

# Different radical initiation techniques of hydrosilylation reactions of multiple bonds in water: dioxygen initiation<sup>†</sup>

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The relevance of radical initiation methodologies for the classical hydrosilylation reactions of organic compounds bearing C—C multiple bonds is due to the need to come up with newer and more efficient methods to effect this reaction, on account of its applications on surface chemistry. In the past, when organic solvents were employed, thermal and photochemical methods for the chain initiation reaction have been documented (thermal and photochemical decompositions of azo compounds). We herein present the dioxygen-initiation technique of the classical radical hydrosilylation reaction of C—C triple bonds with tris(trimethylsilyl)silane ((Me<sub>3</sub>Si)<sub>3</sub>SiH) in water. This initiation technique is confronted with the photochemical radical initiation in the absence of a chemical radical precursor other than the silane and also confronted with the classical thermal initiation triggered by the decomposition of an azo compound, both performed in water. The radical-based dioxygen initiation methodology studied in water is shown to afford the highest Z:E stereoselective ratios of hydrosilylated alkenes. Copyright © 2010 John Wiley & Sons, Ltd.

Supporting information may be found in the online version of this article.

**Keywords:** dioxygen initiation; hydrosilylation; radical reactions in water; reaction mechanisms; tris(trimethylsilyl)silane

## INTRODUCTION

The majority of organic radical transformations employing Si-centered radicals take place in organic solvents, neat media, and on surface chemistry,<sup>[1–3]</sup> and only recently has water been used as a convenient reaction medium for these radicals.

The development of novel water-soluble organosilane compounds and their applications to radical reactions in water is constantly being paid attention to, as a means to producing effective radical organic reactions in water, such as reductions of hydrophilic organic halides, and hydrosilylation of multiple bonds.<sup>[4–6]</sup>

In the radical chain processes, the initial silyl radicals are generated by some initiation. The most popular initiator is 2,2-azobisisobutyronitrile (AIBN), with a half life of 1 h at 81°C, generating the incipient radicals that commence the radical chain reaction. Other azo-compounds are used from time to time<sup>[4]</sup> as well as the thermal decomposition of di-*tert*butyl peroxide<sup>[5]</sup> depending on the reaction conditions. Et<sub>3</sub>B<sup>[6]</sup> in the presence of very small amounts of oxygen is an excellent initiator for low temperature reactions (down to –78°C). Also air-initiated reactions have recently been reported.

It is known that in organic solvents, tris(trimethylsilyl)silane, (Me<sub>3</sub>Si)<sub>3</sub>SiH, is both an efficient reducing agent for organic halides and an excellent hydrosilylation agent of multiple bonds. Also, the reported methodology of polarity-reversal catalysis is well documented in organic solvents. The thiol/silane couple not only shows an efficient synergy of radical production and regeneration, but could also provide for the use of an amphiphilic thiol, in order to enhance the radical reactivity at the interface. For the reduction of an organic halide (RX) by the couple (Me<sub>3</sub>Si)<sub>3</sub>SiH/HOCH<sub>2</sub>CH<sub>2</sub>SH under radical conditions, the propagation steps depicted in

Scheme 1 are expected. That is, the alkyl radicals abstract hydrogen from the thiol and the resulting thiyl radicals abstract hydrogen from the silane, so that the thiol is regenerated along with the chain carrying silyl radical for a given RX.<sup>[10,11]</sup>

Recently, Postigo *et al.*<sup>[12]</sup> tested the reducing agent (Me<sub>3</sub>Si)<sub>3</sub>SiH in water and observed its high stability in deaerated aqueous media and high temperatures. They subjected a series of organic halides to reduction with (Me<sub>3</sub>Si)<sub>3</sub>SiH in water with different initiators, azo compounds, and Et<sub>3</sub>B.

The same authors<sup>[13]</sup> also effected the hydrosilylation reaction of unsaturated bonds in water, using different hydrophobic compounds such as aldehydes, alkenes, and alkynes under light initiation and by thermal decomposition of azo compounds.

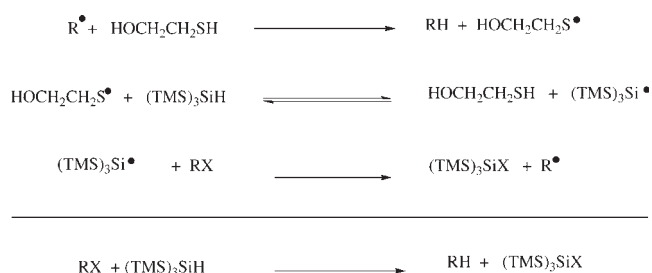
Again, the efficiency of the reaction was very good, and in all cases, good to quantitative formation of the hydrosilylation

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**Scheme 1.** Polarity reversal catalysis of silanes with thiols

products was achieved. It is worth mentioning the higher *cis* stereoselectivity observed in water vs. toluene at 90 °C.

These results showed that the nature of the reaction medium does not play an important role either in influencing the efficiency of the radical transformation or in the ability to dissolve the reagents. The authors attribute the success of the radical transformations of all water-insoluble materials suspended in the aqueous medium to the vigorous stirring that creates an efficient vortex and dispersion. Probably, the radical initiation benefits from the enhanced contact surface of tiny drops containing  $(\text{Me}_3\text{Si})_3\text{SiH}$  and the azo initiator 1,1'-azobis(cyclohexyl)carbonitrile (ACCN).<sup>[13]</sup>

When hydrophilic substrates were subjected to hydrosilylation reaction with  $(\text{Me}_3\text{Si})_3\text{SiH}$  in water, and ACCN as an initiator, excellent results of hydrosilylation of multiple bonds were achieved by adding the amphiphilic thiol  $\text{HOCH}_2\text{CH}_2\text{SH}$  to the system. A heterogeneous mixture of water-soluble starting material, the system  $(\text{Me}_3\text{Si})_3\text{SiH}/\text{HOCH}_2\text{CH}_2\text{SH}$ , and ACCN is flushed with Ar and heated. The treatment of hydrophilic substrates in water has the additional advantage of an easy separation of the silane by-products by partition between water and organic phases.

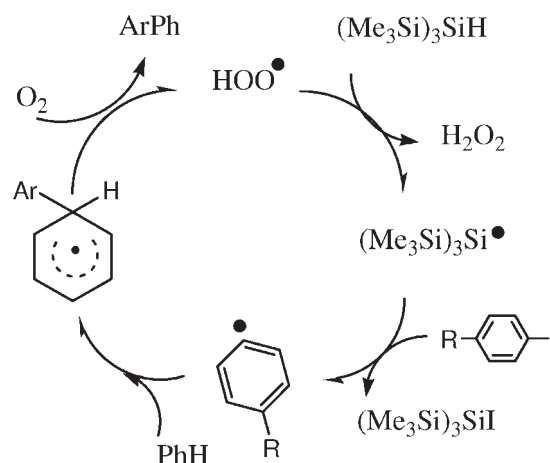
In another report<sup>[14]</sup> by the same authors, alkynes such as 1-octyne, 1-cyclohexylacetylene, 1-phenylacetylene, and propiolic acid were treated with  $(\text{Me}_3\text{Si})_3\text{SiH}$  in water under dioxygen initiation and yielded the respective alkenes stereoselectively in high yields. Normally *Z* alkenes (*Z*:*E* ratios >99:1, isolated alkene yields >95%) are formed. In the case of propiolic acid, 2-mercaptoethanol is needed as a chain carrier. Comparison of these data with the analogous reactions carried out in toluene at 80–90 °C and AIBN as an initiator,<sup>[15]</sup> not only shows better product yields but also a higher stereoselectivity in favor of the *Z* isomer.

Recently, Zhou and coworkers<sup>[16]</sup> reported that phenylacetylene is hydrosilylated in water in 1 h through air initiation to render the hydrosilylated product in 86% yield.

$(\text{Me}_3\text{Si})_3\text{SiH}$  as a pure material or in solution reacts spontaneously and slowly at ambient temperature with molecular oxygen from air, to form the siloxane. The mechanism of this unusual process has been studied in some detail.<sup>[17]</sup> Absolute rate constants for the spontaneous reaction of  $(\text{Me}_3\text{Si})_3\text{SiH}$  with molecular oxygen (reaction 1) have been determined to be  $3.5 \times 10^{-5} \text{ M}^{-1} \text{ s}^{-1}$  at 70 °C, and theoretical studies elucidated the reaction coordinates.<sup>[17]</sup>



In organic solvents (benzene), Curran and Keller<sup>[18]</sup> reported the  $(\text{Me}_3\text{Si})_3\text{SiH}/\text{dioxygen}$ -mediated radical initiation reaction in



**Scheme 2.** Dioxygen initiation in  $(\text{Me}_3\text{Si})_3\text{SiH}$ -mediated reactions in benzene

the absence of an azo compound or light. Thus, it was shown that  $(\text{Me}_3\text{Si})_3\text{SiH}$  mediates in the radical addition reaction of aryl iodides to benzene, and the rearomatization is achieved through oxygen. The mechanism of this reaction in benzene is described in Scheme 2.

Silyl radicals, generated from reaction of  $(\text{Me}_3\text{Si})_3\text{SiH}$  with oxygen, abstract the iodine atom from iodobenzene generating aryl radicals that suffer intramolecular addition to benzene (solvent) to form the cyclohexadienyl radical. Oxygen-induced rearomatization affords products along with hydroperoxyl radicals ( $\text{HOO}^\bullet$ ). This radical abstracts hydrogen from the silane yielding  $(\text{Me}_3\text{Si})_3\text{Si}^\bullet$  radicals completing the chain reaction.

Though it has been established that the thermal decomposition of ACCN is an excellent method for initiating the hydrosilylation reaction of unsaturated organic compounds in water, the high temperature needed for the decomposition of the initiator (ACCN, 70–100 °C) precludes the treatment of thermally labile substrates and compromises the stability of products. Also, the photochemical initiation is very sensitive to the nature of the alkyne studied, since only alkynes with low absorptivities at 254 nm can be employed. The photostability of the hydrosilylated alkenes at the irradiation wavelength is also a compromising and limiting factor in choosing this latter initiation technique. Therefore, the need to explore and expand another different and milder radical initiating technique of the well-known radical hydrosilylation reaction with  $(\text{Me}_3\text{Si})_3\text{SiH}$ , this time performed in water, becomes a challenging synthetic goal. We herein present a series of light and thermal sensitive alkyne substrates and hydrosilylated products where the dioxygen initiation is deemed the most convenient radical triggering event.

## METHODS OF RADICAL INITIATION IN WATER

### Dioxygen initiation

A balloon filled with pure oxygen connected to the vessel where no apparent bubbling resulted allowed dioxygen to be introduced up to its solubility limits in water.

The dioxygen-initiated radical-induced hydrosilylations of lipophilic alkynes in Ar-degassed water are carried out by adding subsequently  $(\text{Me}_3\text{Si})_3\text{SiH}$  ( $6 \times 10^{-5} \text{ mol}$ ) and the substrate

( $5 \times 10^{-5}$  mol). The vessel is tight-sealed, connected with a balloon filled with 99.99% dioxygen, and vigorously stirred at 20 °C (24 h). As a slight positive oxygen pressure is exerted on the reaction vessel, air does not leak in the system. For hydrophilic alkynes, HOCH<sub>2</sub>CH<sub>2</sub>SH (0.3 equiv.) is employed as the chain propagating agent. The isolation and purification of products are described in the Experimental section.

### Photochemical initiation and thermal initiation

These methods have been described previously.<sup>[12–14]</sup>

## RESULTS

In this account, we report an expansion on the hydrosilylation reactions with a new series of alkynes in water using dioxygen initiation, and provide a piece of mechanistic detail.

The water-soluble prop-2-yn-1-ol<sup>[13]</sup> (**1**) and prop-2-yn-1-amine (**3**) have been tested under dioxygen initiation conditions employing the amphiphilic 2-mercaptoethanol as the chain carrier. The reactions proceed efficaciously (24 h) affording the respective hydrosilylated alkenes in optimal reaction yields (98%, Scheme 1, Table 1, column 3, entries 1 and 3). These hydrosilylated alkenes are obtained with *Z:E* isomeric ratios equal to 99:1 and 96:4, respectively. Water-soluble hydrosilylated alkene products are rinsed with pentane (to discard silane excess), lyophilized, and column-chromatographed by reverse-phase silica gel with ethyl acetate-methanol (90:10) as eluant. In some cases, the products are obtained sufficiently pure for spectral characterization (Supplementary Material).

For comparison, the hydrosilylation reaction of propiolic acid (**4**) with (Me<sub>3</sub>Si)<sub>3</sub>SiH in water initiated by dioxygen is reported, where a high *Z:E* stereoselectivity ratio is obtained (Table 1, column 3, entry 4).<sup>[14]</sup>

The hydrosilylation of water-insoluble 3-chloroprop-1-yne (**2**) with (Me<sub>3</sub>Si)<sub>3</sub>SiH initiated by dioxygen (24 h) affords a high yield of the corresponding hydrosilylated alkene product (97%), in a *Z:E* ratio equal to 99:1 (Table 1, column 3, entry 2). Retention of the chlorine atom is observed in this hydrosilylated alkene product.

It should be pointed out that a small minor by-product (*ca.* 5%) detected from the oxygen-initiated reactions in water corresponds to a compound observed by mass spectrometry of mass 280 and formula minima C<sub>9</sub>H<sub>28</sub>SiO<sub>2</sub> whose structure has been assigned to (Me<sub>3</sub>SiO)<sub>2</sub>Si(H)SiMe<sub>3</sub>, arising from the autoxidation of silane.<sup>[15]</sup> This by-product was confirmed by GC-co-injection with an authentic sample which has been synthesized according to a reported procedure.<sup>[15]</sup>

When hydrosilylation reactions of substituted phenylacetylenes (**5–9**) are attempted under dioxygen initiation (Table 1, column 3, entries 5–9) in water, the respective hydrosilylated styrene derivatives are obtained in high yields, ranging from 88% yield (that derived from 1-chloro-4-ethynylbenzene (**9**)) to 96% yield (that from 4-ethynyltoluene (**5**)), and 75% yield from 3,4-dimethyl-ethynylbenzene (**7**). Notably, the stereoselectivity observed in all tris(trimethylsilyl)silyl-substituted styrenes is  $\geq 95\%$  in favor of the *Z* isomers. For comparison, the hydrosilylation in water of the parent phenylacetylene (**10**) initiated by dioxygen is shown in Table 1, where the hydrosilylated styrene is obtained quantitatively in the *Z* geometric isomer exclusively (Table 1, column 3, entry 10).<sup>[14]</sup> Hydrosilylated styryl derivatives are isolated and purified by silica-gel column chromatography (CH<sub>2</sub>Cl<sub>2</sub>:ethyl acetate 78:22).

The hydrosilylation reactions of water-soluble<sup>[13]</sup> (**1**) and (**3**) initiated by ACCN have been tested under the conditions described in subsection 'Photochemical initiation and thermal initiation', although in this case, 2-mercaptoethanol is added as the chain carrier. The reactions proceed efficaciously affording the respective hydrosilylated alkenes in optimal reaction yields (98 and 89%, respectively, Scheme 1, Table 1, column 4, entries 1 and 3). These alkenes are obtained with *Z:E* isomeric ratios equal to 88:12 in both cases (determined by <sup>1</sup>H NMR spectroscopy).

The hydrosilylation of (**2**) in water with (Me<sub>3</sub>Si)<sub>3</sub>SiH initiated by ACCN affords a high yield of the corresponding hydrosilylated alkene product (89%), in a *Z:E* ratio equal to 89:11 (Table 1, column 4 entry 2).

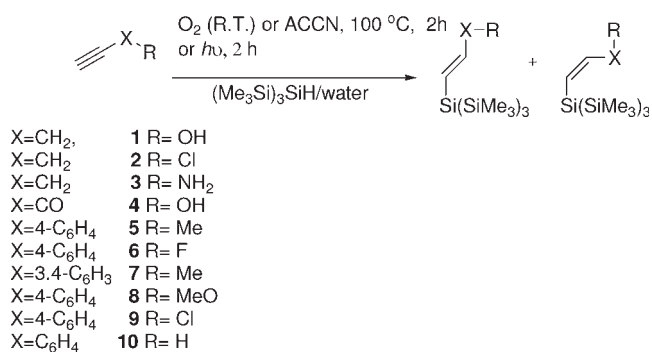
When substituted phenylacetylenes (**5–9**) are subjected to hydrosilylation reactions in water initiated by ACCN, the respective hydrosilylated styryl derivatives are obtained in good

**Table 1.** Hydrosilylation reactions of C—C triple bonds. Organic solvent-soluble substrates and hydrophilic substrates (10 mm) in water with (Me<sub>3</sub>Si)<sub>3</sub>SiH (12 mm) under different initiation conditions

Entry	Substrate	O <sub>2</sub> (R.T.) isolated yield, % ( <i>Z:E</i> ratio)	ACCN isolated yield, % ( <i>Z:E</i> ratio)	<i>hν</i> isolated yield, % ( <i>Z:E</i> ratio)
1 <sup>a, [10]</sup>	Prop-2-yn-1-ol ( <b>1</b> )	98 (99:1)	98 (88:12)	99 (95:5)
2	3-chloroprop-1-yne ( <b>2</b> )	97 (99:1)	89 (89:11)	95 (93:7)
3 <sup>a</sup>	Prop-2-yn-1-amine ( <b>3</b> )	98 (96:4)	89 (88:12)	99 (91:9)
4 <sup>[13,11]</sup>	Propiolic acid ( <b>4</b> )	99 (99:1)	95 (99:1)	95 (97:3)
5 <sup>[16,20]</sup>	4-ethynyl toluene ( <b>5</b> )	96 (99:1)	90 (85:15)	83 (79:21)
6 <sup>[17,21]</sup>	1-ethynyl-4-fluorobenzene ( <b>6</b> )	89 (95:5)	85 (87:13)	80 (85:15)
7 <sup>b</sup>	3,4-dimethyl-ethynyl benzene ( <b>7</b> )	75 (99:1)	71 (80:20)	67 (66:34)
8	4-ethynyl anisole ( <b>8</b> )	95 (99:1)	89 (85:15)	90 (79:21)
9	1-chloro-4-ethynylbenzene ( <b>9</b> )	88 (95:5)	90 (71:29)	91 (79:21)
10 <sup>[13,11]</sup>	Phenylacetylene ( <b>10</b> )	99 (99:1)	93 (70:30)	98 (75:25)

<sup>a</sup> HOCH<sub>2</sub>CH<sub>2</sub>SH (0.3 equiv.) was added as a chain carrier.

<sup>b</sup> 24 mM (Me<sub>3</sub>Si)<sub>3</sub>SiH used, 4 h-reaction. Isolated yield.



**Scheme 3.** Hydrosilylation ((Me<sub>3</sub>Si)<sub>3</sub>SiH) reactions of triple-bonded substrates in water by different initiation methods

yields albeit with lower stereoselectivities than those observed under dioxygen initiation (Table 1, column 4, entries 5–10). The stereoselectivities are nevertheless in favor of the *Z* alkenes, ranging from 71:29 to 87:13. For comparison, the hydrosilylation in water of the parent phenylacetylene (**10**) initiated by ACCN is reported in Table 1 (entry 10, column 4) from previous studies, where the hydrosilylated styrene is obtained almost quantitatively (93%) with a *Z:E* stereoisomeric ratio equal to 70:20.<sup>[13]</sup>

The hydrosilylation reactions of water-soluble (**1**) and (**3**) have also been tested under photochemical initiation conditions employing 2-mercaptoethanol as the chain carrier. The reactions proceed efficaciously affording the respective hydrosilylated alkenes in optimal reaction yields (99%, Scheme 1, Table 1, column 5, entries 1 and 3). These hydrosilylated alkenes are obtained with *Z:E* isomeric ratios equal to 95:5 and 91:9, respectively, determined by <sup>1</sup>H NMR spectroscopy. For comparison, the hydrosilylation reaction of (**4**) with (Me<sub>3</sub>Si)<sub>3</sub>SiH in water initiated by light is also reported, where a high *Z:E* stereoselectivity ratio is obtained (Table 1, entry 4).<sup>[13,14]</sup>

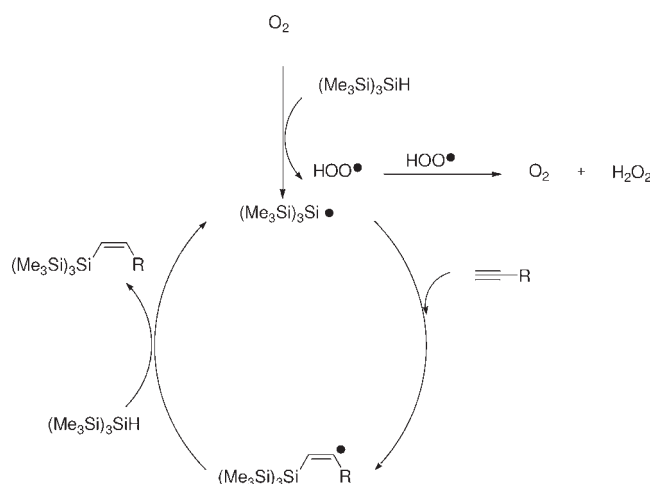
The hydrosilylation of (**2**) with (Me<sub>3</sub>Si)<sub>3</sub>SiH initiated by light affords a high yield of the corresponding hydrosilylated alkene product (95%), in a *Z:E* ratio equal to 93:7 (Table 1, column 5 entry 2). Retention of the chlorine atom is again observed in this hydrosilylated alkene product obtained under light-induced initiation.

When substituted phenylacetylenes (**5–9**) are subjected to hydrosilylation reactions in water initiated by light, the respective hydrosilylated styryl derivatives are obtained in good yields albeit with poorer stereoselectivities as compared to those obtained under dioxygen (Table 1, column 5, entries 5–10). The stereoselectivities in favor of the *Z* alkenes range from 66:34 to 85:15. For comparison, the hydrosilylation yield in water of the parent phenylacetylene (**10**) induced by light is shown in Table 1 (entry 10, column 5), where the hydrosilylated styrene is obtained almost quantitatively (98%) with a *Z:E* stereoisomeric ratio equal to 75:25.<sup>[14]</sup>

## DISCUSSION

For the dioxygen initiation, we postulate a mechanism as shown in Scheme 4 as operative in water for the hydrosilylation of C—C triple bonds.

Upon reaction of dioxygen with (Me<sub>3</sub>Si)<sub>3</sub>SiH (in water), silyl radicals along with hydroperoxyl radicals are generated.



**Scheme 4.** Mechanism for the dioxygen-initiated hydrosilylation reactions of C—C triple bonds in water

Hydroperoxyl radicals are known to be poorly reactive towards closed-shell compounds, and probably expected to recombine to form oxygen and hydrogen peroxide (or else abstract hydrogen from the silane to render (Me<sub>3</sub>Si)<sub>3</sub>Si• radicals that add to C—C triple bonds). No product derived from an addition reaction of hydroperoxyl radicals on C—C triple bonds has been detected under our reaction conditions. Nevertheless, hydrogen peroxide is expected to be a by-product of the reaction. The latter was detected by adding to the aqueous reaction mixture (24 h reaction of 2-chloro-1-propyne or phenylacetylene, (Me<sub>3</sub>Si)<sub>3</sub>SiH, dioxygen and water, where the hydrosilylated alkene product was previously detected by gc) a fresh colorless solution of Fe(SCN)<sup>+</sup> (10 mM) which immediately turned light orange due to the formation of Fe(SCN)<sup>2+</sup>. A blank experiment considering a freshly prepared oxygen-saturated aqueous mixture of the respective alkyne and (Me<sub>3</sub>Si)<sub>3</sub>SiH did not lead to a change in color when Fe(SCN)<sup>+</sup> was added to the aqueous mixture, purporting that the chain reaction initiates very slowly. As a matter of fact, the radical chain reaction under oxygen initiation is known to have a poor initiation yield, and the effectiveness of the overall radical hydrosilylation transformation relies on a very efficient propagation step. Another experiment carried out by adding H<sub>2</sub>O<sub>2</sub> (5%) to a 10 mM solution of Fe(SCN)<sup>+</sup>, isolated hydrosilylated alkene product (10 mM) and (Me<sub>3</sub>Si)<sub>3</sub>SiH (10 mM) produced an orange solution.

The silyl radicals perform the well-known addition reaction to C—C triple bonds. Unconjugated  $\sigma$  vinyl radicals are known to be sp<sup>2</sup> hybridized and to invert with a very low barrier (Eqn 2). Although (Me<sub>3</sub>Si)<sub>3</sub>Si• radicals have been shown to isomerize alkenes, the post-isomerization of the hydrosilylation adduct is not observed due to steric hindrance. The higher *Z*-stereoselectivity observed upon the addition of (Me<sub>3</sub>Si)<sub>3</sub>Si• to triple bonds is rationalized in terms of the *E*  $\sigma$  vinyl silylated radical being more hindered to abstract hydrogen from (Me<sub>3</sub>Si)<sub>3</sub>SiH than the *Z*  $\sigma$  vinyl silylated radical (Eqn 2). The higher stereoselectivity in favor of the *Z* isomer observed in water *versus* organic solvents, under the experimental conditions, suggests that additional factors play a role in water. It could be hypothesized that the hindrance of approach of the bulky silane to the radicals may also be influenced by the organization of the organic material dispersed in water. Further work is in

progress in our laboratory to disclose the effect of water on the higher stereoselectivity observed in this medium in the hydrosilylation reaction of alkynes. It is evident that the higher *Z* stereoselectivity observed upon dioxygen initiation in water (as compared to light-induced or thermal) is related to the stability of substrates and products under the experimental conditions. The milder dioxygen-initiated hydrosilylation reaction in water, as compared to the thermal and light-induced methods, circumvents issues associated with the stability of substrates and products under the reaction conditions. In the photochemical initiation, light is partially absorbed by the substrate (e.g., phenylacetylenes).



It is worth mentioning that under our experimental procedure, initiation with oxygen does not take place under O<sub>2</sub> purging of the solution, nor with slow, continuous bubbling of O<sub>2</sub> or air. Oxygen or air introduced slowly by syringe-pump techniques resulted in a less efficient initiation of the chain radical reaction. Probably, the slow oxygen addition into the solution with the balloon technique described above allows for sufficient oxygen to be dissolved in the water environment, thus initiating the radical chain (the solubility of oxygen in water is  $1.34 \times 10^{-3}$  M at 22 °C; taking into account that the substrate and (Me<sub>3</sub>Si)<sub>3</sub>SiH concentrations are *ca.* 10 times higher, limiting working initiator concentrations could be reached by the methodology).

## CONCLUSIONS

The scope of the hydrosilylation reaction of C—C triple bonds in water with (Me<sub>3</sub>Si)<sub>3</sub>SiH has been expanded from the use of the classical radical initiation attained through the thermal decomposition of azo compounds and photochemical initiation to the radical initiation reactions employing dioxygen.

Unlike the results known from air initiation of silanes in organic solvents<sup>[19]</sup> and in the absence of solvent,<sup>[16]</sup> it is likely that, in water, the silyl radical production represents an important and clean route for generating these species.<sup>[19]</sup> We are currently exploring this silyl radical production in water with other starting silanes.

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## REFERENCES

- [1] A. Langner, A. Panarello, S. Rivilio, O. Vassilyev, J. G. Khinast, Y. J. Chabal, *J. Am. Chem. Soc.* **2005**, *127*, 12798.
- [2] J. M. Schmeltzer, L. Porter, Jr., M. P. Stewart, J. M. Buriak, *Langmuir* **2002**, *18*, 2971.
- [3] M. P. Stewart, J. M. Buriak, *J. Am. Chem. Soc.* **2001**, *123*, 7821.
- [4] B. Marciniec, *Comprehensive Handbook on Hydrosilylation*, Pergamon Press, Oxford, **1992**.
- [5] B. Marciniec, *Silicon Chem.* **2002**.
- [6] I. Ojima, Z. Li, J. Zu, in *The Chemistry of Organic Silicon Compounds*, Vol. 2, (Eds: Z. Rappoport, Y. Apeloig), Wiley, Chichester, **1998**.
- [7] H. Yasuda, Y. Uenoyama, O. Nobutta, S. Kobayashi, I. Ryu, *Tetrahedron Lett.* **2008**, *49*, 367.
- [8] K. Miura, K. Oshima, K. Utimoto, *Bull. Chem. Soc. Jpn.* **1993**, *66*, 2356.
- [9] A. Naka, H. Ohnishi, J. Ohsita, A. Ikadai, A. Kunai, M. Ishikawa, *Organometallics* **2005**, *24*, 5356.
- [10] B. P. Roberts, *Chem. Soc. Rev.* **1999**, *28*, 25.
- [11] C. Chatgililoglu, *Organosilanes in Radical Chemistry*, Wiley, Chichester, **2004**.
- [12] A. Postigo, C. Ferreri, M. L. Navacchia, C. Chatgililoglu, *Synlett* **2005**, *18*, 2854.
- [13] A. Postigo, S. Kopssov, C. Ferreri, C. Chatgililoglu, *Org. Lett.* **2007**, *9*, 5159.
- [14] A. Postigo, S. Kopssov, S. Zlotsky, C. Ferreri, C. Chatgililoglu, *Organometallics* **2009**, *28*, 3282.
- [15] B. Kopping, C. Chatgililoglu, M. Zehnder, B. Giese, *J. Org. Chem.* **1992**, *57*, 3994.
- [16] J. Wang, Z. Zhu, W. Huang, M. Deng, X. Zhou, *J. Organomet. Chem.* **2008**, *693*, 2188.
- [17] A. B. Zaborovskiy, D. S. Lutsyk, R. E. Prystansky, V. I. Kopylets, V. I. Timokhin, C. Chatgililoglu, *J. Organomet. Chem.* **2004**, *689*, 2912.
- [18] D. P. Curran, A. I. Keller, *J. Am. Chem. Soc.* **2006**, *128*, 13706.
- [19] UV-Irradiation of (Me<sub>3</sub>Si)<sub>3</sub>SiH is known to generate silylenes rather than silyl radicals. We suggest that a minor photolytic path accounts for the formation of silyl radicals that initiate the radical chain hydrosilylation in water.
- [20] Z. Wang, J.-P. Pittelaud, L. Montes, M. Rapp, D. Derane, S. F. Wnuk, *Tetrahedron* **2008**, *64*(22), 5322.
- [21] Y. Liu, S. Yamazaki, S. Yamabe, Y. Nakato, *J. Mater. Chem.* **2005**, *15*(46), 4906.