Supporting Information

Catalytic hydrogen evolution from hydrolytic oxidation of organosilanes with silver nitrate catalyst

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Experimental

General Considerations

Glassware was oven-dried for 3 hours at 150 °C prior to use. $CDCl_3$ and D_2O were purchased from Cambridge Isotope Laboratory Inc. All other chemicals were obtained from Aldrich and Alfa Aesar and were used as received. NMR (^1H and ^{13}C) spectra were recorded with a Bruker AC 300 Fourier transform spectrometer at room temperature. The chemical shifts (δ) were internally referenced to the residual solvent signals relative to tetramethylsilane. Hydrogen gas was detected using a Balzer Prisma QMS 200 residual mass analyzer and calibrated with known concentrations of pure hydrogen gas. The organic product yields were calculated from the ^1H NMR spectra using reagent grade toluene or *n*-hexane as internal standard.

Typical Procedure for Catalytic Reaction

To a stirred tetrahydrofuran (6 mL) solution containing the silver nitrate catalyst (20 μmol) and excess water (60 mmol), organosilane (2 mmol, 1 equiv) was carefully added. Strong effervescence was observed and hydrogen gas was detected using a Balzer Prisma QMS 200 residual mass analyzer by sampling the headspace above the catalytic mixture throughout the reaction. A calibration curve using a known amount of pure hydrogen gas was used for the yield measurement. The yields of organosilanols were determined by ^{1}H NMR using reagent grade toluene or *n*-hexane as internal standard.

Product Identification

The generated gas in the oxidation reaction of organosilanes was identified to be hydrogen gas by MS. The organosilanol products were identified by NMR through the comparison of their ^{1}H and ^{13}C NMR signals with the literature data: Et_3SiOH[1], *i*-Pr_3SiOH[2], $PhMe_2SiOH$[3], $Ph_2Si(OH)_2$[3], Ph_3SiOH[1].

Typical Procedure for Kinetic Studies

Triethylsilane was added into a tetrahydrofuran solution containing the catalyst and excess water. The reaction mixture was stirred under ambient conditions and the hydrogen released was measured volumetrically via the displacement of water from an inverted measuring cylinder. 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. For high concentrations such as 0.25M in Figure 1a, the linear fit only extends to the first 5 seconds while for smaller concentrations, the fit generally extends to longer duration. Reaction orders were obtained by

following the reaction rate at different concentration of reactants at 299.5 ± 0.3 K. Kinetic isotope effect was determined by the ratio of the reaction rate of triethylsilane with H_2O and D_2O, and H_2O with triethylsilane and triethyl(silane-d) respectively. Total kinetic isotope effect was determined by the ratio of the reaction rate of triethylsilane with H_2O and that of triethyl(silane-d) with D_2O. Activation parameters were calculated from the rate constants measured at different reaction temperature. The temperature was controlled by carefully adding ice into water.

References:

1   Y. Lee, D. Seomoon, S. Kim, H. Han, S. Chang, P. H. Lee, *J. Org. Chem.*, 2004, **69**, 1741-1743.

2   W. Adam, C. M. Mitchell, C. R. Saha-Mo1ller, O. Weichold, *J. Am. Chem. Soc.*, 1999, **121**, 2097-2103.

3   J. John, E. Gravel, A. Hagege, H. Li, T. Gacoin, E. Doris, *Angew. Chem. Int. Ed.*, 2011, **50**, 7533-7536.