Hydrogen generation: catalytic acceleration and control by light[†]

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The ruthenium-catalyzed generation of hydrogen from formic acid is significantly accelerated by light.

The sufficient and sustainable supply of energy remains one, if not the most, important challenge for our future. An abundant source of energy is sunlight, which provides about 2.9×10^{24} J per year, of which about 50% (UV/Vis) can be used for photochemistry.¹ In the coming years it will be vital to develop novel efficient processes to convert the energy of light into chemical energy. Among the various energy carriers hydrogen is a promising candidate, which can be efficiently used in fuel cells generating electricity and water. Nevertheless, advancements in hydrogen technology such as the generation of hydrogen from suitable starting materials, its storage and conversion to electrical energy are needed.

Recently, we² and the group of Laurenczy³ have demonstrated for the first time that hydrogen can be generated from formic acid at ambient conditions and directly applied in fuel cells. While the reverse reaction (hydrogenation of carbon dioxide) has been studied extensively since then,⁴ the whole idea of using formic acid as an energy carrier has received considerable attention only lately.⁵ Based on the hydrogen evolution from alcohols,⁶ we showed that the commercially available [RuCl₂(*p*-cymene)]₂ catalyst is suitable for hydrogen generation from formic acid in the presence of amines at ambient conditions. Improved catalytic activity can be obtained with $[RuCl_2(PPh_3)_3]$ as catalyst,² while Laurenczy and co-workers reported a system based on a water soluble ruthenium catalyst.³ More recently, we demonstrated an increase of the catalyst activity with in situ-generated ruthenium phosphine catalyst systems at room temperature.⁷ Notably, both Fukuzumi et al.⁸ and Laurenczy and co-workers⁹ reported details of the mechanism of formic acid/formate decomposition in aqueous solution. In addition, Zhou et al. presented heterogeneous catalysts for hydrogen supply from formic acid/sodium formate.¹⁰

Here, we demonstrate for the first time that visible light significantly accelerates and controls the ruthenium-catalyzed hydrogen generation from HCO_2H in the presence of amines (Scheme 1). Although the photochemistry of ruthenium phosphine complexes has been investigated extensively in the past,¹¹ the catalytic exploitation of these properties has been scarce.^{6d,e} Also, only a few light-accelerated hydrogen generation reactions in the presence of other metal catalysts are known. For example, Onishi reported in 1993 an increase of the turnover number

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Scheme 1 Light-accelerated hydrogen generation from formate.

(TON) of 0.09 to 1.6 within 3 hours in the HCo(PhP(Et)₂)₄catalyzed H₂ evolution upon applying a 400 W Hg vapor lamp with a pyrex filter.¹² At the same time, King *et al.* showed that hydrogen is evolved from aqueous formate solutions with chromium hexacarbonyl under irradiation (TON = 18 after 1 h).¹³ In addition, (UV-)photooxidation of formic acid and other organic compounds with heterogeneous catalysts is used in environmental chemistry, *e.g.* for wastewater treatment.¹⁴ Clearly, in all these examples only small amounts of hydrogen are generated, which makes a combination with fuel cells or the direct use in energy applications not applicable.

In order to investigate the influence of light on our hydrogen generation reaction in detail, we exposed a solution of 5HCO₂H·2NEt₃ (5 mL) and various in situ-generated ruthenium catalysts to irradiation. The reactions were performed at 40 °C in the presence of 320 ppm Ru (Ru : P = 1 : 6). As light source a PerkinElmer Cermax 300 W xenon-arc lamp with a filter designed to approximate the spectrum of sunlight in the UV/Vis region has been applied. The filter cuts off UV below 380 nm and IR wavelengths between 780 and 1200 nm.¹⁵ Additionally, we performed experiments in the dark. Selected results are summarized in Fig. 1. In control experiments in the presence of triphenylphosphine without any ruthenium precursor or using [RuCl₂(benzene)]₂ alone no positive influence of light is observed (Fig. 1, entries 1 and 2). Remarkably, in the presence of both [RuCl₂(benzene)]₂ and



Fig. 1 The influence of light on the decomposition of $5 \text{ mL } 5\text{HCO}_2\text{H}/2\text{NEt}_3$ with ruthenium catalyst systems (320 ppm Ru). ^aNo hydrogen detected by GC; ^bno dark experiment, performed under lab conditions, environmental light.

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arvl phosphines a considerable accelerating effect of irradiation is seen (Fig. 1, entries 3-6). For example in the presence of PPh₃ the turnover number increased from 322 to 1649 during irradiation (Fig. 1, entry 3). Likewise with substituted triphenylphosphines, both with electron-donating or electron-withdrawing substituents (Fig. 1, entries 4 and 5), the positive effect of light is observed. Compared to triphenylphosphine, catalyst activities in the dark are only about 24% and 63% for these ligands, respectively. Notably, the combination of bidentate ligand 1,2-bis-(diphenyl-phosphino)ethane (dppe) and [RuCl₂(benzene)]₂ showed the best activity (TON: 2804 vs. 407 in the dark) reaching 90% conversion after 2 h (Fig. 1, entry 6). Tricyclohexylphosphine as a common electron-donating alkyl-phosphine ligand retains its inhibiting effect also upon irradiation (Fig. 1, entry 7). Catalysts containing triphenylphosphite showed only low activity and no significant effect of irradiation is detected (Fig. 1, entry 8).

Clearly, the observed effects do not simply rely on the metal precursor. With other ruthenium complexes (Fig. 1, entries 10 and 11), a photoactivation of the catalyst is observed, too. The active species derived from [Ru(cod)(methylallyl)₂] even showed the most pronounced effect upon irradiation (1160% increase of gas evolution), but is not very active in the dark (TON = 115). A positive effect (39% increase of gas evolution) of light is observed with the catalyst derived from RuCl₃·*x*H₂O. Also when the molecular-defined ruthenium hydrido complex [RuH₄(PPh₃)₃] is used, irradiation accelerates the reaction by 27% (Fig. 1, entry 12). However, [RuH₄(PPh₃)₃] is overall less active than a comparable *in situ* system (Fig. 1, entries 3, 10 and 11).

In the presence of light significant amounts of hydrogen are generated even at 0 °C (Table 1). This is an interesting observation because the system can be combined with a fuel cell for low temperature applications, *e.g.* appliances in colder areas. To the best of our knowledge this is the first example of hydrogen generation from organic compounds at such low temperatures (Table 1, entries 1–4). At all temperatures studied the influence of light is observed. Obviously, by increasing the temperature the hydrogen generation can be increased. Thus, the observed photochemical activation can be used to save thermal energy.

A careful analysis of the gas evolution in the presence of $[RuCl_2(benzene)]_2$ reveals that irradiation has at least two effects in different phases of the reaction: first, within the induction period of 10 to 20 minutes, a photoinductive effect occurs generating the active catalyst species; and second, when the catalyst is almost deactivated in the dark a reactivation takes place under irradiation (Fig. 2, curve C and D); thus the reaction is photoassisted. Irradiating the pre-catalyst solution for 30 min prior to addition of the substrate, the initial photoinductive effect can be mimicked. Indeed, a catalyst is formed which is highly active under both conditions (Fig. 2, curve A and B). However,

Entry	$T/^{\circ}\mathrm{C}$	Dark		Irradiation	
		$V_{\rm gas}/{\rm mL}$	TON	$V_{\rm gas}/{\rm mL}$	TON
1	0	25	26	182	195
2	25	203	217	1238	1321
3	40	302	322	1545	1649
4	45	399	426	1863	1987



Fig. 2 Typical curves for gas evolution from $5HCO_2H\cdot 2 \text{ NEt}_3$ with $[RuCl_2(benzene)]_2 + 12PPh_3$ (320 ppm Ru).

the second effect, which prevents catalyst deactivation, is more evident: in the dark, there is almost no activity after 1 h, while gas evolution is stable under irradiation.

In order to elucidate the mechanism of the photoactivation ¹H NMR studies simulating the pretreatment with [RuCl₂(benzene)]₂ and 6 equivalents of PPh₃ (3 equiv. PPh₃ per Ru) were performed in DMF-d₇. The signal of η^6 -coordinated benzene, a singlet at 5.79 ppm, is shifted upfield to become a doublet at 5.55 ppm ($J_{PH} = 0.78$ Hz; Fig. 3, A and B) directly after addition of PPh₃. These values are within the same range as those reported by Zelonka and Baird and by Bennett and Smith for [RuX₂(benzene)(PR₃)] complexes.¹⁶

Apparently, a similar ruthenium phosphine complex is formed. The reaction is completed by heating to 80 °C for 2 h, which is underlined by the new multiplet at 7.8 ppm that is attributed to protons of triphenylphosphine. Traces of non-coordinated benzene at 7.38 ppm which appear after heating are due to the beginning of the displacement of the η^6 -coordinated benzene and/or to equilibrium in solution. After 30 min irradiation, however, no η^6 -coordinated benzene is left, and the singlet at 7.38 ppm increases dramatically. Such a photochemical displacement of η^6 -arene ligands in the presence of other ligands is in agreement with previous organometallic studies.^{16b,17}

The proposed photo-assisted dissociation of the η^6 -benzene from the metal center is also supported by the fact that gas evolution with pre-irradiated [RuCl₂(benzene)]₂ + 12PPh₃ catalysts (curve A and B in Fig. 2) is similar to gas evolution with catalysts formed from RuCl₃·*x*H₂O (see ESI†) both in the dark and under irradiation. In addition to the photo-induced activation of the ruthenium arene complexes, there is also a clear photo-assisted regeneration of the active catalyst



Fig. 3 ¹H NMR of the irradiated pre-catalyst solution. (A) [RuCl₂(benzene)]₂ in DMF-d₇; (B) 9.55 μmol [RuCl₂(benzene)]₂, 6 equiv. PPh₃, dissolved in 1.0 mL DMF-d₇; (C) after 2 h at 80 °C; (D) after 30 min irradiation with Xe-arc lamp with filter.



Fig. 4 (A) Light-triggered gas evolution from 5 mL 5HCO₂H·2NEt₃ with $[RuCl_2(benzene)]_2/12PPh_3$ (320 ppm Ru); (B) differential plot of gas evolution in a light-triggered experiment.



Scheme 2 Proposed mechanism for the Ru-catalyzed decomposition of formic acid with a [RuCl₂(benzene)]₂/PAryl₃ catalyst.

occurring (Fig. 4). While the origin of this effect is not fully clear, it offers the opportunity to trigger hydrogen generation. In fact, it is possible to control the formation of hydrogen with light!

As depicted in Fig. 4A the experiments were run for 45 min with light irradiation and then without irradiation (continuous line). In addition, the dashed lines represent typical experiments under permanent irradiation and in the dark, respectively. After an initial formation of a stable photoactive catalyst, gas evolution can be almost stopped switching off the light source, and restarted after turning it on again. In a complementary experiment irradiation with light after 45 min further activates the catalyst (Fig. 4B) in the first cycle of irradiation. In the following irradiation cycles, hydrogen generation is started and stopped by turning the light on or off. This possibility of triggering the reaction with light provides further evidence for a photo-assisted reaction.

According to all these observations, we propose the mechanism shown in Scheme 2. The initial pre-catalyst is activated by irradiation with visible light to give an aryl phosphine-ligated ruthenium hydride species. Deactivation of this active catalyst is prevented by light. Furthermore, the release of hydrogen and/or carbon dioxide from the catalyst is also influenced by light.

In summary, we present the first light-accelerated hydrogen generation reaction from formic acid with a catalyst system based on a ruthenium precursor and aryl phosphines. The overall activity of our light-accelerated ruthenium complex is more than 100 fold higher compared to systems previously reported by Onishi and by King *et al.*^{12,13} In comparison to the non photo-assisted system, a more than one order of magnitude increase of gas evolution is achieved in the light-accelerated

reaction. The best catalyst productivity is observed with a [RuCl₂(benzene)]₂/dppe catalyst. Here, the catalyst activity is almost double the activity of the best non-light activated system. Notably, we demonstrated for the first time that hydrogen evolution can be triggered by switching on and off the light source.

Notes and references

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