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COMMUNICATION

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

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In the light of uncertainty over the amount of recoverable fossil fuel reserves, hydrogen is touted to be a promising energy carrier in the future. Nevertheless, hydrogen storage remains a daunting challenge but a potential reaction for the generation of hydrogen on demand is the hydrolytic oxidation of organosilanes. Here, we demonstrate that silver nitrate, a readily available ionic salt, can catalyze the hydrolysis of organosilanes to produce hydrogen and organosilanols. In particular, turnover numbers and turnover frequencies in excess of 5×10^3 and 10^2 min^{-1} respectively are obtainable for the hydrolysis of triethylsilane at room temperature. This proposed silver nitrate mediated system is, by far, the simplest and cheapest catalytic hydrolysis of organosilanes. Results from the kinetic studies suggested a mechanistic scenario in which the hydrolysis of organosilanes is third order overall and first order in organosilane, water, and catalyst. The high hydrogen yield observed makes the silver nitrate catalyst an attractive material for hydrogen evolution.

There is no doubt that hydrogen (H_2) is an important chemical feedstock in today's industry. With an estimated annual production of 50 billion kg per year, hydrogen has found its applications in the processing of petroleum products to break down crude oil and synthesis of NH_3 for fertilizer.¹ In the wake of a growing global population with dwindling fossil fuel resources, hydrogen is viewed as a potential energy carrier in future energy systems² and the pathway to this proposed hydrogen economy will most likely proceed via hydrogen for portable applications first.³ Indeed, the ability to generate hydrogen on demand is crucial because whether the proposed hydrogen economy can be successfully implemented depends critically on the storage ability of the energy sources. In this regard, the most feasible and currently preferred storage method is in the form of energy-rich compounds³ and organosilanes with the potential of meeting the revised U.S. Department of Energy (DOE) 2015 system target of 5.5 wt% hydrogen⁴ through the rich Si-H groups in $\text{C}(\text{SiH}_3)_4$ and cyclo- $(\text{CH}_2\text{SiH}_2)_3$ are suitable candidates⁵ and, as such, significant attention was being devoted to clean hydrogen production through the catalytic hydrolysis of

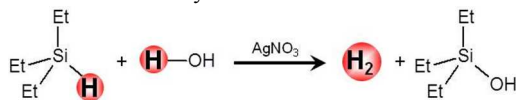
organosilanes. Even though this interest has seemed to fade away because of the difficulty in regenerating organosilanes from silanols (and their derivatives), the reaction is still of value as a useful synthetic route for organosilanols as these byproducts of organosilanes hydrolysis serve as important building blocks for polymeric and other organic materials.^{6,7}

The hydrolytic oxidation of organosilanes to produce hydrogen and organosilanols constitutes half of water splitting. Unfortunately, even though the Si-H bond is relatively weak and can undergo thermodynamically favourable protolytic cleavage with water, this reaction is kinetically slow⁸ and active catalysts are required to increase the process efficiency. Over the years, both homogeneous catalysts based on rhodium,⁹ iridium,¹⁰ rhenium,¹¹ and ruthenium¹² metal complexes and heterogeneous catalysts prepared with varying metal sources and supports¹³ have been developed. While most of these catalysts exhibited good mediating capabilities, the time consuming and costly laborious synthetic procedures for these catalysts make it difficult for routine hydrogen evolution in a real setting. Therefore, for any sustainable and economically viable future application, the ideal catalyst is one which is of low cost, readily available (or practically synthesis-free), and does not compromise on the desired catalytic efficiency. Herein, we wish to report the use of a commercially available inorganic salt, silver nitrate, for the hydrolytic oxidation of organosilanes to produce hydrogen and organosilanols. This work is poised to open brand new frontiers and revolutionize the development of simple, safe, cost-effective, and highly efficient hydrogen on-demand generation strategies. Furthermore, an environmentally friendly, carbon neutral catalytic system is also technically possible through the usage of silane (SiH_4) or trichlorosilane (HSiCl_3) substrate.

Strong effervescence was immediately observed when triethylsilane was added into a solution containing the silver nitrate catalyst and excess water (see the ESI† for typical procedures). Yet, virtually no gas was observed when the catalyst was substituted by each of the following salts: CuCl , CuCl_2 , FeCl_2 , FeSO_4 , NiBr_2 , NiCl_2 , $\text{Ni}(\text{NO}_3)_2$, and NiSO_4 . This immediately prompted us to suspect that Ag^+ must have played

an active role in the catalysis. In order to verify this hypothesis, the experiment was repeated by substituting the catalyst with AgBF_4 and AgPF_6 respectively. Indeed, strong effervescence was again immediately observed. In fact, gas bubbles were also observed when the catalyst was further substituted by Ag_2SO_4 and Ag_2O respectively, although these two reactions appeared sluggish due to the poor solubility of Ag_2SO_4 and Ag_2O catalysts in the system which resulted in a heterogeneous catalysis.

Table 1 Product details for the hydrolysis of triethylsilane catalyzed by silver nitrate.^a



Entry	Silane	Solvent	Catalytic Loading (%)	Time (min)	H ₂ Yield (%) ^b	Silanol Yield (%) ^c
1	-	Anhydrous THF	1.00	30	0	0
2 ^d	Et ₃ SiH	Anhydrous THF	1.00	30	0	0
3	Et ₃ SiH	Anhydrous THF	-	30	0	0
4	Et ₃ SiH	THF	1.00	5	>99	>99
5	Et ₃ SiH	THF	0.20	15	>99	>99
6	Et ₃ SiH	THF	0.10	30	>99	>99
7	Et ₃ SiH	THF	0.04	40	67	68
8	Et ₃ SiH	THF	0.02	50	66	65
9	Et ₃ SiH	THF	0.01	60	63	61
10	Et ₃ SiH	Hexane	1.00	30	0	0
11	Et ₃ SiH	CHCl ₃	1.00	30	0	0

^a Catalytic runs involved 2 mmol of organosilane and 60 mmol of H₂O at 298 K. ^b Total H₂ yields derived from mass analyzer using a calibration curve obtained from a known amount of H₂. ^c ¹H NMR triethylsilanol yield calculated with respect to triethylsilane, using toluene as internal standard. ^d Without addition of water.

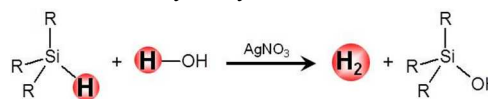
Mass spectroscopic analysis of the headspace of the reaction vessel involving triethylsilane, water, and silver nitrate catalyst revealed an intense signal at m/z 2 (H₂). When water was replaced by D₂O, this signal diminished and an intense signal at m/z 3 (HD) was observed instead. Upon further substituting triethylsilane with triethyl(silane-d), an intense signal was observed at m/z 4 (D₂), with diminished signals at m/z 2 and 3. Furthermore, no hydrogen gas was detected when anhydrous tetrahydrofuran (distilled from sodium benzophenone ketyl) was used and when either triethylsilane (Table 1, Entry 1), water (Table 1, Entry 2), or the catalyst (Table 1, Entry 3) was removed. These observations tallied with our previous studies that water was one of the substrates in the reaction and that hydrogen was formed as a result of both organosilane and water supplying one H atom each.^{12b}

The mediating power of silver nitrate in a solution containing triethylsilane and excess water with varying catalytic loading was studied (Table 1, Entries 4 to 9). All hydrolysis was carried out in air and after each of these experiments, the solvent and remaining water were carefully removed via slow evaporation and a colorless liquid was obtained and found to be triethylsilanol, based on ¹H and ¹³C NMR analysis. Interestingly, even with a decreased catalytic loading, the mediating power of the catalyst remained high. All in all,

turnover numbers and turnover frequencies in excess of 5×10^3 and 10^2 min^{-1} respectively were obtainable for the hydrolysis of triethylsilane consistently. This was made possible by the presence of a polar solvent, tetrahydrofuran, which ensured good miscibility of triethylsilane with water. On the other hand, no hydrogen gas was detected when the reaction was performed in a solvent with low dielectric constant such as hexane (Table 1, Entry 10) and chloroform (Table 1, Entry 11).

The scope of the catalytic oxidation reaction was then investigated on a panel of aliphatic and aromatic organosilanes. While the reaction of sterically less-hindered triethylsilane was completed within 5 min with >99% hydrogen and triethylsilanol yields, reactions involving sterically hindered trialkylsilanes (i.e. triisopropylsilane) proceeded slower with noticeably lower hydrogen and organosilanol yields (Table 2, Entries 1 and 2). The same reactivity trend was also observed with increasing number of phenyl substituent on the organosilane (Table 2, Entries 3 to 5). Nevertheless, it is worth mentioning that the oxidation of the sterically hindered triisopropylsilane was well known to be problematic and would require either extensive reaction time of 24 h^{13d} or high catalytic loading of 3%.^{13a} In our case, a significantly shorter reaction time of 40 min with 1% catalytic loading was sufficient for the majority of the triisopropylsilane to be oxidized. In addition, considerably higher organosilanol yield was also obtained, through the conversion of triphenylsilane into triphenylsilanol, for the silver nitrate catalyst (49%, 30 min) as compared to the previously reported supported-gold catalyst (<1%, 24 h).^{13d}

Table 2 Product details for the hydrolysis of various organosilanes catalyzed by silver nitrate.^a



Entry	Silane	Silanol	Time (min)	H ₂ Yield (%) ^b	Silanol Yield (%) ^c
1	Et ₃ SiH	Et ₃ SiOH	5	>99	>99
2	<i>i</i> -Pr ₃ SiH	<i>i</i> -Pr ₃ SiOH	40	53	55
3	PhMe ₂ SiH	PhMe ₂ SiOH	20	80	80
4	Ph ₂ SiH ₂	Ph ₂ Si(OH) ₂	25	88	85
5	Ph ₃ SiH	Ph ₃ SiOH	30	45	49

^a Catalytic runs involved 2 mmol of organosilane and 60 mmol of H₂O with 1.00% catalytic loading at 298 K. ^b Total H₂ yields derived from mass analyzer using a calibration curve obtained from a known amount of H₂. ^c ¹H NMR calculated with respect to organosilane, using toluene or *n*-hexane as internal standard.

In order to further our current understanding of the reaction pathway for the hydrolytic oxidation of organosilanes, a detailed kinetic study (see the ESI† for typical procedures) was performed via the monitoring of the initial rate of hydrogen evolution, through the displacement of water from an inverted measuring cylinder, for triethylsilane hydrolysis. The initial rate of hydrolysis was found to be $0.334 \pm 0.025 \text{ cm}^3 \text{ s}^{-1}$ or $(1.37 \pm 0.12) \times 10^{-5} \text{ mols}^{-1}$. Successive doubling of the concentration of organosilane increases the initial rates to $0.664 \pm 0.037 \text{ cm}^3 \text{ s}^{-1}$ (or $(2.72 \pm 0.15) \times 10^{-5} \text{ mols}^{-1}$) and $1.327 \pm 0.073 \text{ cm}^3 \text{ s}^{-1}$ (or $(5.43 \pm 0.29) \times 10^{-5} \text{ mols}^{-1}$) respectively (Fig. 1a). This represents an average increase of 1.99 ± 0.05 times in the initial rates of hydrolysis when the concentration of organosilane was doubled successively. Similarly, successive doubling of the

concentration of water and catalyst recorded an average increase of 1.98 ± 0.06 (Fig. 1b), and 2.00 ± 0.08 (Fig. 1c) times in its initial rate of hydrolysis respectively. These experimental data strongly suggest the first order dependence on organosilane, water, and catalyst respectively, since the observed rate constants k_{obs} would be independent of the concentrations at the same temperature. This would also imply that each of these species was involved in the rate determining step(s). Supporting evidence was drawn from the observed kinetic isotope effect, where the initial rate of hydrolysis ($k_{\text{D}}/k_{\text{H}}$) was slowed down by about 2.5 and 2.6 times when

triethylsilane was substituted with triethyl(silane-d) (Fig. 1a), and when H_2O was substituted by D_2O (Fig. 1b), respectively. The overall reaction rate of triethyl(silane-d) with D_2O was found to be almost 6 times slower than that of triethylsilane with H_2O . Evaluation of the activation parameter from the Arrhenius plot, by means of measurement of the rate constant over the temperature range of 277–299 K, yielded $\Delta H^\ddagger = 67.8 \text{ kJ mol}^{-1}$, $\Delta S^\ddagger = -220 \text{ J K}^{-1} \text{ mol}^{-1}$, and $\Delta G^\ddagger(298 \text{ K}) = 133 \text{ kJ mol}^{-1}$ for the hydrolysis of triethylsilane (Fig. 1d).

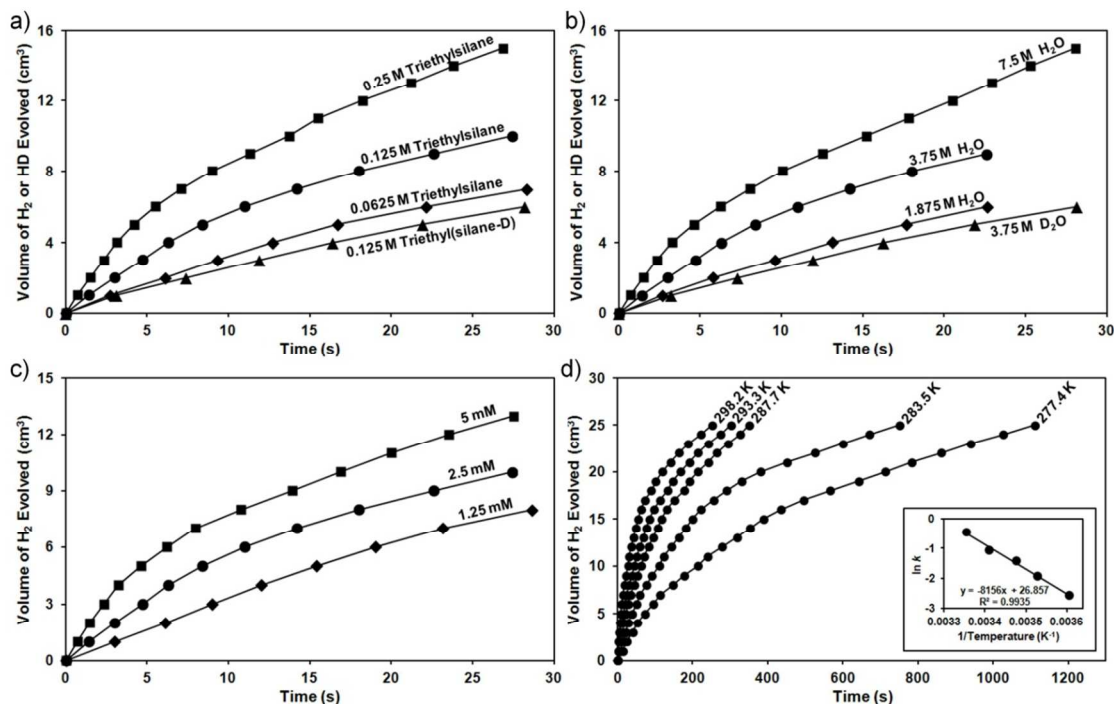


Fig. 1 The effect of (a) triethylsilane, (b) water, (c) catalyst, and (d) temperature on the hydrogen evolution for the hydrolysis of triethylsilane catalyzed by silver nitrate. Conditions: (a) $c(\text{H}_2\text{O}) = 3.75 \text{ M}$ and $c(\text{catalyst}) = 2.5 \text{ mM}$; (b) $c(\text{organosilane}) = 0.125 \text{ M}$ and $c(\text{catalyst}) = 2.5 \text{ mM}$; (c) $c(\text{organosilane}) = 0.125 \text{ M}$ and $c(\text{H}_2\text{O}) = 3.75 \text{ M}$; (d) $c(\text{organosilane}) = 0.125 \text{ M}$, $c(\text{H}_2\text{O}) = 3.75 \text{ M}$, and $c(\text{catalyst}) = 2.5 \text{ mM}$.

Conclusions

In this report, we have demonstrated a novel homogeneous catalytic system for the clean hydrolytic oxidation of organosilane and water into hydrogen and organosilanol. This readily available inorganic salt not only acts as a scalable catalyst with extremely high activity and excellent stability, but is also a simple, convenient, and cost-effective catalyst for the generation of hydrogen on-demand, since no further synthesis or manipulations were needed for the catalysis. We studied this catalyst extensively and found that high turnover numbers and turnover frequencies in excess of 5×10^3 and 10^2 min^{-1} respectively were obtainable for triethylsilane. The kinetics and activation parameters were studied via the monitoring of hydrogen evolution rate. We believe these results may guide future research efforts, specifically in the development of hydrogen storage materials derived from organosilanes.

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Highly efficient silver nitrate mediated hydrogen generation from the hydrolysis of organosilanes.

