Mechanistic Aspects of Hydrosilane/Potassium tert-Butoxide (HSiR₃/KO₄Bu)-Mediated Reactions

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ABSTRACT: The hydrosilane/potassium tert-butoxide reagent system has attracted significant attention over the last 5 years since the discovery of its ability to silylate heteroarene C–H bonds. Numerous useful HSiR₃/KO₄Bu-mediated transformations are now known, including silylation of sp, sp², and sp³ C–H bonds, reductive cleavage of C–O, C–S, and C–N bonds, reduction of polycyclic arenes, and hydrosilylation and polymerization of styrenes. This mini-review surveys the rich diversity of reaction mechanisms, both ionic and free radical and including hydride transfer, H atom transfer, and electron transfer, that have been uncovered during recent studies on the HSiR₃/KO₄Bu reagent system. Several mechanistic phenomena that remain to be explained are also highlighted.

1. INTRODUCTION

In 2015, Grubbs, Stoltz, et al. reported a remarkable reaction.¹ They showed that the C–H bonds of heteroarenes (e.g., 1, Scheme 1) could be transformed into C–Si bonds by reaction with a hydrosilane and an unusual C–H activation catalyst: potassium tert-butoxide.

The practical advantages of this transformation were immediately obvious. It takes place under mild conditions without the need for any precious metal catalysts or pyrophoric reagents. What was less obvious was how the reaction takes place. Mechanistically, it appeared to be unlike any other heteroarene C–H functionalization process. The reaction triggered great interest among physical organic chemists who have applied a range of approaches to explore the reaction mechanism. In this mini-review, we highlight some of the reaction pathways and reactive intermediates that have been uncovered in HSiR₃/KO₄Bu-mediated reactions during the 5 years since Grubbs’ and Stoltz’s original report. We discuss the most extensively studied reactions first, followed by newer reactions that still await a deeper mechanistic characterization. Taken together, the examples presented in this mini-review embody a remarkably rich diversity of reactive species and mechanistic processes.

2. SILYLATION OF HETEROARENE C(sp²)–H BONDS: HETEROLYTIC AND HOMOLYTIC PATHWAYS

Grubbs and Stoltz, together with a large international team, conducted an extensive experimental and theoretical investigation to uncover the details of the C–H silylation mechanism.²,³ They utilized a multifaceted approach, applying mass spectrometry, nuclear magnetic resonance, infrared, electron paramagnetic resonance, conductivity, kinetics, substrate dependence, isotope labeling, radical trapping agents, radical clock probes, a stereochemical probe, and density functional theory calculations. The finding that emerged from their studies was that the reaction appears to have a complex underlying mechanism. Multiple heterolytic and homolytic pathways were found to be consistent with the experimental data.

Key evidence for a heterolytic mechanism came from desorption electrospray ionization mass spectrometry experiments,³ which identified several transient ionic intermediates formed in the reaction mixture. These include the deprotonated heteroarene 3, pentacoordinate silicate 4, and a cation–π complex of K⁺ with the heteroarene, 5 (Scheme 2a).

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Anion 3 provided strong evidence that the heteroarene undergoes deprotonation in the reaction mixture. Complexation of the heteroarene with K⁺ (as in 5) would make the C−H bond more acidic. A hydridic species was proposed to act as the base (Scheme 2b). Two options were considered plausible: the H− ion itself or the silane/tert-butoxide adduct 6. The regioselectivity of deprotonation was confirmed through isotope labeling. After the deprotonation, anion 3 adds to silyl ether 7 to form 4 containing the new C−Si bond.

Theoretical calculations showed that this sequence of events represented a low-energy pathway. Computations also identified another pathway, similar to the one just described but involving only neutral species (Scheme 3). In this neutral pathway, the deprotonation of the heteroarene was executed by the coordinated hydride 9, which was formed by the reaction of the silane with the KO'Bu tetramer. The tetramer1 is the dominant form of KO'Bu in solvents such as THF (a common solvent for the silylation), but conductivity studies showed that some dissociation into ions occurs over a period of 1 h. Hence, both neutral and ionic pathways seem plausible.

The neutral and ionic pathways in Schemes 2 and 3 successfully account for many of the key features of the reaction. For example, both pathways predict that the reaction is cross-dehydrogenative, that the heteroarene C−H bond and silane hydrogen participate in the rate-determining step, and that C2 silylation is kinetically favored relative to C3 silylation. In these pathways, the rate of reaction and the regioselectivity are both determined by the deprotonation step; C2 is more acidic than C3.5

At the same time as characterizing these heterolytic pathways, the same research team uncovered strong evidence for a radical mechanism.2 For example, the radical trapping agent TEMPO inhibited the reaction and led to the formation of the TEMPO−SiR₃ adduct, suggesting the involvement of silyl radicals. A mixture of KO'Bu and HSiEt₃ was found to be EPR-active. The silylation of a probe substrate, 12 (Scheme 4), took place with opening of the cyclopropyl ring, indicative of the transient formation of a radical at the C3 position of the indole under the reaction conditions. All of this evidence led the team to propose a radical chain mechanism involving silyl radicals. The propagation steps of the chain are shown in Scheme 4. They comprise the addition of SiR₃ to the indole to give intermediate 13 followed by the loss of the C2 hydrogen atom through a β-scission step. The hydrogen atom acceptor was proposed to be either the KO'Bu tetramer or the silicate 6; both options were computed to be facile. The β-scission step determined both the rate and the regioselectivity, kinetically favoring C2. It is noteworthy to comment that the heteroarene silylation is reversible. Over long reaction times, or at high temperatures, the C3-silylated product is favored.

What was most difficult to understand was how silyl radicals could be generated in the first place.6−8 The reported bond dissociation energy of the Si−H bond in triethylsilane is 90 kcal/mol.9 Visible light did not promote the reaction nor did the direct addition of sources of tert-butyl radicals such as di-tert-butyl peroxide. Ultimately, it was proposed that radical formation involves traces of oxygen. Two possible initiation processes were proposed based on computations (Scheme 5).2,3 One involved the reaction of O₂ with KO'Bu to give BuO• and the potassium peroxide radical 14; the other involved the reaction of O₂ with the coordinated hydride 9 to give HO• and the coordinated oxyl radical 15. The latter process reflects that the coordinated hydride in 9 is not only a strong base but also a good hydrogen atom donor. Hydrogen atom abstraction from the silane by the
be decreased to very low levels. The corresponding reductive C–O bond cleavage of dibenzofurans behaves differently: only one of the C–O bonds is cleaved (Scheme 6b). Small quantities of silylated dibenzofurans (e.g., Scheme 6a) are obtained. These minor products become significant at lower temperatures and played a very important role in the story of the arene sp² silylation reaction (sections 1 and 2).

Two mechanisms, both involving silyl radicals, were suggested to take place in these C–X (X = S or O) cleavage reactions (Scheme 6c). In the first mechanism, SiR₃• adds to one of the aromatic rings at the position adjacent to X. The C–X bond then cleaves, and SiR₃• is transferred from C to X to give the aryl radical 24. Hydrogen atom abstraction from the silane, followed by addition of SiR₃• to X and elimination of R₃SiXSiR₃, gives the biphenyl radical 26. Hydrogen atom abstraction from the silane then gives the hydrocarbon product. The second mechanism shares some of the steps of the first but is more direct; in it, the SiR₃• radical effects a homolytic displacement at X to give 24. Computations showed that, for dibenzothiophenes, both pathways have similar barriers. For dibenzofurans, on the other hand, the C-attack pathway is greatly favored, as the attack by SiR₃• on O (21 → 24) has a high barrier. The different products formed from dibenzofurans and dibenzothiophenes are explained because the conversion of 25 to 26 is difficult when X = O. The reaction is thus arrested at the stage of silyl ether 25, leading (after hydrolysis) to the biphenyl alcohol 19.

3. REDUCTIVE C–O AND C–S BOND CLEAVAGE

An industrially relevant application of the HSiEt₃/KO'Bu reagent system involves the reductive C–S bond cleavage of dibenzothiophenes. This reaction, which gives biaryl products through cleavage of both C–S bonds, has been found to offer a way to deal with refractory dibenzothiophenes in hydrocarbon fuels (e.g., Scheme 6a), enabling the sulfur content of the fuels to be decreased to very low levels. The corresponding reductive C–O bond cleavage of dibenzofurans behaves differently: only one of the C–O bonds is cleaved (Scheme 6b). Small quantities of silylated dibenzofurans (e.g., 20, 3%) are also obtained. These minor products become significant at lower temperatures and played a very important role in the story of the hydrosilane/KO'Bu reagent system, as their detection stimulated the discovery of the heteroarene silylation reaction (sections 1 and 2).

Two mechanisms, both involving silyl radicals, were suggested to take place in these C–X (X = S or O) cleavage reactions (Scheme 6c). In the first mechanism, SiR₃• adds to one of the aromatic rings at the position adjacent to X. The C–X bond then cleaves, and SiR₃• is transferred from C to X to give the aryl radical 24. Hydrogen atom abstraction from the silane, followed by addition of SiR₃• to X and elimination of R₃SiXSiR₃, gives the biphenyl radical 26. Hydrogen atom abstraction from the silane then gives the hydrocarbon product. The second mechanism shares some of the steps of the first but is more direct; in it, the SiR₃• radical effects a homolytic displacement at X to give 24. Computations showed that, for dibenzothiophenes, both pathways have similar barriers. For dibenzofurans, on the other hand, the C-attack pathway is greatly favored, as the attack by SiR₃• on O (21 → 24) has a high barrier. The different products formed from dibenzofurans and dibenzothiophenes are explained because the conversion of 25 to 26 is difficult when X = O. The reaction is thus arrested at the stage of silyl ether 25, leading (after hydrolysis) to the biphenyl alcohol 19.

4. REDUCTIVE C–N BOND CLEAVAGE AND REDUCTIONS OF POLYCYCLIC ARENES: SINGLE-ELECTRON TRANSFER AND HYDRIDE TRANSFER

In 2017, Murphy, Tuttle, et al. added two ground-breaking contributions to the hydrosilane/KO'Bu mechanistic picture. They showed that this reagent system possessed single-electron donor and hydride donor ability. Their computations predicted that the radical anion 27 (Scheme 7a), possibly formed from a SiR₃• radical precursor, was a potent electron donor (E = −3.74 V vs SCE in MeCN). It could readily transfer an electron to N-benzylindole to generate the radical anion 28. Subsequent loss of the benzyl radical would then swiftly follow. This type of reactivity was observed in experiments on a range of N-benzyl indoles, N-allyl indoles, and NBnPhMe with HSiEt₃/KO'Bu at 130 °C (Scheme 7b). These results are distinct from the earlier report by Grubbs, Stoltz, et al., who had obtained the regular C₂ hydrogenation product in 82% yield at lower temperature (45 °C).

The powerful electron donor 27 was also predicted to be capable of donating an electron to polymeric aromatic hydrocarbons, such as naphthalene 32. These arenes were indeed reduced to dihydro derivatives such as 33 (Scheme 7c). However, an even more facile pathway for the reduction of arenes was found to involve hydride ion transfer to the arene from the silicate 6.

5. HYDROSILYLATION AND POLYMERIZATION OF STYRENES: HYDROGEN ATOM TRANSFER

In 2019, Jeon et al. reported that styrenes (in particular, electron-neutral and electron-rich styrenes) undergo hydrop-
silylation by H₂SiR₂/KO'Bu (Scheme 8a).13 They provided strong evidence for a mechanism involving hydrogen atom transfer (HAT) from the pentacoordinate silicate 6 to the vinylarene–K⁺ complex 36 (Scheme 8b). This led to a caged intermediate 37 in which the benzylic radical was closely associated with radical anion 27. Dissociation of tBuO⁻ from 27 in the caged intermediate would liberate a silyl radical, which would then combine with the benzylic radical to give the hydrosilylation product. In this mechanism, radical anion 27 serves as a protected form of the silyl radical. It appears likely that the benzylic radical and radical anion would be somehow tethered to each other by the K⁺ ion. Consistent with this idea, when the reaction was carried out in the presence of 18-crown-6 or with an electron-deicient styrene, polymerization took place instead of hydrosilylation. Theoretical computations indicated that the HAT transition state and intermediate 37 possessed substantial multiconfigurational character (i.e., both closed-shell and biradical character). This feature was proposed to account for the multiple mechanistic manifolds generally displayed by hydrosilane/KO'Bu reagent systems.

6. SILYLATION OF ALKYNE C(sp)−H BONDS

In 2017, Grubbs, Stoltz, et al. showed that the C−H bonds of terminal alkynes could be silylated in high yield by hydrosilane/KO'Bu (Scheme 9).14,15 Unlike heteroarene C(sp²)−H silylation (section 2), this alkyne C(sp)−H silylation worked even better with bases such as KOH and NaOH than with KO'Bu. The mechanism was not clear. The evidence suggested that multiple manifolds may play a role. For example, base-catalyzed isomerization of the acetylene was observed. The reaction was inhibited to varying degrees by TEMPO and galvinoxyl. Curiously, 18-crown-6 did not inhibit the KOH-catalyzed reaction with HSiEt₃, but it inhibited the corresponding reaction of HSi(OEt)₃.

7. SILYLATION OF BENZYLIC C(sp³)−H BONDS

In the original 2015 report,1 the hydrosilane/KO'Bu-mediated silylation was not restricted to only sp² C−H bonds. Several benzylic substrates, such as toluene and 2,6-lutidine, were also silylated, albeit under slightly more forcing conditions and in lower yields (Scheme 10). No mechanism was proposed for this reaction. It is difficult to see how a radical chain mechanism (Scheme 4) could bring about benzylic silylation. However, an ionic mechanism analogous to that in Scheme 2 or 3 is a possibility.

8. SILYLATION OF AMINES

In 2019, Murphy, Tuttle, et al. reported the application of HSiR₃/KO'Bu to the conversion of amines into N-silyl amines (Scheme 11a).16 They proposed that the active catalyst was not KO'Bu but was KH, generated in situ (Scheme 11b). KH would be a strong enough base to deprotonate the amine, leading to a nucleophilic potassium amide that would then attack the silane. Commercial KH was not an effective catalyst for the silylation. However, the authors pointed out that a KH molecule formed in situ would be a much more reactive species than the solid aggregate form of KH.

9. OUTLOOK

The recent work surveyed herein has uncovered a number of important reactive intermediates and mechanistic pathways that operate in the HSiR₃/KO'Bu reagent system. Indeed, each type of transformation mediated by this system appears to have its own distinct mechanistic characteristics, which may be heterolytic, homolytic, or a combination of the two. Despite the significant advances made over the last 5 years, there are
several features that cannot be explained by our current mechanistic understanding.

For example, in the heterorearene C–H silylation chemistry (section 2), it remains unclear why the silylation does not perform well with electron-poor heteroarenes such as pyridine.1 Ordinarily, silyl radicals are “nucleophilic” radicals that react readily with electron-poor substrates.2 It is also not clear why an experiment in which silyl radicals were independently generated under silica-Minisci-type conditions did not give the expected C2 silylation product from N-methylindole. Third, the reason why certain additives such as iodobenzene and bromobenzene were observed to suppress the silylation is also difficult to rationalize. These observations, and indeed the exact mechanism of silyl radical generation, remain unclear.

In the reductive C–S bond cleavage of dibenzo thiophenes (section 3), it is puzzling that HSiEt3 afforded an 83% yield of the desulfurized product (17, Scheme 6a), but H2SiEt2 gave a much lower yield of 13%.10 The relative reactivities of the respective silyl radicals, SiEt3• and SiEt2H•, in the proposed reaction mechanism (Scheme 6c) would be expected to be comparable.

An intriguing aspect of the HSiR3/KOtBu reagent system is that both dehydrogenative and hydrogenative pathways are possible. For example, in the C–N debenzylination chemistry (section 4), N-benzylindoles undergo debenzylation at high temperatures (hydrogenative pathway) but C2 silylation (dehydrogenative pathway) at low temperatures. Silylation is known to be reversible.2 It therefore appears likely that, in the reaction at high temperature, the C2-silylated and C3-silylated products are both formed and then undergo debenzylisation en route to the observed product. In other examples, such as C–O and C–S bond cleavage (section 3), the hydrogenative pathway also seems to require higher temperatures, whereas lower temperatures favour silylation (dehydrogenative pathway). Perhaps not surprisingly, the reduction of naphthalene (section 4) required more forcing conditions—high temperature and 10–100-fold increase in the concentration of KOtBu catalyst (which would increase the concentration of reactive silane/tert-butoxide adduct 6).

In the arene reduction chemistry (section 4), the ability of silicate 6 to transfer a hydride ion to the arene was demonstrated by computations. One feature that remains unclear is where the proton comes from to quench the intermediate aryl anion. The two mechanistic alternatives for arene reduction—hydride transfer from 6 or single electron transfer from 27—are potentially distinguishable in this respect.

Finally, in the styrene hydrosilylation/polymerization (section 5), the >90% yields of hydrosilylation products are remarkable when one takes into account that the reaction is performed under neat conditions with the styrene itself effectively serving as the solvent. Even tiny concentrations of escaped radicals (benzylic or silyl radicals) would be expected to trigger polymerization in this scenario. One possibility, which seems likely but was not explicitly discussed by Jeon et al., involves the intermediate 40 depicted in Scheme 8c. Direct radical recombination of the caged intermediate 37 to give 40 could help to explain why polymerization is suppressed.

These questions reveal that there is much more to be learned about the chemistry of the fascinating HSiR3/KOtBu reagent system.

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Notes
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■ REFERENCES

(1) (a) Toutou, A. A.; Liu, W.-B.; Betz, K. N.; Fedorov, A.; Stoltz, B. M.; Grubbs, R. H. Silylation of C—H bonds in aromatic heterocycles by an Earth-abundant metal catalyst. Nature 2015, 518, 80–84. (b) Toutou, A. A.; Liu, W.; Grubbs, R. H.; Stoltz, B. M.; Betz, K.; Schuman, D. P. Patent Appl. WO/2016/100606, 2016.
(2) Liu, W.-B.; Schuman, D. P.; Yang, Y.-F.; Toutou, A. A.; Liang, Y.; Klare, H. P. T.; Nesnas, N.; Oestreich, M.; Blackmond, D. G.; Virgil, S. C.; Banerjee, S.; Zare, R. N.; Grubbs, R. H.; Houk, K. N.; Stoltz, B. M. Potassium tert-Butoxide-Catalyzed Dehydrogenative C—H Silylation of Heteroarenes: A Combined Experimental and Computational Mechanistic Study. J. Am. Chem. Soc. 2017, 139, 6867–6879.
(3) Banerjee, S.; Yang, Y.-F.; Jenkins, I. D.; Liang, Y.; Toutou, A. A.; Liu, W.-B.; Schuman, D. P.; Grubbs, R. H.; Stoltz, B. M.; Krenske, E. H.; Houk, K. N.; Zare, R. N. Ionic and Neutral Mechanisms for C—H Bond Silylation of Aromatic Heterocycles Catalyzed by Potassium tert-Butoxide. J. Am. Chem. Soc. 2017, 139, 6880–6887.
(4) Chisholm, M. H.; Drake, S. R.; Naini, A. A.; Streib, W. E. Synthesis and X-Ray Crystal Structures of the One-Dimensional Ribbon Chains [MOBu’Bu’OH]n and the Cubane Species [MOBu’]4 (M = K and Rb). Polyhedron 1991, 10, 337–345.
(5) Shen, K.; Fu, Y.; Li, J.-N.; Liu, L.; Guo, Q.-X. What are the pKa values of C—H bonds in aromatic heterocyclic compounds in DMSO? Tetrahedron 2007, 63, 1568–1576.
(6) Prior to the publication of Liu and Banerjee et al.’s extensive mechanistic studies, Shang and Liu proposed an alternative mechanism for the heteroarene silylation. In their mechanism, KO\textsubscript{t}Bu donates an electron to the silane, causing it to dissociate to give a silyl radical and hydride ion. The silyl radical adds to the heteroarene, and the resulting radical adduct is then deprotonated by the hydride. Redox potentials\textsuperscript{8} and entropic considerations make this mechanism appear less likely than those depicted in Schemes 2–5.

(7) Shang, X.; Liu, Z.-Q. Recent developments in free-radical-promoted C–Si formation via selective C–H/Si–H functionalization. Org. Biomol. Chem. 2016, 14, 7829–7831.

(8) Barham, J. P.; Coulthard, G.; Emery, K. J.; Doni, E.; Cumine, F.; Nocera, G.; John, M. P.; Berlouis, L. E. A.; McGuire, T.; Tuttle, T.; Murphy, J. A. KO\textsubscript{t}Bu: A Privileged Reagent for Electron Transfer Reactions? J. Am. Chem. Soc. 2016, 138, 7402–7410.

(9) Kanabus-Kaminska, J. M.; Hawari, J. A.; Griller, D.; Chatgilialoglu, C. Reduction of Silicon–Hydrogen Bond Strengths. J. Am. Chem. Soc. 1987, 109, 5267–5268.

(10) Toutov, A. A.; Salata, M.; Fedorov, A.; Yang, Y.-F.; Liang, Y.; Cariou, R.; Betz, K. N.; Couzijn, E. P. A.; Shabaker, J. W.; Houk, K. N.; Grubbs, R. H. A potassium tert-butoxide and hydrosilane system for ultra-deep desulfurization of fuels. Nat. Energy 2017, 2, 17008.

(11) Fedorov, A.; Toutov, A. A.; Swisher, N. A.; Grubbs, R. H. Lewis-base silane activation: from reductive cleavage of aryl ethers to selective ortho-silylation. Chem. Sci. 2013, 4, 1640–1645.

(12) Smith, A. J.; Young, A.; Rohrbach, S.; O’Connor, E. F.; Allison, M.; Wang, H.-S.; Poole, D. L.; Tuttle, T.; Murphy, J. A. Electron-Transfer and Hydrode-Transfer Pathways in the Stoltz–Grubbs Reducing System (KO\textsubscript{t}Bu/Et\textsubscript{3}SiH). Angew. Chem., Int. Ed. 2017, 56, 13747–13751.

(13) Asgari, P.; Hua, Y.; Bokka, A.; Thiamsiri, C.; Prasitwatcharakorn, W.; Karedath, A.; Chen, X.; Sardar, S.; Yum, K.; Leem, G.; Pierce, B. S.; Nam, K.; Gao, J.; Jeon, J. Catalytic hydrogen atom transfer from hydrosilanes to vinylarenes for hydrosilylation and polymerization. Nat. Catal. 2019, 2, 164–173.

(14) Toutov, A. A.; Betz, K. N.; Schuman, D. P.; Liu, W.-B.; Fedorov, A.; Stoltz, B. M.; Grubbs, R. H. Alkali Metal-Hydrosilane–Catalyzed C(sp)-H Bond silylation. J. Am. Chem. Soc. 2017, 139, 1668–1674.

(15) For a related reaction incorporating CO\textsubscript{2} to give acetylene-carboxylates, see: Yu, B.; Yang, P.; Gao, X.; Yang, Z.; Zhao, Y.; Zhang, H.; Liu, Z. Sequential protocol for C(sp)-H carboxylation with CO\textsubscript{2}: KO\textsubscript{t}Bu-catalyzed C(sp)-H silylation and KO\textsubscript{t}Bu-mediated carboxylation. Sci. China: Chem. 2018, 61, 449–456.

(16) Palumbo, F.; Rohrbach, S.; Tuttle, T.; Murphy, J. A. N-Silylation of Amines Mediated by Et\textsubscript{3}SiH/KO\textsubscript{t}Bu. Helv. Chim. Acta 2019, 102, No. e1900235.

(17) Chatgilialoglu, C.; Ingold, K. U.; Scaiano, J. C. Absolute Rate Constants for the Addition of Triethylsilyl Radicals to Various Unsaturated Compounds. J. Am. Chem. Soc. 1983, 105, 3292–3296.