, FID). Typically a ratio of hydrogen and carbon dioxide of 1:1 ± 5% is detected. *Typical procedure for the decomposition of formic acid/amine adducts*: The premixed solution of HCO_2H/amine (5.0 mL) was warmed to 40.0 °C in a double-walled thermostated reaction vessel. The vessel is purged with argon to remove any other gas before the reaction is started by addition of the catalyst either as powder in a Teflon crucible $[RuCl_2(p\text{-cymene})]_2$ (18.23 mg, 29.75 μmol) or as a solution in DMF (4.78 mg, 9.55 μmol $[RuCl_2(\text{benzene})]_2$/30.06 mg, 114.6 μmol PPh_3) via septa and a small polyethylene tube.