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Radical-Initiated Dismutation of Hydrosiloxanes by Catalytic Potassium-Graphite

Xavier Frogneux,^{[a],[b]} Antoine Pesesse,^[a] Simon Delacroix,^[a] François Ribot,^[a] Sophie Carencó*^[a]

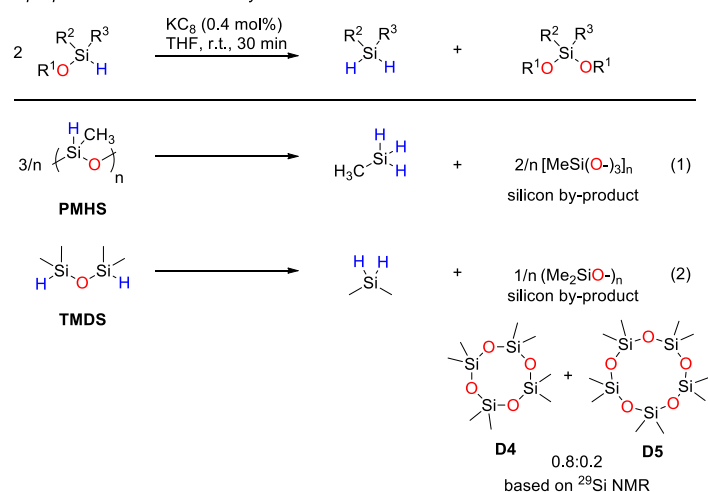
Formation of higher-value products from cheaper silicone precursors such as polymethylhydrosiloxane (PMHS) is a challenge for silicon chemistry. Here, we show that catalytic amount (<0.5 mol%) of potassium graphite (KC₈) can be used as an efficient radical initiator for the cleavage of Si–O bonds of hydrosiloxanes. Methylsilane and dimethylsilane are quantitatively obtained from PMHS and TMDS (1,1,3,3-tetramethyldisiloxane), respectively. Taking advantage of the high reactivity of the newly formed silane, the reduction of carbonyl functionalities with KC₈ in catalytic amount was further performed. Mechanistic investigations suggest that both the dismutation of the initial hydrosiloxane and the reduction of carbonyl derivatives by hydrosilylation are initiated with a radical pathway.

Hydrosilanes are convenient reagents in reduction reactions thanks to their polarized Si–H bond, which make them good hydride donors.^[1] They can be used in multiple reduction reactions using organometallic complexes or organic catalysts of inorganic salts.^[2–17] Among the most reactive hydrosilanes, silane (or monosilane), SiH₄, can be obtained from the disproportionation of triethoxysilane (TES). Silane has been used as precursor for the production of high purity silicon applications,^[18–20] and for the hydrosilylation of olefins.^[21,22] The disproportionation of TES has been studied with Ti-based catalysts such as Ti(O-iPr)₄,^[23] various metal-oxides supports,^[24–27] or with stoichiometric amount of glycol ethers derivatives.^[28] More recently, the use of anion exchange resins (Amberlite[®]) resulted in excellent conversion of TES into (EtO)₄Si and SiH₄, at 40 °C.^[29] However, silane being an extremely hazardous chemical,^[30,31] efforts have been made to circumvent the utilization of TES with more attractive, low-cost and air-stable hydrosilanes such as polymethylhydrosiloxane (PMHS) or 1,1,3,3-tetramethylhydrosiloxane (TMDS) in reduction reactions.^[32,33] Both Lewis acid, such as tris(pentafluorophenyl)borane (B(C₆F₅)₃) and Lewis base (such as fluoride species, KO^tBu, K₂CO₃) proved to be highly efficient for the disproportionation of siloxanes.^[5,34,35] In the presence of nucleophiles, two mechanisms have been proposed. Lawrence *et al.* suggested a “zipper” mechanism in which the silicate species formed shifts along the silicon chain during the course of the hydrosilylation.^[36,37] More recently, a base-catalyzed rearrangement mechanism was proposed by the group of Nikonov, involving a complete redistribution of the polysiloxane into methylsilane and silicone gel.^[5] Although the ionic pathway

seems favored, Stoltz *et al.* have detailed the three possible pathways (ionic, radical or neutral) for the KO^tBu-catalyzed dehydrogenative coupling of indoles with triethylsilane.^[38,39] Their studies showed that a radical mechanism seemed favored, *via* the generation of a silyl radical. Electron-donors may also be used as radical initiators. Among them, potassium-graphite (KC₈) is well-known to be a very strong single-electron donor.^[40] It is commonly used as a stoichiometric reducing agent in organometallic or organic syntheses.^[41,42] It was also used in the preparation of nanoscaled metallic carbides^[43] or under the form of a graphenide solution to generate supported metallic nanoparticles on graphite.^[44] Herein, we investigate the radical-initiated dismutation of hydrosiloxanes with KC₈.

To a suspension of KC₈ (1.4 mg, 0.01 mmol) in anhydrous THF (2.5 mL), PMHS was added (2.5 mmol of Si–H). Bubbles formed within seconds. ¹H NMR of the reaction crude revealed the presence of solubilized methylsilane (CH₃SiH₃, bp = -57.5 °C) from the quartets at 3.51 and 0.17 ppm in THF-*d*₆. Similarly, dimethylsilane (bp = -19.6 °C) was obtained from the dismutation of TMDS (Scheme 1) and identified from a septet at 3.76 ppm and a triplet at 0.14 ppm in THF-*d*₆. In this case, cyclic silanes **D4** and **D5** (see Scheme 1) were identified as side-products of the reaction by ²⁹Si NMR, with a 0.8:0.2 ratio.

Disproportionation reaction of hydrosiloxanes



Scheme 1. (Top) General equation for disproportionation reaction of hydrosilanes. (Bottom) Reaction conditions for the disproportionation of PMHS (1) and TMDS (2). For (2), the main cyclic products are represented on the bottom.

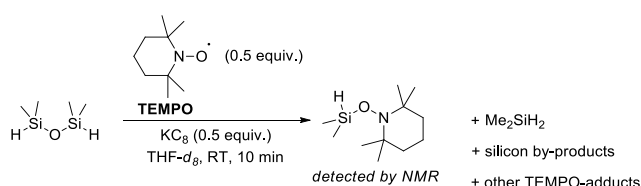
In order to clarify the catalytic role of KC₈ in this disproportionation reaction, an attempt to trap silyl radical species from TMDS was conducted in the presence of a radical scavenger. A stoichiometric quantity of KC₈ was mixed with TEMPO in THF-*d*₆ and then 2 equiv. of TMDS were added (Scheme 2). By NMR, the formation of at least four species

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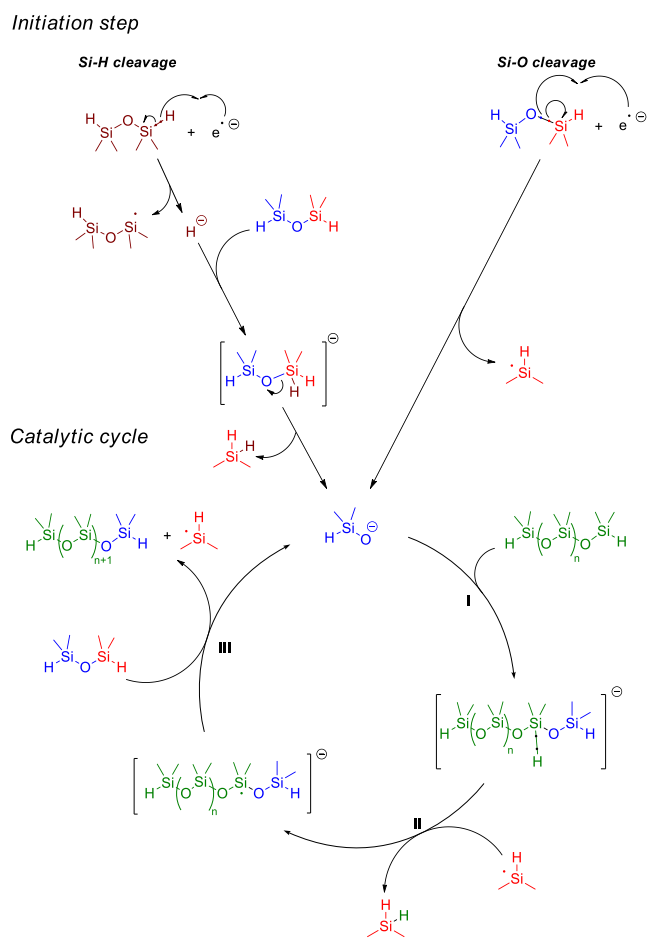
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containing TEMPO moieties was observed (see ESI, Figure S2-11). In order to identify the major TEMPO-adduct, ^1H - ^1H NOESY was performed (Figure S8). A correlation indicating a spatial proximity was found between the Si-H signal at 4.76 ppm and the methyl groups of TEMPO at 1.08 ppm. Moreover, ^1H DOSY NMR showed that only one Me_2Si moiety, corresponding to a doublet at 0.23 ppm, has the same diffusion coefficient (i.e. $14.0 \cdot 10^{-10} \text{ m}^2 \cdot \text{s}^{-1}$) as the Si-H at 4.76 ppm and the methyl groups of TEMPO at 1.08 ppm. Consequently, the major adduct was identified as $\text{TEMPO-Me}_2\text{SiH}$. Mass spectrometry was performed in order to gain information on the other species. Several silyl-TEMPO adducts (e.g. $\text{TEMPO-SiMe}_2\text{OSiMe}_2\text{H}$, $\text{TEMPO-SiMe}_2\text{OSiMe}_2\text{-OTEMP}$, see ESI, Figure S12-22), were identified in the spectrometer.



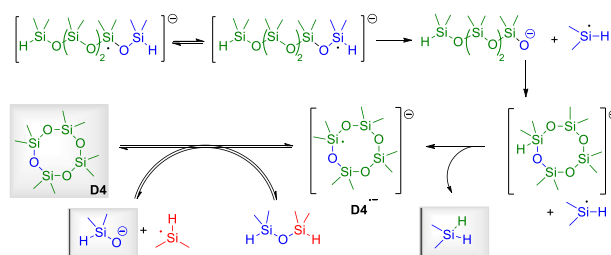
Scheme 2. Formation of a silyl-TEMPO species in the presence of TEMPO

We explain our observations by a radical initiation during which one electron is transferred to the TMDS. This transfer could occur either by the cleavage of a Si-H or a Si-O bond ($\text{BDE}(\text{Si-H}) = 318 \text{ kJ} \cdot \text{mol}^{-1}$ vs. $\text{BDE}(\text{Si-O}) = 452 \text{ kJ} \cdot \text{mol}^{-1}$ (BDE stands for Bond Dissociation Energy))^[45-47] (Scheme 3, initiation step). In the first case, it leads to the formation of a free hydride and a silyl species. This free hydride forms a pentavalent silicon species after nucleophile addition on a second TMDS. By releasing one Me_2SiH_2 , the generation of a silanolate species occurs. On the other hand, if we consider first a Si-O bond cleavage, it results in the direct formation of a silyl radical $\text{Me}_2\text{SiH}^\cdot$ and a silanolate species. At this moment, there is no direct argument that allows stating which mechanism is the dominant one: high BDE of Si-O bond pledges for an unfavourable homolytic cleavage, but the trapping experiment with TEMPO indicates that this does happen to some extent. Moreover, preliminary electron spin resonance (ESR) experiments to detect silyl radicals were so far inconclusive, possibly due to the presence of KC_8 . Theoretical calculations comparing the ionic and radical pathways, although technically challenging, might shed light on this question in the future. Regardless of its origin, this silanolate acts as a nucleophile in the same way than potassium *tert*-butoxide and generates a pentavalent silicon species after nucleophilic addition on a silicon atom from TMDS (or a longer silicon chain) (Scheme 3, I), thus enhancing the polarity of the Si-H bond on the pentavalent Si center. The H^\cdot radical can be trapped by the previously formed $\text{Me}_2\text{SiH}^\cdot$, leading to the formation of Me_2SiH_2 (Scheme 3, II). In the presence of another equivalent of TMDS, the silanolate species is regenerated along with one $\text{Me}_2\text{SiH}^\cdot$ radical, and the silicon by-product length is increased by one $-\text{OSiMe}_2-$ unit (Scheme 3, III).



Scheme 3. Proposed mechanism for TMDS dismutation

To explain the formation of cyclic by-products, we propose that from the silicon chain formed at the end of step II in the catalytic cycle, the radical center is in equilibrium between the silicon centers. The formation of a silanolate can occur *via* the cleavage of a Si-O bond, generating one equivalent of a $\text{Me}_2\text{SiH}^\cdot$ radical. Ring closure is achieved by the intramolecular nucleophilic attack of the silanolate onto the $\text{HSiMe}_2\text{O}-$ moiety of the silicon chain, forming a pentavalent Si-H species. This later species reacts with the remaining $\text{Me}_2\text{SiH}^\cdot$, yielding Me_2SiH_2 and the radical D4^\cdot . By single electron transfer (SET) of D4^\cdot to one equivalent of TMDS, the final cyclic siloxane **D4** is formed.



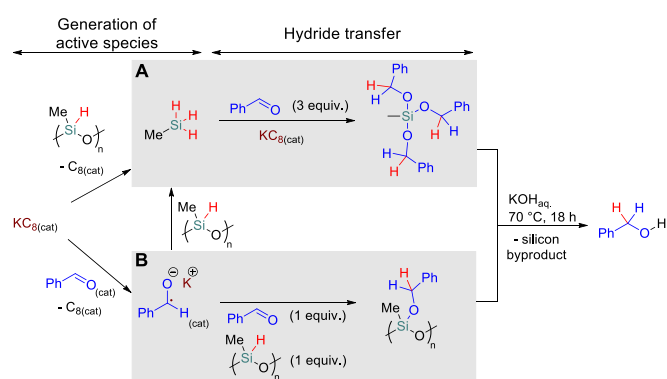
Scheme 4. Formation of D4 from the catalytic cycle

Noticeably, we experimentally verified that other single electron donor such as sodium, potassium, or sodium naphthalenide can also be used as radical initiators for the disproportionation of both TMDS and PMHS.

At this stage, we realized that this methodology allowed the clean generation of methylsilane from PMHS. Although it cannot be stored on the shelf, methylsilane was easily trapped in a second vessel, thus becoming available as highly reactive silane to perform reduction reactions (Scheme 5, route **A**).

Initial trials were conducted on benzaldehyde. In a trap-to-trap setup (Figure S1), MeSiH₃ was generated from PMHS in the presence of KC₈ in a first vessel, and then transferred through the vapor phase in a second one, containing a solution of benzaldehyde in THF. In the absence of catalyst, benzaldehyde did not react with methylsilane after 1 h at room temperature or even at 70 °C. However, when a catalytic amount of KC₈ was present in the second vessel, complete conversion of the carbonyl into the corresponding silylated alcohol was obtained after 30 min at room temperature.

Moreover, considering that carbonyl compounds are keen to form an acyl radical with a strong electron donor such as K (or KC₈),^[48] we hypothesized that the acyl species generated *in situ* could act as an initiator for the dismutation of PMHS thanks to its alkoxide moiety (Scheme 5, **B**→**A**). By adding PMHS to a solution containing catalytic amounts of potassium and benzaldehyde in THF, complete conversion into methylsilane was observed after 5 min. It is also possible to directly use PMHS in one-pot reaction with benzaldehyde and KC₈ (Scheme 5, route **B**). The acyl radical catalyzes the direct reduction of benzaldehyde with PMHS. In any case (route **A** or route **B**), benzyl alcohol was obtained after cleavage of the Si–O bond under basic conditions.



Scheme 5. KC₈ radical-initiated pathways from benzaldehyde to benzyl alcohol using PMHS.

We further extended the scope of this reaction to other moieties, as reported in Table 1. Aromatic aldehydes (or heteroaromatic)

were converted in good to excellent yields (entries 1, 2, 4). However, the presence of electron withdrawing group completely shut down the reactivity of KC₈: both PMHS and the substrate were recovered (entry 3). Octanal was not reduced by this methodology (entry 5). Aromatic and aliphatic ketones were reduced in the corresponding silylated alcohol in good yields (entries 6-8). Amides and ester groups could not be reduced in these conditions, even by heating at 70 °C for 18 h, and with a larger excess of Si–H (entries 9, 10).

Table 1. Reduction of carbonyl derivatives.

| Entry | Substrate ^[a] | NMR yield (%) |
|-------------------|--------------------------|-------------------------|
| 1 | | >99 (70) ^[b] |
| 2 | | >99 |
| 3 | | N.R. |
| 4 | | 90 |
| 5 | | N.R. |
| 6 | | 89 |
| 7 | | >99 |
| 8 | | 96 |
| 9 ^[c] | | N.R. |
| 10 ^[c] | | N.R. |

[a] Reaction conditions: under Ar in a 10 mL vial, KC₈ (1.4 mg, 0.01 mmol) in THF (2.5 mL), substrate (2.5 mmol), PMHS (3.0 mmol Si–H), agitation at r.t. for 30 min; N.R. = No reaction [b] isolated yield of benzyl alcohol [c] PMHS (7.5 mmol Si–H), r.t. or 70 °C.

This difference of reactivity between the substrates can be linked to the relative stability of the acyl radical generated from the reaction between the carbonyl moiety and KC₈. Ketones and (hetero)aromatic aldehydes bearing sufficient electron-donating groups can generate acyl radicals that can act as initiator for reaction reductions with hydrosiloxanes. However, with aliphatic aldehydes or aromatic aldehydes bearing an electron withdrawing group, no reactivity was observed, which may be due to the lower stability of the acyl radical. Ester and amides are also unreactive which may be due to the attractive inductive

effect of the oxygen or nitrogen atom, respectively.

In conclusion, the dismutation of hydrosiloxanes proved to be feasible by radical initiation with KC_8 in low catalyst loading (0.4 mol%). Particularly, this methodology enables the use of PMHS, a cheap byproduct of silicone polymer industry, and yields quantitatively $MeSiH_3$, which can be used for chemical reduction, as well as semi-conductor or silicide synthesis. The one-pot reduction of carbonyl compounds with PMHS, initiated with KC_8 , was tackled and proved to be selective to ketones and (hetero)aromatic aldehydes.

Experimental Section

All experimental details can be found in the ESI.

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