

Palladium on Carbon-Catalyzed Gentle and Quantitative Combustion of Hydrogen at Room Temperature

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Abstract: A quantitative and gentle oxidation (combustion) of hydrogen in the presence of oxygen in a variety of solvents was achieved under palladium on carbon (Pd/C)-catalyzed conditions at ordinary pressures and temperatures. A quantitative generation of water accountable for the consumed oxygen was observed. While hydrogen peroxide (H₂O₂), which would form as an intermediate, was extremely unstable under the Pd/C-catalyzed conditions to be converted into water with accompanying oxygen generation, the stability of H₂O₂ was found to be increased in cold (0°C) trifluoroacetic acid, and the formation of 64% H₂O₂ based on the consumed oxygen could be detected. A mechanistic elucidation study revealed that the single electron transfer and generation of the hydroxyl radical are involved in the gentle combustion process. The reactive oxygen species generated during the process was effectively utilized for the chemical oxidation of sulfides and phosphines to afford the corresponding sulfoxides and phosphine oxides, respectively.

Keywords: heterogeneous catalysis; hydrogen; oxidation; oxygen; palladium

The usual hydrogen-oxygen chemical reaction, i.e., combustion, is induced by ignition associated with the liberation of an enormous amount of energy, such as an explosion and flames, based on common sense. The gentle chemical uniting of hydrogen with oxygen has recently attracted much attention in various fields of chemistry due to the connection with the direct synthesis of hydrogen peroxide (H₂O₂),^[1–27] which is widely used as an oxidant, bleach, and disinfectant, since its industrial manufacturing method based on

the sequential hydrogenation and oxidation of the 2-alkylanthraquinone derivative consumes a huge amount of energy.^[28] Most methods for the oxidation of hydrogen gas in the literature require flowing (bubbling) or highly pressurized hydrogen and oxygen gases in aqueous or alcoholic media in the presence of a palladium catalyst,^[1–22] and no quantitative conversion of hydrogen or oxygen under ordinary pressures and temperatures has been reported. Furthermore, the electron transfer process during the combustion of hydrogen gas was never elucidated.

In this paper, we demonstrate an effective and quantitative gentle combustion of hydrogen gas in organic and aqueous solvents using commercially available palladium on carbon (Pd/C) under ordinary pressures and temperatures, involving the hydroxyl radical during the reaction for the generation of H₂O₂ based on the single electron transfer (SET) process, and an effective *in-situ* application of the resulting reactive oxygen species to organic synthesis as mild and transient oxidizing reagents.

A 17-mL test tube containing a suspension of 10% palladium on carbon (Pd/C) in deuterated methanol (CD₃OD, 1 mL) was filled with hydrogen gas (16 mL) and connected to an oxygen gas burette through flexible Tygon tubing (Figure 1). The smooth absorption of oxygen gas through the gas burette under ordinary pressures and temperatures was observed, and the nearly quantitative generation of water relative to the quantity of consumed oxygen was confirmed by the ¹H NMR analysis in CD₃OD (Figure 2a). The amount of generated water (solid line, closed diamond) was virtually identical to the theoretical quantity of water production (dashed line, closed square), which was calculated based on the assumption that 2 equiv. of water are formed from the consumed oxygen, indicating that hydrogen gas in CD₃OD was effectively and quantitatively united with the oxygen in the presence

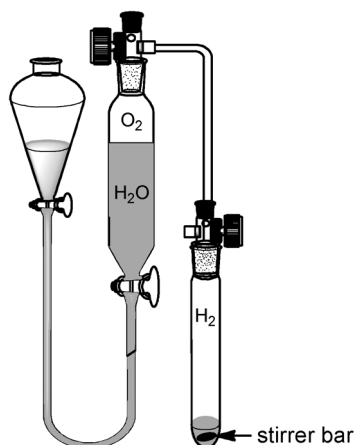


Figure 1. Reaction apparatus using a gas burette.

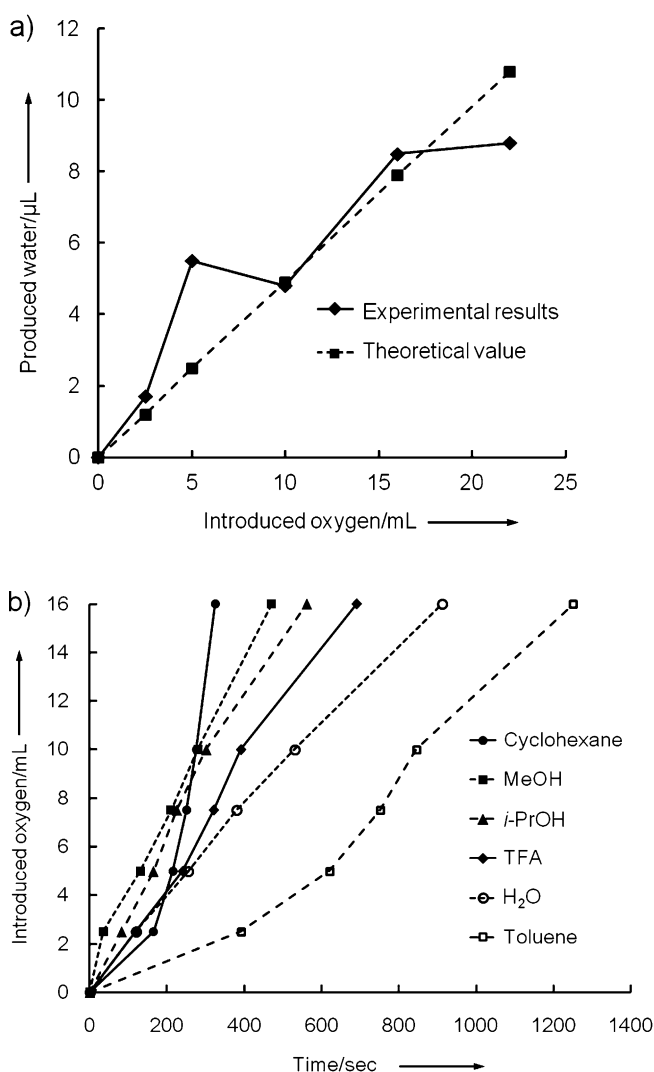


Figure 2. Consumption of oxygen gas during the 10% Pd/C-catalyzed oxidation of hydrogen gas. a) Generation of water in CD_3OD . b) Solvent effect.

of 10% Pd/C under ordinary temperatures and pressures.^[29,30] The gentle combustion of hydrogen gas with oxygen gas could be achieved in a variety of solvents, such as hydrocarbons, alcohols, trifluoroacetic acid (TFA), and water; Figure 2b shows that the oxygen gas was smoothly consumed in each solvent.^[31,32] Since hydrogen peroxide (H_2O_2), which would be a possible intermediate leading to water, was not detected in the filtrates of all samples after the removal of the 10% Pd/C by iodometric analysis, H_2O_2 would be quantitatively converted to water.

The stability of H_2O_2 in water, MeOH, and TFA in the presence of the 10% Pd/C was then evaluated. A mixture of 10% Pd/C and commercially obtained aqueous H_2O_2 , the concentration (24%, 26.9 mg in 100 μL) of which was determined by iodometry prior to use, in each solvent was stirred at 0 °C, 25 °C and 40 °C for 5 min under an argon atmosphere. The residual quantity of H_2O_2 in the filtrates after removal of the Pd/C and the consumed amount of 0.1 M $\text{Na}_2\text{S}_2\text{O}_3$ for iodometric titration are shown in Table 1. Although H_2O_2 was stable in all the solvents at 25 °C without the 10% Pd/C (entries 1, 4, and 7), its stability in the presence of the 10% Pd/C depended on the type of solvents and temperatures.^[33] While the H_2O_2 was readily decomposed at 25 °C in water and MeOH (entries 3 and 6), the stability of H_2O_2 was somewhat improved at 0 °C (entries 2 and 5). Furthermore, the H_2O_2 was relatively stable in TFA (entries 8–10), and almost no decomposition was observed at 0 °C for at least 5 min (entry 8).

Table 1. Stability of H_2O_2 in the presence of 10% Pd/C based on iodometry.

		24% H_2O_2 100 μL 26.90 mg (H_2O_2)		10% Pd/C (2 μmol) Ar, 5 min	remaining H_2O_2 iodometry
Entry	Solvent	T [°C]	0.1 M $\text{Na}_2\text{S}_2\text{O}_3$ [mL] ^[a]	Quantity of H_2O_2 [mg]	
1 ^[b]	H_2O	25	14.5	24.95	
2	H_2O	0	8.3	14.28	
3	H_2O	25	0.5	0.86	
4 ^[b]	MeOH	25	15.3	26.33	
5	MeOH	0	3.2	5.51	
6	MeOH	25	0.7	1.20	
7 ^[b]	TFA	25	16.6	28.57	
8	TFA	0	15.9	27.36	
9	TFA	25	10.2	17.55	
10	TFA	40	5.5	9.46	

^[a] The consumed amount of 0.1 M $\text{Na}_2\text{S}_2\text{O}_3$ ($f=1.012$) during the iodometric titration.

^[b] A mixture of 24% H_2O_2 in each solvent was stirred at 25 °C without Pd/C.

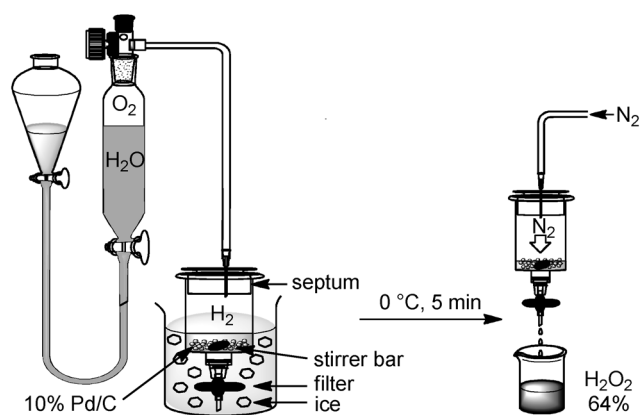


Figure 3. Detection of H_2O_2 as an intermediate.

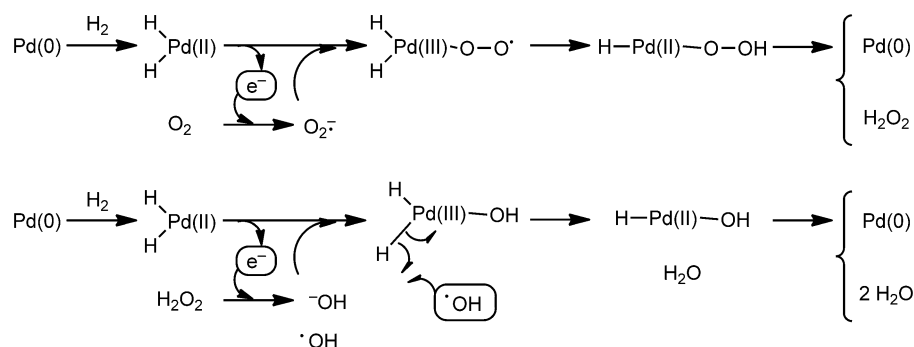
The gentle Pd/C-catalyzed hydrogen–oxygen chemical reaction was then carried out using TFA as a solvent at 0°C .^[34] The resulting reaction mixture was quickly passed through the membrane filter under N_2 gas pressure to remove the Pd/C after the consumption of 0.35 mL of oxygen during a 5 min period, and 64% H_2O_2 based on the consumed oxygen gas was detected in the filtrate by iodometry (Figure 3).

We next investigated the reaction mechanism of the gentle hydrogen combustion leading to the generation of water *via* H_2O_2 (Scheme 1) specifically about the involvement of the single electron transfer (SET) process, generation of the hydroxyl radical, and identification of the oxygen source. The uptake of oxygen gas to a 17-mL test tube containing a suspension of 10% Pd/C (2 μmol , 0.3 mol% *vs.* H_2) in CD_3OD (1 mL) under a hydrogen atmosphere (16 mL) at 25°C was significantly suppressed by the addition of tetracyanoquinodimethane (TCNQ, 20 μmol , 3 mol% *vs.* H_2) as a single electron scavenger, and only 2.5 mL of oxygen were absorbed during 11.5 min, although 16 mL oxygen were smoothly absorbed without TCNQ (see the Supporting Information). The generation of the hydroxyl radical was also confirmed by the ESR spectroscopy-spin trapping method using 5,5-dimethyl-1-pyrroline *N*-oxide (DMPO) as a trapping reagent (see the Supporting Information). These results

strongly suggest the involvement of an SET process during the reaction. Furthermore, it was clarified that the oxygen atom in the generated water was derived from the molecular oxygen by the detection of the incorporated ^{18}O in the generated water when ^{18}O -labelled oxygen gas ($^{18}\text{O}_2$) was used instead of the unlabelled oxygen gas (see the Supporting Information).

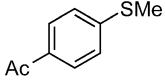
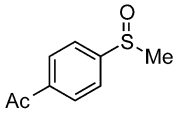
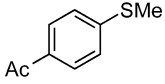
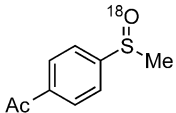
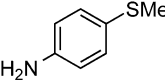
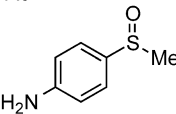
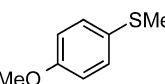
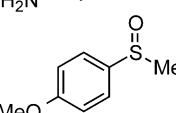
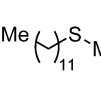
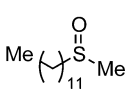
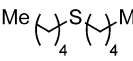
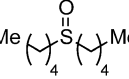
Based on these experiments, the hydroxyl radical and H_2O_2 are obviously generated during the reaction. We then investigated the use of such reactive oxygen species in organic synthesis (Table 2). When 1.8 equiv. of oxygen gas were introduced into a mixture of 10% Pd/C and 4-methylthioacetophenone in TFA at room temperature under a hydrogen atmosphere, the sulfide was selectively monooxidized to give the corresponding sulfoxide in good yield (entry 1).^[35,36] The use of $^{18}\text{O}_2$ instead of O_2 led to smooth incorporation of an ^{18}O atom into the 4-methylthioacetophenone, indicating that the oxygen gas functions as the oxygen source (entry 2, see also the Supporting Information). Either electron-sufficient aryl alkyl sulfides (entries 3 and 4) or dialkyl sulfides (entries 5 and 6) readily underwent the selective *S*-monooxidation to afford the corresponding sulfoxides without any formation of sulfones. Furthermore, the oxygenation method utilizing *in-situ* reactive oxygen species could be used for the synthesis of phosphine oxides from trisubstituted phosphines (entries 7 and 8). Therefore, the present oxidation method would be expected to be a safe and effective protocol for the oxygenation of sulfides and phosphines using a short-lived reactive oxygen species generated from only 1.8 equiv. of oxygen gas during the Pd/C-catalyzed gentle combustion of hydrogen gas under the apparent hydrogen gas-dominated hydrogenation conditions.

In conclusion, hydrogen was gently and quantitatively reacted by the consecutive supply of oxygen in various solvents in the presence of commercially available 10% Pd/C as a catalyst under ordinary pressures and temperatures. Although the intermediary H_2O_2 in the reaction mixture was quite instable and readily decomposed to water with the release of



Scheme 1. Proposed mechanism for the Pd/C-catalyzed combustion of hydrogen.

Table 2. Oxygenation of sulfides and phosphines.

10% Pd/C (2 mol%) H_2 (6.6 equiv.) O_2 (1.8 equiv.) substrate $\xrightarrow{\text{TFA, 25 } ^\circ\text{C}}$ product				
Entry	Substrate	t [h]	Product	Yield [%]
1		8		81
2 ^[a]		6		91
3		6		70
4		1		71
5		1		91
6 ^[b]		3		100
7 ^[c]	Bu_3P	6	$\text{Bu}_3\text{P} \cdot \text{O}$	96
8 ^[c]	Ph_3P	24	$\text{Ph}_3\text{P} \cdot \text{O}$	75

^[a] A small balloon of $^{18}\text{O}_2$ was used instead of 1.8 equiv. of O_2 .

^[b] 10 mol% of 10% Pd/C were used.

^[c] 50 mol% of 10% Pd/C and 9.2 equiv. of O_2 were used.

oxygen, H_2O_2 was detected when the reaction was carried out in cooled (0°C) TFA. The involvement of SET in the reaction process was clarified by the significant suppression of the reaction progress in the presence of a single electron scavenger (TCNQ), and generation of the hydroxyl radical was directly demonstrated by the use of DMPO as a spin trapping reagent in the ESR analysis. The reactive oxygen species was utilized for the *in-situ* oxygenation of sulfides and phosphines, and the corresponding sulfoxides and phosphine oxides were obtained in good yields.

Experimental Section

Generation of Water in CD_3OD during the 10% Pd/C-Catalyzed Oxidation of Hydrogen (Figure 2a)

A suspension of 10% Pd/C (2.1 mg, $2\text{ }\mu\text{mol}$) in CD_3OD (1 mL) in an oven-dried 17-mL test tube under a hydrogen

atmosphere (16 mL, 0.655 mmol, headspace) was stirred at 25°C , and oxygen gas was introduced into the mixture through a gas burette at 25°C and ordinary pressures. After a specific amount of oxygen was introduced (2.5, 5, 10, 16, and 22 mL), the mixture was filtered by a well-dried and small cotton-packed Pasteur pipette, then the amount of water was measured by the ^1H NMR analysis of the filtrate.

Solvent Effect of the 10% Pd/C-Catalyzed Oxidation of Hydrogen Gas (Figure 2b)

A suspension of 10% Pd/C (2.1 mg, $2\text{ }\mu\text{mol}$) in a variety of solvents (1 mL) in an oven-dried 17-mL test tube under hydrogen atmosphere (16 mL, 0.655 mmol, headspace) was stirred at 25°C , then oxygen gas was introduced into the mixture through a gas burette at 25°C and ordinary pressures. The time for the introduction of a specific amount of oxygen was recorded.

Stability of Hydrogen Peroxide (H_2O_2) in the Presence of 10% Pd/C (Table 1)

The concentration of commercially available aqueous 30% H_2O_2 was determined to be 24% by iodometry using 0.1 M $\text{Na}_2\text{S}_2\text{O}_3$ ($f=1.012$) for the titration. The 24% H_2O_2 (26.90 mg, $100\text{ }\mu\text{L}$) was added to a suspension of 10% Pd/C (2.1 mg, $2\text{ }\mu\text{mol}$) in water, MeOH, or TFA (1 mL) in an oven-dried 17-mL test tube under an argon atmosphere. The mixture was stirred at 0, 25, or 40°C for 5 min, then filtered using a $0.45\text{ }\mu\text{m}$ membrane filter. The remaining H_2O_2 in the resulting filtrate was measured by iodometry using 0.1 M $\text{Na}_2\text{S}_2\text{O}_3$ ($f=1.012$) for the titration.

Detection of H_2O_2 as an Intermediate (Figure 3)

A suspension of 10% Pd/C (2.1 mg, $2\text{ }\mu\text{mol}$) in TFA (1 mL) in a 10-mL plastic syringe, which was connected to a $0.45\text{ }\mu\text{m}$ membrane filter, under a hydrogen atmosphere (12.1 mL, 0.4952 mmol, headspace) was stirred at 0°C , then oxygen gas (0.70 mL) was introduced into the mixture through a gas burette in 5 min at 25°C and ordinary pressures. Half of the amount of oxygen (0.35 mL, 0.01432 mmol) out of the introduced oxygen should be consumed for the reaction with hydrogen gas in the ratio of 1 to 1 for the production of H_2O_2 . The mixture was filtered ($0.45\text{ }\mu\text{m}$, Milipore Corporation, Billerica, MA, USA), and the generated H_2O_2 was measured by iodometry of the resulting filtrate. 1.81 mL of 0.01 M $\text{Na}_2\text{S}_2\text{O}_3$ ($f=1.007$) were used for titration; the amount of the generated H_2O_2 was calculated to be 0.3099 mg [$9.113\text{ }\mu\text{mol}$ ($1.007 \times 0.01 \times 1.81 \times 0.5$)]. Since the amount of the consumed oxygen was 0.01432 mmol ($1 \times 0.35 \div 0.082 \div 298$), the yield of the generated H_2O_2 based on the consumed oxygen was calculated to be 64% ($0.009113 \div 0.01432 \times 100$).

General Procedure for the Oxygenation of Sulfides and Phosphines (Table 2)

A suspension of 10% Pd/C (2.1 mg, $2\text{ }\mu\text{mol}$) and sulfide or phosphine (0.1 mmol) in TFA (1 mL) in an oven-dried 17-mL test tube under a hydrogen atmosphere (16 mL,

0.655 mmol, headspace) was stirred at 25°C, then oxygen gas (4.5 mL, 0.184 mmol) in a 10-mL plastic syringe was connected to the test tube and introduced into the mixture. After a specific time, CH₂Cl₂ (10 mL) was added, and the mixture was filtered using a 0.45 µm membrane filter. The filtrate was concentrated under reduced pressure, and the residue was extracted with CH₂Cl₂ (10 mL × 2) and saturated aqueous NaHCO₃ (1 mL). The combined organic layers were dried over MgSO₄, filtered, and concentrated under reduced pressure, and the residue was purified by flash column chromatography on silica gel (CHCl₃:MeOH, 20:1) to afford the corresponding oxygenated product.

Acknowledgements

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- [29] The amount of the consumed oxygen was calculated from the amount of produced water, which was measured from ¹H NMR, based on the assumption that 2 equiv. of water are formed from the consumed oxygen. Theoretical amounts of consumed oxygen and produced water were also calculated from the amount of the introduced oxygen; one-third and two-third of the amount of the introduced oxygen should be the theoretical amounts of consumed oxygen and produced water, respectively. Also see the Supporting Information.
- [30] The gaps between experimental results and theoretical values in the cases of 5 mL and 22 mL of oxygen introduction in Figure 2a could be attributed to a minor detection error of water observed in the ¹H NMR spectra.
- [31] The properties of the 10% Pd/C hardly changed after the oxygenation of hydrogen gas in H₂O. The following data of 10% Pd/C after the reaction are virtually the same as those before the reaction. The surface area of activated carbon of the 10% Pd/C was 1054 m² g⁻¹ [Brunauer–Emmett–Teller (BET) analysis]. The palladium particle size was estimated to be 3–6 nm by scanning transmission electron microscopy (STEM). The X-ray photoelectron spectroscopy (XPS) indicates that the palladium species exist as Pd(0) species, and no palladium oxide was detected. See the Supporting Information.
- [32] Various types of palladium species were used for the water generation in cyclohexane at 25°C by the introduction of oxygen gas into the hydrogen-filled test tube (see the Supporting Information). While Pd(OAc)₂ hardly catalyzed the reaction, 5% Pd/C and 5% Pd/Al₂O₃ indicated a similar and good catalyst activity. The more highly loaded Pd/C basically catalyzed the reaction more effectively (1% Pd/C < 5% Pd/C < 10% Pd/C), although 30% Pd/C was significantly less active,

presumably due to the low distribution of the active palladium species on the activated carbon.

- [33] H_2O_2 was more stable in less polar solvents, such as cyclohexane and toluene; a half amount of H_2O_2 remained in cyclohexane or toluene even at 40°C under an argon atmosphere in the presence of 10% Pd/C. See the Supporting Information.
- [34] The H_2O_2 detection was carried out in cooled TFA in a short reaction period in view of the stability of generated H_2O_2 in the presence of Pd/C.
- [35] The effect of the kinds of the palladium catalyst on the oxygenation of 4-methylthioacetophenone in TFA was closely parallel to that on the H_2O_2 generation mentioned in the ref.^[32] 10% Pd/C was the most effective. See the Supporting Information.
- [36] The oxygenation of 4-methylthioacetophenone hardly proceeded in cyclohexane or toluene, although H_2O_2 was relatively stable in both solvents as noted in the ref.^[33]