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# Metal-free visible-light-mediated aerobic oxidation of silanes to silanols

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Oxidation of silanes into silanols using water/air has attracted considerable attention. The known methods with no exception required a metal catalyst. Herein we report the first metal-free method: 2 mol% Rose Bengal as the catalyst, air  $(O_2)$  as the oxidant, water as the additive and under visible light irradiation. While this method produces various silanols in a simple, cost-effective, efficient (92%–99% yields) and scalable fashion, its reaction mechanism is very different than the reported ones associated with metal catalysis.

metal-free, photoredox, aerobic oxidation, silanes

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# 1 Introduction

Visible light photoredox catalysis has received rapidly growing attention because it may constitute an ideal platform for sustainable chemistry. It has many conceived advantages due to the characteristics of light (abundant, non-toxic and generating no waste) as well as the related process (operationally simple and scalable) [1]. The past decade has witnessed the development of various powerful photoredox catalyst systems [2]. Among them, transition metal dyes [2a-2d] are extensively studied and most successful. In comparison, the application of organic dyes [2e-2j] is still limited but warrant further investigations since they are more costeffective and environmental benign.

Silanols are ubiquitous building blocks in silicone industry [3a,3b]. They are also versatile synthons in organic synthesis [3c,3d], serving as nucleophilic partners in cross-coupling reactions [4], organocatalysts for activating carbonyl compounds [5] and directing groups for C–H bond activation reactions [6]. In medicinal chemistry, the Si–OH moiety has

been ingeniously exploited as enzyme inhibitors [7] and isosteres of pheromones [8]. The classic syntheses of silanols involve hydrolysis of chlorosilanes [9] and less commonly nucleophilic substitution of siloxanes [10]. The direct oxidation of hydrosilanes into silanols represents a more desirable approach since it produces less byproducts [11]. Conventional methods entail stoichiometric oxidants [11a,11b]. The focus has now shifted to the usage of water and air as the green oxidants [11c–11f]. Our longstanding interest in silicon chemistry has also led to the single-site Au(I) catalyzed water oxidation of silanes [11f]. While these methods provide greener access to silanols, the universal employment of a transition metal catalyst [11g] causes burdens in product purification and waste treatment.

We thus became curious if it is possible to develop a metalfree aerobic oxidation of slianes using photoredox catalysis. In this context, Fu's group [12] has reported the first photoredox oxidation of silanes with water using a Rh(III) porphyrins photocatalyst. Herein, we reported the first examples of metal-free visible-light-mediated oxidation of silanes to silanols (Scheme 1). Thus, with low loading (2 mol%) of Rose Bengal [13] as the photocatalyst under white LED ir-

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Scheme 1 Synthetic methods for silanols (color online).

radiation at room temperature, an array of silanes was converted into the corresponding silanols in exceptionally high yields (92%–99%) within 12 h. Moreover, our studies uncovered a reaction mechanism that is very different than the ones reported in metal catalysis including Fu's work.

# 2 Experimental

To a solution of Rose Bengal (0.008 mmol, 2 mol%) in THF 2 mL was added silane **1** (0.4 mmol, 1 equiv.) and  $H_2O$  (50  $\mu$ L). The reaction mixture was open to the air (with a syringe needle inserted into the rubber cover to intoduce the air into the system and avoid the solvent evaporation heavily, the same below), and stirred under the irradiation of a household 200 W white LED at room temperature for 12 h. After completion of the reaction (monitored by GC-MS or TLC), the solvent was removed under reduced pressure, the crude product was purified by column chromatography with petroleum ether/ethyl acetate (10:1) as eluent to give the desired silanol **2**.

### **3** Results and discussion

We started our investigation using the less reactive triphenylsilane 1a as the model substrate. In the presence of 2 mol% of Rose Bengal in tetrahydrofuran (THF) at room temperature in open air, triphenvlsilanol 2a was isolated as the single product in 67% yield (70% conversion as monitored by crude <sup>1</sup> H NMR) after 12 h irradiation of white LED (Table 1, entry 1). Gratifyingly, complete conversion of 1a was obtained when 7 equiv. of water was added to the reaction (Table 1, entry 2). Three other photocatalysts were also examined but none of them appeared to be effective (Table 1, entries 3–5). Importantly, very minimal conversion was observed when the reaction was carried out in the absence of a photocatalyst (Table 1, entry 6) or without light (Table 1, entry 7). The catalyst loading of the Rose Bengal was examined, showing that increased loading from 2 mol% to 5 mol% to 10 mol% slightly diminished the yields (cf. Table 1, entry 2, 8, 9). When 1 equiv. of Rose Bengal was added, the yield drastically dropped to 43% (Table 1, entry 10), probably due to the shield of light resulting from the incomplete resolution of catalysts. A number of solvents were tested but none of them is comparable with THF (Table 1, entries 11–17). By note, the reaction in methanol only produced the alcoholysis product  $Ph_3SiOMe$  but not silanol **2a** (Table 1, entry 15).

A number of controlled experiments were carried out to dissect the roles of oxidants. Under nitrogen atmosphere, water alone could not oxidize the silane (Table 1, entry 18). Consistent with this observation, when an oxygen balloon was used instead of open air, 90% conversion was achieved in dry THF (i.e., without appreciable amount of water) after 72 h (Table 1, entry 19) and complete conversion could be achieved within 12 h when water is added which gave silanol 2a (Table 1, entry 20). These experiments collectively suggested that molecular oxygen but not water was likely the oxidant. This is remarkably different from metal catalysis [11c] as well as Rh(III) mediated photochemistry [12], where water itself was a competent oxidant. Rose Bengal, visible light and oxygen were all necessary for the success of this transformation. The optimal conditions were thus identified as listed in entry 2 (Table 1). The reaction time could be shorten to 3 h when heating at 60 °C, which might be more desirable for industrial application.

With the optimal conditions in hand, we successfully extended the reaction to a scope of silane substrates. In all the reactions, silanols were obtained as the only isolable product and the formation of troubling siloxanes was not observed. In the case of the hindered silane 1b, the reaction was more sluggish: the desired silanol 2b was obtained in 78% yield after 12 h irradiation (Table 2). However, extending the reaction time to 24 h could achieve complete conversion and an excellent yield (95%). Replacing one of the phenyl group with either bulky tert-butyl group (1c) or smaller methyl group (1d) did not affect the reaction, giving the product in 97% and 99% vield, respectively. Further introducing of a second alkyl group was also well tolerated as shown in the case of 1e (97% yield). Trialkylsilanes are also amenable to this reaction despite of the alkyl group sizes, giving silanols 2f, 2g and 2h in excellent yields. Unsaturated carbon-carbon bonds were compatible with this method: alkynyl silane 1i and alkenyl silane 1j furnished the desired products in almost quantitative yields, albeit the former required longer reaction time. It is worthy to point out that dihydrosilane 1k, as well as silane bearing an electron withdrawing group 1m, reacted smoothly under the current reaction conditions. Importantly, without tuning of reaction conditions except for reaction

#### Table 1 Optimization of reaction conditions<sup>a)</sup>

	Ph <sub>3</sub> SiH <b>1a</b>	catalyst, white LED solvent, additive, oxydant, r.t.	► Ph <sub>3</sub> SiOH <b>2a</b>	
Entry	Catalyst	Solvent	Oxidants	Conversion/Yield (%) <sup>b)</sup>
1	Rose Bengal	THF	Air	70/67
2	Rose Bengal	THF	Air/H <sub>2</sub> O	>99/98
3	Eosin B	THF	Air/H <sub>2</sub> O	<5/-
4	Eosin Y	THF	Air/H <sub>2</sub> O	<5/-
5	Fluorescein	THF	Air/H <sub>2</sub> O	<5/-
6	-	THF	Air/H <sub>2</sub> O	<5/-
7 <sup>c)</sup>	Rose Bengal	THF	Air/H <sub>2</sub> O	<5/-
8 <sup>d)</sup>	Rose Bengal	THF	Air/H <sub>2</sub> O	>99/97
9 <sup>e)</sup>	Rose Bengal	THF	Air/H <sub>2</sub> O	>99/95
10 <sup>f)</sup>	Rose Bengal	THF	Air/H <sub>2</sub> O	47/43
11	Rose Bengal	DME	Air/H <sub>2</sub> O	90/86
12	Rose Bengal	DMF	Air/H <sub>2</sub> O	50/47
13	Rose Bengal	DMA	Air/H <sub>2</sub> O	13/10
14	Rose Bengal	MeCN	Air/H <sub>2</sub> O	<5/-
15 <sup>g)</sup>	Rose Bengal	MeOH	Air/H <sub>2</sub> O	60/53
16	Rose Bengal	Acetone	Air/H <sub>2</sub> O	77/72
17	Rose Bengal	DMSO	Air/H <sub>2</sub> O	55/51
18	Rose Bengal	THF	$N_2/H_2O$	<5/-
19	Rose Bengal	Dry THF	$O_2$	90/86 <sup>h)</sup>
20	Rose Bengal	Dry THF	$O_2/H_2O$	>99/97

a) Reaction conditions unless otherwise stated: triphenysilane **1a** (0.4 mmol),  $H_2O$  (50  $\mu$ L), photocatalyst (2 mol%), otherwise noted, solvent (2 mL) without anhydrous treatment, using a 200 W white LED as the visible light source, 12 h. b) Yields after chromatography. c) Reaction performed in dark. d) 5 mol%, e) 10 mol% and f) 100 mol% catalyst was used, respectively. g) Alcoholysis product was isolated. h) The reaction time was 72 h.

time, this operationally simple method gave universally excellent yields to all types of silanes. We also demonstrated its applicability to gram scale reaction of silane **1a** as example (1.04 g, 4 mmol), which gave silanol **2a** in 99% yield.

A series of controlled experiments were carried out to better understand the reaction mechanism. H<sub>2</sub><sup>18</sup>O was added to a reaction performed under <sup>16</sup>O<sub>2</sub> atmosphere and the reaction products were monitored by gas chromatographymass spectrometer (GC-MS) (Table 3). It was observed that in the initial stage of the reaction (entry 1), mainly the Ph<sub>3</sub> Si<sup>16</sup>OH was produced. However, as the reaction proceeded Ph<sub>3</sub>Si<sup>18</sup>OH started to dominate (Table 3, entries 2–4). Importantly, our control experiments showed that there was no oxygen exchange between H<sub>2</sub>O and the silanol under reaction conditions (see Supporting Information online). Altogether these indicated that in the initial stage the oxygen in the silanol was mainly originated from the oxygen molecule  $({}^{16}O_2)$  and then gradually from the water (H<sub>2</sub><sup>18</sup>O). The deuterium kinetic isotope effect (KIE) was measured to be a small KIE ( $k_{\rm H}/k_{\rm D}$  is about 1.21), suggesting that Si–H bond cleavage was not the rate-limiting step.

Addition of 2,2,6,6-tetramethyl-1-piperdinyloxy (TEM-



Scheme 2 Controlled Experiments to Verify <sup>1</sup>O<sub>2</sub> (color online).

PO), a radical scavenger, completely inhibited the production of the silanol (Scheme 2, Eq. (1)), suggesting a radical pathway might be operative in this reaction. It is well recognized that Rose Bengal could react with molecular oxygen [2g, 13e-13f, 14] under visible light irradiation to

 Table 2
 Substrate scope of the organocatalytic oxidation of silane

	R <sup>1</sup> R <sup>2</sup> -Si-H R <sup>3</sup> THF, air (O <sub>2</sub> ), white L <b>1a–1j</b>	$(2.0 \text{ mol }\%) \qquad \qquad$	
Ph   Ph—Si—OH   Ph	Ph Ph Si-OH Ph	Ph <sup> </sup> Bu— <mark>Si</mark> —OH   Ph	Ph I — Si—OH I Ph
2a	2b	2c	2d
98% (12 h)	78% (12 h)	97% (12 h)	99% (12 h)
99% (gram scale)	95% (24 h)		
Рһ —_Si—ОН 	Et Et—Si—OH Et	'Pr   'Pr—Si—OH   'Pr	<sup>n</sup> Hex Hex <sup>n</sup> −Si−OH <sup>n</sup> Hex
2e	2f	2g	2h
97% (12 h)	92% (12 h)	97% (12 h)	99% (12 h)
Ph— <u>—</u> Si–OH	Ph I SI-OH Ph	OH Ph_si_OH Ph	F <sub>3</sub> C
2i	2j	2k	2m
81% (12 h)	98% (12 h)	98% (12 h)	97% (12 h)
97% (24 h)			

a) Standard conditions unless otherwise stated: silane (0.4 mmol), Rose Bengal (2.0 mol%), H<sub>2</sub>O (50 µL), THF (2 mL), 200 W white LED, air, r.t., 12 h or 24 h. b) Isolated yields.

generate singlet oxygen.

To verify the presence of  ${}^{1}O_{2}$  in our reaction, we carried out the trapping and quenching experiments. The trapping experiment [15] with 9,10-dimethylanthracene 3 under the standard conditions furnished the endoperoxide product 4 (Scheme 2, Eq. (2)), while such an adduct product 4 was not observed in the reactions performed in the dark or without Rose Bengal. The reaction was completely quenched in the presence of DABCO, which is known as a strong physical quencher of singlet oxygen (Scheme 2, Eq. (3)). These experiments indicated that <sup>1</sup>O<sub>2</sub> was produced in the reaction system. The reaction didnot take place in the dark and can be switched on by turning on the light, suggesting that a photocatalytic pathway but not the chain propagation is likely the main mechanism. Such a notion was further supported by fact the quantum yield of the oxidation of 1a was measure to be around 0.017 (see Supporting Information online). In addition, fluorescence quenching experiments showed that the emission intensity of excited Rose Bengal (RB\*) was not affected by the silane concentration, which suggested that there was no energy transfer between silane 1a and Rose Bengal.

On the basis of the above experimental observations as well as literature examples [16], a plausible reaction mechanism is proposed (Figure 1). First, Rose Bengal (RB) was excited under visible light irradiation to produce its excited



Figure 1 Proposed reaction mechanism (color online).

state species RB\*, which interacted with  ${}^{3}O_{2}$  to generate  ${}^{1}O_{2}$  via the energy transfer (ET). In this process, the excited state RB\* returned to its ground state RB. Subsequently, the generated  ${}^{1}O_{2}$  abstracted an electron from silane 1 to give the radical cation **A** along with superoxide anion  $O_{2}^{-}$ . The abstraction of a proton from the radical cation **A** by the superoxide radical anion produced a hydroperoxy radical HOO' and a silyl radical **B**. The oxidation of Si–H bond by  $O_{2}^{-}$  is a good analogue to the proposed oxidation of S–H bond under similar conditions, reported independently by Wang's group [16a] and the Barman's group [16b] in their inspiring work. The silyl radical **B** and the HOO' radical formed a Si–O bond in the form of silylperoxide **C**. The

**Table 3** Controlled Experiments of Reaction with  $H_2^{18}O$  and  ${}^{16}O_2^{a}$ 

	Ph <sub>3</sub> SiH - 1a	Rose Bengal (2 mol%) white LED Dry THF, <sup>16</sup> O <sub>2</sub> , H <sub>2</sub> <sup>18</sup> O, r.t.	Ph <sub>3</sub> Si <sup>18</sup> OH/Ph <sub>3</sub> Si <sup>16</sup> OH <b>2</b> a	
Entry	Time (h)	Conversion (%)	$Ph_{3}Si^{18}OH$ in <b>2a</b> (%) <sup>b)</sup>	$Ph_{3}Si^{16}OH$ in <b>2a</b> (%) <sup>b)</sup>
1	0.3	2.7	33	67
2	1	5.8	66	34
3	6	71.5	65	35
4	12	100	67	33

a) Reaction conditions: triphenysilane 1a(0.4 mmol),  $H_2^{18}O(50 \mu L)$ , Rose Bengal (2 mol%), dry THF (2 mL), 200 W white LED, reacting in a freshly dried Schlenk tube under the  ${}^{16}O_2$  atmosphere. b) The relative amount of Ph<sub>3</sub>Si<sup>18</sup>OH and Ph<sub>3</sub>Si<sup>16</sup>OH in **2a** was analyzed by GC-MS.

direct excursion of an oxygen atom from silylperoxide C to form the silanol product 2 has not been reported, which is also very unlikely. Instead, we propose that water acted as a nucleophile to attack the silicon, forming a pentavalent ate complex **D**. Such types of pentavalent Si complex has been documented in many previous studies [17]. This would explain the rate difference of the reaction with and without external water (cf. entries 19 and 20, Table 1). The decomposition of intermediate **D** into the silanol product **2** should involve several different  $\sigma$  metatheses pathways, where either of the two Si–O bonds could be cleaved. It is possible that the O–O bond can also be cleaved, which accounts for the 2:1 statistical ratio of Ph<sub>3</sub>Si<sup>16</sup>OH/ Ph<sub>3</sub>Si<sup>18</sup>OH in the initial stage of the reaction (cf. entry 1, Table 3).

The production of silanol 2 is accompanied with the production of equal molar of hydrogen peroxide E. As the reaction proceeded, accumulated hydrogen peroxide E started to react with silvl radical B, which also produced intermediate C. In other words, the OOH group in silvlperoxide C can come from either dioxygen (pathway a) or HOOH (pathway b). In the early stage, as there was little HOOH, pathway a was dominant, while in later stage pathway b became significant. This could explain the increasing percentages of the Ph3Si<sup>18</sup>OH as the reaction proceeded. Even though we know that the Si-H cleavage is not the rate determining step, it is hard to deduce the rate limiting step. Much more in-depth kinetic studies are required to uncover the mechanistic aspects of this interesting reaction. Nonetheless, the known aspects of the reaction mechanism is very different than the reported ones [11,12].

# 4 Conclusions

We have developed the first metal-free, visible-light-mediated oxidation of silanes to silanols. This method featured a low cost, readily available organic dyes, Rose Bengal, as the photocatalyst and oxygen in air as the green oxidant. The reaction operates under simple, mild conditions yet produces a wide scope of silanols in extremely high efficiency. Given these advantages and the conceived advantage of visible light photoredox catalysis in mass scale production, we believed this method might serve as the first step to produce silanols by photocatalysis at industrial scale.

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**Conflict of interest** The authors declare that they have no conflict of interest.

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