

Supplementary Information

Metal-free catalytic hydrogen production from a polymethylhydrosilane-water mixture

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Experimental Section

General Procedures.

Glassware was cleaned and oven-dried overnight at 80°C prior to use. CDCl_3 and D_2O were purchased from Cambridge Isotope Laboratory Inc., and all other chemicals were obtained from Aldrich and used without further purification. Hydrogen gas was collected and measured volumetrically by the displacement of water from an inverted measuring cylinder. NMR (^1H) spectra were recorded with a Bruker AMX 300 NMR spectrometer at room temperature, using CDCl_3 as solvent. Hydrogen gas was detected by sampling the headspace above the catalytic mixture using a Balzer Prisma QMS 200 residual mass analyzer.

Typical Procedures for Catalytic Reaction.

A 25 mL two-necked round bottom flask sealed with rubber septum was charged with 4.4 mL of THF and 0.06 mL of PMHS (1 mmol, 1 equiv). Aqueous KOH solution (18.5 mM, 1% cat.) was prepared and 0.54 mL (30 mmol of water and 10 μmol of KOH) was injected into the flask. The flask was connected to an inverted measuring cylinder, where the hydrogen gas is collected and measured. The cylinder was not heated and positioned about 20cm away from the flask. Thus all hydrogen gas measurements and subsequent calculations have been performed assuming constant room temperature. For each catalytic run, the total volume of mixture was maintained at 5 mL. The reaction mixture was stirred under ambient conditions.

Typical Procedure for Kinetic Studies.

The kinetics of the OH-catalysed reaction of PMHS with water were studied with respect to four parameters ; (1) catalyst concentration, (2) silane concentration, (3) water concentration and (4) temperature. For any individual set of experiment, only one parameter was varied while the rest of the parameters were kept constant.

Various concentrations of KOH solutions were prepared (0.5 mM, 1.0 mM and 2.0 mM). A 25 mL two-necked round-bottom flask sealed with a rubber septum was charged with THF, PMHS (fixed at 0.1 M) and water (fixed at 3.0 M). Aqueous KOH solution was then injected into the flask to make up a total volume of 10 mL. Note that the volumes of all the solutions have been carefully measured prior to mixing. The reaction mixture was stirred while the temperature of the flask was maintained with a water bath. The reaction rate was determined by the initial rate of hydrogen evolution, by carrying out a linear fit to the curve and then determining the gradient of the fit. Generally, all linear fits extend to the first 30 seconds of the reaction. The same reaction was typically carried out 3 times to obtain average values.

Reaction orders were obtained by following the reaction rate at different concentration of reactants namely PMHS or water at 298.5 ± 0.2 K. The experimental procedure was similar to that mentioned above except that the silane concentration was varied (0.05M, 0.1M and 0.2M) at a fixed $[\text{OH}^-] = 1.0$ mM and $[\text{H}_2\text{O}] = 3.0$ M. Likewise when the water concentration was varied (1.5M, 3.0M and 6.0M), [silane] and $[\text{OH}^-]$ were fixed at 0.1M and 1.0 mM respectively.

The presence of kinetic isotopic effect was also determined by the ratio of the reaction rate of PMHS with H_2O (3.0 M) or with D_2O (3.0 M) while keeping all other conditions constant.

Activation parameters were calculated from the rate constants measured at different reaction temperatures. The temperature was controlled by gentle heating for higher temperatures ($>298\text{K}$) and careful adding of ice into a water bath for lower temperatures ($<298\text{K}$). Generally the temperature variation could be maintained to within $\pm 0.5\text{K}$ of the required temperature.

Calculations

Activation Parameters:

From the plot of $1/T$ against $\ln k$, the slope ($-E_a/R$) and intercept ($\ln A$) were obtained.

$$\text{Arrhenius Equation: } \ln k = \frac{\ln A - \frac{E_a}{R}}{T}$$

From the value of $\ln k$ at temperature T , we were then able to obtain ΔG^\ddagger , and subsequently ΔH^\ddagger and ΔS^\ddagger .

$$\text{Eyring - Polanyi Equation: } k = \frac{k_B T}{h} e^{\frac{-\Delta G^\ddagger}{RT}} \Rightarrow \Delta G^\ddagger = RT \left[\ln \left(\frac{k_B T}{h} \right) - \ln k \right]$$

$$\Delta H^\ddagger = E_a - RT$$

$$\Delta S^\ddagger = - \frac{\Delta G^\ddagger - \Delta H^\ddagger}{T}$$

Mass Spectrum

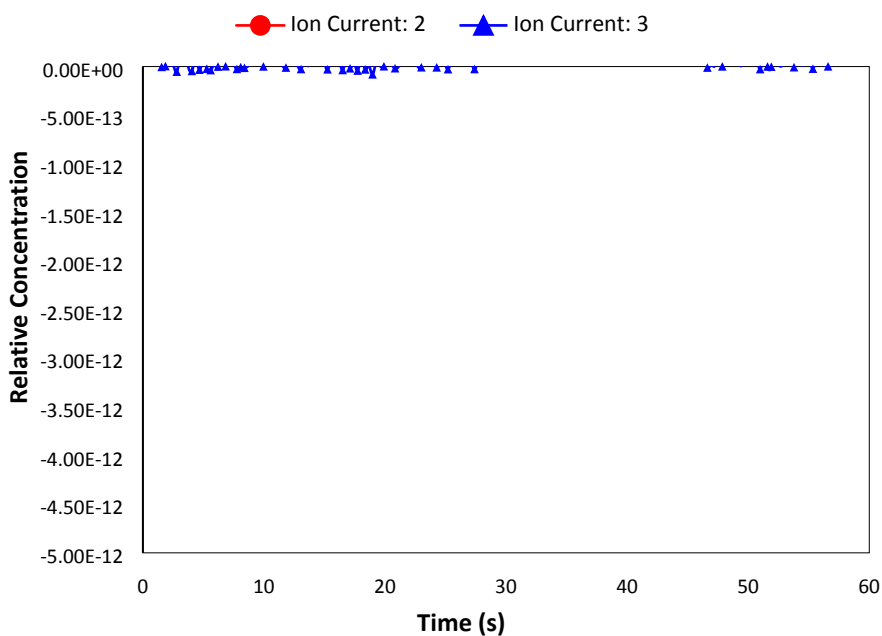


Figure S1: Mass Spectrum of HD when D₂O was used in place of H₂O. The m/e=3 signal showed the definite production of HD while the signal at m/e=2 could likely be contributions from (a) D⁺ as a result of fragmentation of HD, and (b) a small amount of H₂⁺ from H₂O residual in the D₂O sample.

¹H NMR Spectrum

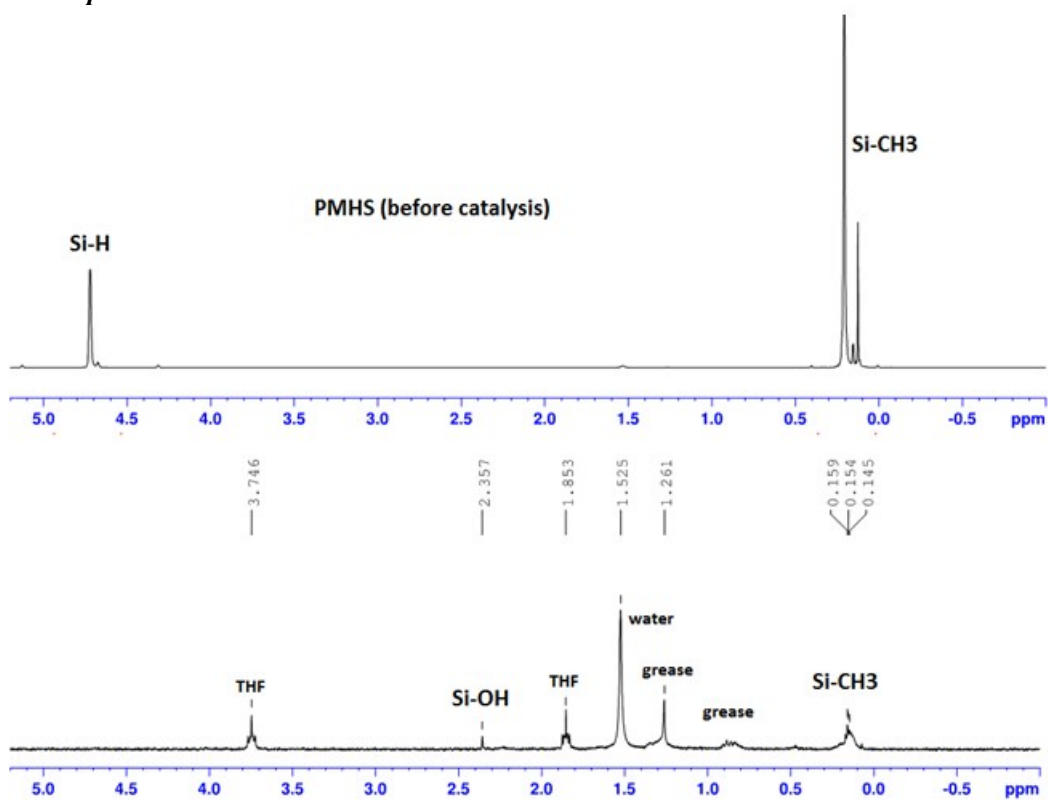


Figure S2: ¹H NMR spectra in CHCl₃ : (top) PMHS before catalysis and (bottom) silanol product after catalysis in THF.