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Physical Chemistry Chemical Physics

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ARTICLE

Received 00th January 20xx, Accepted 00th January 20xx DOI: 10.1039/x0xx00000x

Mechanistic Investigation of Zinc-Promoted Silylation of Phenylacetylene and Chlorosilane: A Combined Experimental and Computational Study

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Zinc prompted silylation method is of great importance to synthesize high-performance silicon-containing arylacetylene (PSA) resins in the industry. However, it is difficult to eliminate the accompanied by-product of terminal alkenes due to the lack of mechanistic understanding of the silylation. The initiation of Zinc-promoted silylation is facilitated by the interaction between zinc and phenylacetylene. Our DFT calculations indicated that the intermolecular hydrogen transfer of phenylacetylene follows an ionic pathway, which generates the phenylacetylene anion and the corresponding alkene moieties on the zinc surface. The styrene by-product is observed in this stage, with its alkene moieties desorbing as radicals into the solvent under the high reaction temperature. Three possible intermediates of surface phenylacetylene anions were proposed including PhC=C-Zn, PhC=CZnCl, and (PhC=C)₂Zn. These carbanion-zinc intermediates undergo an SN₂ reaction with Me₃SiCl to afford the alkynylsilane on the zinc surface, which is calculated to be the rate-determining step for zinc promoted silylation reaction.

Introduction

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High heat resistant materials have been developed rapidly over the last decades, especially in the field of aerospace.^{1, 2} Since the first industrial production of phenolic resin in 1910, heat resistant resins have been widely used for its excellent properties. A variety of heat resistant materials like polyimide polyarylacetylene (PAA)⁴, and silicon-containing resin.³ arylacetylene(PSA)⁵ resin were successively synthesized in order to improve the thermal and mechanical performance. With the introduction of silicon element into the PAA backbone, PSA resin shows higher thermal stability and less volatile component with better mechanical properties. Besides, PSA resin has an excellent dielectric property and high-temperature ceramic performance, which exhibits potentials in wave transmitting materials and semiconductor materials used in areas such as electronic, information, and aerospace industries, et al..⁶ Currently, various methods have been developed to synthesize the silicon-containing polymers. The Itoh group first reported a successful synthesis of siliconcontaining polymers by the dehydrogenation coupling of alkynes and hydrosilanes with MgO as the catalyst.^{7, 8} Then organolithium⁹ and Grignard reagents^{10, 11} were successively applied to synthesize the PSA. However, there are some challenges including uncontrollable reaction temperatures, and extremely high molecular weight and poor thermostability of the products. A recent study showed that zinc powder promoted method could yield the product with better thermal and mechanical properties and processability, while the reaction remains simple and controllable.12

Electronic Supplementary Information (ESI) available:

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Alkynylsilanes are the precursors of the PSA resin¹³⁻¹⁵, and are also extensively used in organic synthesis as protecting reagents for terminal alkynes,¹⁶ important synthons of C-C and C-N bond formation¹⁷⁻¹⁹ as well as the precursors of other conjugated functional oligomers and polymers. Typically, alkynylsilanes are prepared by deprotonating terminal alkynes with organolithium²⁰ or Grignard reagents²¹ to form alkynylmetal species, followed by the addition of silyl electrophiles. However, it is challenging to control the reaction temperature to carry out the large-scale production of alkynylsilanes in the industry due to the strong exothermicity of the reaction. Some other catalysts or promoters have been developed for the alkynylsilanes formation, consisting of transition metal complexes,²²⁻²⁵ base metal compounds^{8, 26, 27}, and Lewis acids^{28, 29} including zinc^{30, 31} and zinc compound³²⁻³⁶. However, there are some limitations in these methods for industrial production, such as the requirement of noble metal catalysts, highly basic conditions, significantly excess amounts of hydrosilanes or base additives, and strict anhydrous and anaerobic environment.

Sugita et al. directly silylated terminal alkynes with chlorosilanes in the presence of zinc powder in acetonitrile to give the corresponding alkynylsilanes in good yields.³⁰ Then this mild, simple, and controllable method using zinc powder to promote the polycondensation reaction of diacetylene to synthesize the PSA resin was reported.¹² However, it is also known that the zinc promoted method would lead to the formation of terminal alkene by-products along with the alkynylsilanes products. The alkene moieties could lower the heat-resistant temperature of the PSA resin by about 100 °C.37 Thus, it is crucial to inhibit the generation of the terminal alkene by-products in order to acquire high-grade PSA resins. Our group investigated the performance of zinc alloy in order to prevent the formation of the terminal alkenes, but effects were not superior. To the best of our knowledge, researches on inhibiting alkene by-products are limited as the mechanism

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Fig. 1 Proposed mechanisms for zinc-promoted silylation of terminal alkynes and chlorosilanes $^{\rm 30,\,31}$

of zinc promoted terminal alkynes silylation remains unclear.

Fig. 1 shows two different pathways proposed for zinc promoted terminal alkynes silylation.^{30, 31} The first mechanism supported by the stoichiometric relationship between reactants involves an alkynylzinc intermediate, which is formed in situ by direct metalation of terminal alkynes with metal zinc.³⁰ Then, chlorosilane reacts with alkynylzinc to afford the alkynylsilane and ZnCl₂. Besides, a verification experiment of benzaldehyde reduction with phenylacetylene by zinc powder also implies the existence of phenylethynylzinc species.³⁰ It is unlikely that the silylzinc is the active species as the attempt to prepare silylzinc by reacting chlorotrimethylsilane with zinc powder in acetonitrile was unsuccessful, and the chlorosilane remained unchanged throughout the reaction.³⁰ It is worthy of note that this mechanism is disapproved by the absence of the hydrogen gas generated in the reaction.³⁰ The second mechanism follows an electron transfer-deprotonation reaction between zinc and phenylacetylene³¹, which is similar to the alkynes reduction using alkali metals in liquid ammonia.^{38, 39} More specifically, the reaction starts with a single electron transfer from Zn to the alkyne to generate the alkene radical anion [R-C=CH]. followed by deprotonation of phenylacetylene to yield the alkynyl anion $[R-C=C]^{-}$ and alkene radical $[R-C=CH]^{\bullet}$. The second electron transfers from Zn to [R-C=CH][•] resulting in the formation of an anion [R-C=CH]⁻, followed by protonation to form the alkene by-product. The alkynyl anion [R-C≡C]⁻ reacts with the silyl electrophile to yield the product alkynylsilane. This mechanism reveals the formation process of alkenes, and is consistent with the molar ratio of alkynylsilanes to alkenes of 2:1. However, this speculation lacks evidence to support while the transformation of zinc remains unclear, which needs further clarification.

So far, the mechanism of zinc promoted terminal alkynes silylation is still unclear. To the best of our knowledge, there is no published work concerning the reaction mechanism. Here, we aim to unravel the mechanism of zinc-promoted silylation through a combined experimental and computational study. The deuterated experiment and intermediate trapping reactions were conducted in order to obtain information about the reaction process and the intermediates. In our DFT calculations, a periodic Zn(0001) surface model was constructed, and phenylacetylene and trimethylchlorosilane (TMSCI) were chosen as representative reactants. The interaction between the reactants and the zinc surface was investigated in detail. Our computational study supports a surface ionic pathway during the initiation stage. Then, the surface alkynyl anion underwent an SN₂ reaction with Me₃SiCl

to generate alkynylsilane. The ionic or radical nature of the surface adsorbed intermediates and desorbed inclusion were discussed. We believe this study provides a thorough insight into the zinc-promoting method, which may shed some light on the design of a better metal-mediated system with an improved selectivity.

Experimental and computational methods

A vacuum glass Schlenk tube (25 mL) equipped with a magnetic stirring bar was evacuated and flushed with argon. The calculated amount of zinc powder and 10 mL of dry acetonitrile were placed in the reactor. Then to the mixture obtained were successively added phenylacetylene and Me₃SiCl under a flow of argon. The reactor was placed in an oil bath, and the reaction was conducted at 100 °C. All manipulations with air-sensitive materials were performed with the exclusion of oxygen and moisture using Schlenk techniques or a glovebox. Acetonitrile solvent was distilled under N_2 with CaH₂. Nitrogen was purified through the Ag oxygen-removal column and a Davison 4 Å molecular sieve column. Phenylacetylene, Me₃SiCl, Styrene, 1-Phenyl-2trimethylsilylacetylene and Toluene were purchased from TCI and the radical scavenger N-tert-Butyl- α -phenylnitrone (PBN) from Sigma-Aldrich. These reagents were used as received without further purification.

The EPR spectra were recorded on a Bruker BioSpin GmbH Xband (v = 9.87 GHz) digital EPR spectrometer. The instrument settings were: microwave power 6.392 mW; microwave frequency 9.872 GHz; modulation frequency 100 kHz; modulation amplitude 1.0 G; sweep time 42 s; and a detector time constant of 163.84 ms. The GC analysis was performed on gas chromatography apparatus equipped with an FID detector and capillary column HP-5 (30 m × 0.32 mm). Products were identified by GC/MS equipped with an HP-5 column (30 m × 0.25 mm) and a quadrupole mass detector. The conversion yields were analyzed by GC using the internal standard calculation method with toluene as an internal standard.

All the structures were optimized by Vienna ab initio simulation package (VASP)⁴⁰, using the PBE functional in combination with core potentials and plane-wave basis sets.⁴¹ The spin-polarized PBE functional was used for radical intermediates. A detailed benchmark was carried out to ensure the quality of the computed barriers and reaction energies, including cut-off energies, K point mesh, and various smearing methods (ESI, section S4). The optimized conditions were under an energy cut-off of 400 eV with a smearing of 0.1 eV by a second-order Methfessel–Paxton scheme. The K point mesh was chosen to be $(1 \times 1 \times 1)$. The electronic wave functions were converged to 1×10^{-6} eV. An implicit solvation effect was implemented in VASPSol⁴², and the dielectric constant of acetonitrile was 37.5. All energies reported herein are electronic energies without entropy correction.

All intermediate structures were relaxed using a quasi-newton algorithm, with the max force 0.02 eV/Å. Transition states were first coarsely located with a climbing image nudged elastic band (CI-NEB) method⁴³, followed by the optimization with dimer methods⁴⁴ as implemented in the VASP transition state tools (VTST) with the same convergence criteria as the

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geometry relaxation. All transition states were verified to have only one imaginary frequency.

Zn(0001) surface is usually considered active for reactions.⁴⁵ A 7×5×4 model of Zn(0001) surface was constructed for calculations with the bottom two layers fixed unless otherwise stated. The determined equilibrium lattice constants for Zn are a = b = 2.6501 Å, c = 4.9783 Å, which are consistent with experimental values (a = b = 2.66 Å, c = 4.95 Å). A vacuum layer of 25 Å was added to avoid interactions between periodic slabs. For calculations of molecular species, a cubic unit cell of 30×30×30 Å was used. Dipole corrections were considered as part of the involved structures had strong charge separation.

Results and Discussion

Description of the reaction

Zinc promoted silylation of phenylacetylene and Me₃SiCl occurs in acetonitrile under 80~120 °C.³⁰ We first investigated the detailed kinetic behaviour of the silylation reaction. In general, a higher reaction rate was obtained at an elevated temperature (ESI, Section S3.1). However, the temperature effect was less pronounced for the reaction at 120 °C in comparison with the rate detected at 100 °C. Thus, considering the reaction rate and efficiency, 100 °C was chosen as the best reaction temperature. In Fig. 2, a very short induction period was observed. Then the reaction quickly entered an active period with the styrene by-product **d** (0-5 h). After about 5 h, the reaction rate was significantly reduced. The conversion rate came up to 98% at 12 h, and rarely changed by prolonging the reaction time.

Investigation on the influence of different ratios between phenylacetylene and Me₃SiCl showed that phenylacetylene was transformed to **c** and **d** at a ratio of 2:1 when Me₃SiCl was in access (Entry 1-2, Table 1). With an increase in the proportion of phenylacetylene, the yield of **c** decreased from its maximum theoretical yield (entry 3-4, Table 1). Some undetermined white precipitate was observed which might be



Fig. 2 Time course for the silvlation of phenylacetylene with Me $_3$ SiCl at 100 °C

Entry	a:b	Yields ^b (%) DOI: 10.1039/D0CP04127H				
		С	d	Theoretical c ^c	c.u	
1	1:2	66	33	66	2.0	
2	2:2	66	33	66	2.0	
3	3:2	60	33	66	1.8	
4	4:2	43	33	50	1.3	

^aAll reactions were carried out with trimethylchlorosilane (3 mmol), and zinc powder (9 mmol) in 10 mL dry acetonitrile at 100 °C. ^bYields were determined by GC with toluene as an internal standard and calculated based on the amount of **a**.



the by-product from dimerization of phenylalkynyl compound.⁴⁶ Interestingly, the yield of **d** kept around 33%, even if changing the ratio between phenylacetylene and Me₃SiCl. This result suggests that the generation of styrene might originate from the reduction of phenylacetylene by zinc powder,⁴⁷ not affected by the amount of Me₃SiCl.

Deuteration experiment

In this reaction, phenylacetylene is the only source of hydrogen as the methyl group is hard to cleavage. Thus, the formation of styrene is related to the hydrogen transfer from the terminal alkyne. To validate this hypothesis, we carried out a reaction using deuterated phenylacetylene to react with Me_3SiCl . The GC-MS analysis of the liquid product indicated that the by-product styrene was deuterated (m/z 107, ESI, Figure S1). From the stoichiometric balance, the formation of one equivalent of styrene requires two additional equivalents of phenylacetylene as the hydrogen source, which is consistent with 33% by-product yield.

X-H bond is usually involved in the rate-determining step of a reaction.^{48, 49} Deuterated phenylacetylene was used to study the kinetic isotope effect (KIE) during the silylation reaction. The parallel reactions of Me₃SiCl with phenylacetylene, and with deuterated phenylacetylene were carried out, respectively (Fig. 3). A primary KIE value was calculated to $k_{\rm H}/k_{\rm D}$ =1.6, which indicated the transformation of C-H bond before or during the rate-determining step.

Intermediates trapping

The zinc promoted silvlation was reported to occur through a free radical way³¹, which was similar to alkynes reduction with alkali metals in liquid ammonia.^{38, 39} However, there is no direct evidence to validate this hypothesis so far. Herein, the electron paramagnetic resonance (EPR) technique was used to study the initiation stage of the reaction as well as the nature of intermediates. N-tert-Butyl- α -phenylnitrone (PBN) is a well-known radical scavenger commonly used to trap the superoxide, hydroxyl, and carbon-centered radicals.^{50, 51} Under

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PBN: a) phenylacetylene and Me₃SiCl; b) phenylacetylene; c) Me₃SiCl.

the same reaction condition (100 °C for 4 h), three experiments were carried out: a) phenylacetylene and Me₃SiCl with zinc powder, b) pure phenylacetylene with zinc powder, and c) Me₃SiCl with zinc powder, respectively. Then, PBN was added to capture the possible radicals before EPR detection.

Fig. 4a shows a six-fold peak detected in the mixture of PBN with the reaction liquid of phenylacetylene and Me₃SiCl in acetonitrile, indicating the possibility of the existence of radical intermediates. In the second experiment of zinc powder to react with pure phenylacetylene, the intensity of the EPR signal was weaker but it was still active for the PBN adduct (Fig. 4b). For Me₃SiCl under the same condition, the sixfold peak from the spin adduct was not observed (Fig. 4c). These experiments implied that the initiation of zinc promoted silylation was possibly due to the interaction between zinc and phenylacetylene, during which radical intermediates were generated. However, the paramagnetic PBN spin adducts all show six-fold peaks in the EPR spectra, it is difficult to determine their detailed structures with the g factors. Besides, due to the limitation of the detection level, we failed to obtain the adduct information with mass spectrometry. Therefore, to gain a deeper mechanistic understanding of this reaction, we carried out a detailed computational study to investigate the zinc promoted terminal alkyne silylation.

Adsorption of phenylacetylene on the Zn surface

The adsorption of phenylacetylene onto the Zn surface takes place in two ways: i) the alkyne-mode adsorption, and ii) the alkene-mode adsorption (Fig. 5a). Here we used a small $4\times4\times4$ Zn model to study the adsorption of alkyne onto the Zn(0001)



Fig. 5 Adsorption of phenylacetylene on the zinc surface. a) adsorption modes; b) adsorption sites

Table 2. Adsorption energies (kcal/mol) of alkyne- /alkene-modes for phenylacetylene adsorbed at different sites

Modes	hcp-1	hcp-2	hcp-3	bridge
Alkyne-mde	-23.2	-23.9	-23.7	-19.7
Alkene-mode	-36.1	-35.5	-28.0	-30.3

surface. The bottom two layers were kept fixed to reduce the computational cost. The adsorption onto the hexagonal close packing (hcp) site with different orientations of the molecular backbone as well as the bridge site was taken into account (Fig. 5b). Clearly, the alkene-mode adsorption is superior in competing with alkyne-mode adsorption, as indicated by the calculated adsorption energies (Table 2). The most stable adsorption was found to be - 36.1 kcal/mol on the hcp-1 site with the phenylacetylene molecule adsorbed parallel to zinc atoms in the alkene-mode adsorption.

Mechanism of the initiation

Chalk Harrod mechanism is widely accepted for hydrosilylation and dehydrogenative silylation, which begins with the oxidative addition of hydrosilane at the metal center.^{52, 53} However, EPR spectra showed that no radicals were induced for Me₃SiCl by interacting with zinc. We calculated the Si-Cl bond dissociation on the periodic zinc surface, and the dissociation energy turned out to be 16.7 kcal/mol with a dissociation barrier of 37.8 kcal/mol. The high dissociation energy and dissociation barrier illustrated that it was scarcely possible for the reaction to start from the Si-Cl bond cleavage on the zinc surface.

The interaction between zinc and phenylacetylene was studied in detail. Fig. 6 depicts five plausible pathways for the cleavage of terminal hydrogen of phenylacetylene to initiate zincpromoted silylation. The route I in Fig. 6 is a literature reported pathway in which a single electron transfers from zinc to phenylacetylene to form an alkene anion radical, followed by deprotonation of phenylacetylene to form the phenylacetylene anion and alkene species.³¹ Bader charge analysis showed that the phenylacetylene adsorbed in alkenemode onto the zinc surface was in an anionic state, without unpaired electrons and spin polarization. The positive charge was distributed among adjacent Zn atoms (Figure S13 in ESI), which was similar to the charge distribution of Grignard reagents formation.⁵⁴ This result suggested that the proposed

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alkene radical anion may not be an appropriate intermediate during the initiation of the silylation. Considering the above experimental results and the fact of high cleavage energy of Si-Cl bond, we proposed four more pathways for the zinc promoted silylation (route II to V, Fig. 6). If the terminal alkyne hydrogen transferred from the phenylacetylene dissolved in acetonitrile to the adsorbed phenylacetylene, the alkene moiety was generated on the zinc surface along with the dissociative phenylacetylene radical (route II, Fig. 6) or the phenylacetylene anion (route III, Fig. 6). Although the phenylacetylene anion route III rather than the radical route II was supported through the analysis of the charge distribution (Fig.7a) and spin polarization (ESI, Section S5.2.2), the energy for the generation of the alkyne anion was 35.3 kcal/mol with a barrier of 37.8 kcal/mol, indicating a prohibitive pathway of route III. Route IV was supposed to be a direct dissociation of C(sp)-H bond on the zinc surface to yield a phenylacetylene anion and a proton. Similarly, this process was also excluded by a high dissociation energy of 18.5 kcal/mol and a high dissociation barrier of 37.1 kcal/mol. The last pathway of route V involves a proton transfer between two phenylacetylene molecules adsorbed on the zinc surface, forming the adsorbed anionic species (Fig. 7b). The activation barrier for the intermolecular hydrogen transfer is 23.1 kcal/mol, which leads to a fast generation of surface alkene and alkynyl intermediates. Therefore, considering the five possible pathways proposed above, the route V of hydrogen transfer between phenylacetylene on the zinc surface was calculated to be a most likely initiation path for the zinc promoted silylation.

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Fig. 7 Bader charges of hydrogen transfer transition states: (a) H transfer from phenylacetylene dissolving in the solvent to the adsorbed phenylacetylene on the zinc surface; (b) H transfer between adsorbed phenylacetylene on the zinc surface.

As different sites of the alkynyl group was able to accept hydrogen, a detailed investigation of hydrogen transfer process in the route V was investigated, during which generating alkene intermediates and styrene by-product. Three possible alkene moieties were considered (Fig. 8): (i) H transferring to the inner carbon site of the alkynyl group to form a trans alkene moiety A; (ii) H transferring to the inner carbon site of the alkynyl group to form a *cis* alkene moiety **B**; (iii) H transferring to the outer carbon site of the alkynyl group to form an alkene moiety **C**. As shown in the energy profiles of Fig. 9, the formation of intermediate C only requires to overcome a low energy barrier of 16.9 kcal/mol, in comparison to the formation of the other two alkene moieties A (23.2 kcal/mol) and B (23.1 kcal/mol). The second hydrogen transferring to the intermediate **C** only has a shallow energy barrier of 4.1 kcal/mol, while the barriers for the second hydrogen transferring to the trans intermediate A and the cis intermediate B are 21.4 kcal/mol and 12.1 kcal/mol, respectively. In general, hydrogen transfer between phenylacetylene on the zinc surface tended to proceed via the intermediate C. Then alkene moiety intermediates would receive a second hydrogen to form the by-product styrene.

Anionic/radical nature of the intermediates

The EPR spectra indicated that the radical intermediates were generated in the zinc promoted terminal alkyne silylation. Intermediates in this reaction include two main categories: the hydrogen transfer intermediates of phenylacetylene as well as the Me₃SiCl dissociated moieties. We calculated their structures both adsorbed on the surface and desorbed into the solvent to unravel the anionic or radical nature of these intermediates. Bader charge analysis shows that the adsorbed alkynyl and alkene moieties are both anionic without spin polarization. The dissociation of Me₃SiCl molecule at the zinc



Fig. 8 Pathways for hydrogen transfer between phenylacetylene on the zinc surfac

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Fig. 9 Activation barriers and reaction energies (kcal/mol) of hydrogen transfer between phenylacetylene on the zinc surface. Energies are relative to reactant structures.

surface leads to similar results with Cl anion and TMS cation. The positive charge is distributed among adjacent Zn atoms (Figure S12&13 in ESI). The surface anions or cations have no unpaired electrons and would not account for the EPR signals of radicals.

Given that the surface species are in a nonmagnetic state, the EPR signals may relate to the species desorbed into the solvents. Table 3 lists the desorption energy for various species. The desorption energy is determined by $E_{des} = E_{slab} +$ E_{M} - $E_{M/slab}\text{,}$ where E_{M} and E_{slab} are the energies of desorbed species M and the clean zinc surface, respectively, and E_{M/slab} refers to the total energy of the slab with adsorbates. The PBN capture energy is determined by $E = E_{M/PBN} - E_M - E_{PBN}$, where $E_{M/PBN}$ is the energy of PBN captured radical adduct, and E_{PBN} is the energy of PBN molecule. The high desorption energies for surface anionic or cationic species indicate that the strongly adsorbed surface species are unlikely to desorb as anions or cations freely. Thermodynamically, the energies are also too high for the sole radical desorption of the surface species. However, the process for the surface alkene anionic moieties and the trimethylsilane cation species desorbing into the solvent as radicals could be facilitated by adding radical scavenger PBN, as the coupling with PBN is strongly exothermic. It is worthy of note that the hydrogen transfer between phenylacetylene dominates the initiation stage, while the cleavage of the Si-Cl bond in Me₃SiCl is hard to occur due

	lon desorption	Radical desorption	DOI: 10.1 PBN capture	039/D0CP04127 Radical desorption & PBN capture
	50.3	75.0	-59.1	15.9
H-c=c-H	56.0	46.1	-47.7	-1.6
H-c=c	55.0	46.9	-43.8	3.1
H>c=c	39.4	37.4	-33.0	4.4
Me 1 MeSi∼me	25.8	38.4	-30.8	7.6
Cl	19.4	75.2	-37.8	37.4

Table 3. Energies (kcal/mol) for intermediates desorption and PBN capture adducts

Note: Take an example of the first entry: the energies for the adsorbate desorbing into MeCN in the form of ion and radical are 50.3 and 75.0 kcal/mol, respectively. When the desorbed radical is captured by PBN, it is exothermic and the adduct energy is -59.1 kcal/mol. The Energy in Radical desorption & PBN capture (15.9 kcal/mol) is the energy of the captured radical adduct relative to the surface adsorbed moiety, considering both desorption and capturing process.

to high dissociation energies. As a result of the low desorption energies of the PBN captured adducts, it is mainly attributed to the alkene adducts to be EPR active.

Formation of alkynylsilane product

The formation of alkynylsilane product was depicted in Fig. 10, which starts from a carbanion-zinc intermediate I (PhC=C-Zn) formed through hydrogen transfer between phenylacetylene on the zinc surface. Then, the PhC=C-Zn intermediate I undergoes an SN₂ reaction with Me₃SiCl on the zinc surface as the dissociation of Si-Cl bond is endothermic. The whole reaction process was calculated to be exothermic by -14.9 kcal/mol with a barrier of 26.1 kcal/mol. Alternatively, it is also possible for the second phenylacetylene anion to be adsorbed on the same zinc site to form (PhC=C)₂Zn intermediate II. The energy barrier for the formation of alkynylsilane through a similar SN₂ reaction of intermediate II and Me₃SiCl is 25.8 kcal/mol, which is very similar to the path via intermediate I. The anion Cl⁻ could diffuse on the surface and be adsorbed onto the same Zn site together with PhC=C⁻ to form the



Fig. 10 Formation pathways for the alkynylsilane via three possible carbanion-zinc intermediates. Energies (kcal/mol) are relative to each reactant structure.

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PhC≡CZnCl intermediate III. Then the intermediate III reacts with Me₃SiCl to afford the product alkynylsilane with a high barrier of 32.2 kcal/mol. At the high reaction temperature of 100 °C, this process also make a significant contribution to the formation of alkynylsilane in the late stage of the reaction. In addition, our previous experiments proved that the synthesis of alkynylsilane with ZnCl₂ and lithium reagents via the PhC≡CZnCl intermediate was accessible.³⁶ Considering both the hydrogen transfer in the initiation stage and the product formation stage, the SN₂ reaction for surface carbanion-zinc species III and Me₃SiCl to give the alkynylsilane contributed to the rate-determining step in the whole reaction of zinc promoted silylation.

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A detailed surface reaction mechanism of zinc promoted silvlation of phenylacetylene and chlorosilane was reported based on combined experimental characterizations and periodic DFT calculations. Specifically, comprehensive experiments including using GC and EPR to study the reaction behaviors and radical trapping as well as deuterated experiments elucidated the silylation reaction to propose reasonable intermediates in the initiation stage. These suggestions were further complemented by periodic DFT calculations. The dissolving zinc promoted silvlation reaction consisted of two main stages: the initiation stage and the product formation stage. The initiation stage was the dissolving zinc reduction of alkynes with hydrogen transfer on the zinc surface, leading to the generation of surface phenylacetylene anion which would further react with Me₃SiCl in the product formation stage as well as alkene moieties to form the styrene by-product. During this period, the alkene moieties were possible to lose electrons and desorb into the solvent as radicals under high reaction temperature, which were EPR active for its PBN capturing adducts. In the SN₂ product formation stage, three possible carbanion-zinc species were proposed, including PhC=CZn, PhC=CZnCl and (PhC=C)₂Zn. The barriers for alkynylsilane formation via PhC=CZn and (PhC=C)₂Zn were very close, around 26 kcal/mol while a higher barrier of 32.2 kcal/mol was needed via PhC=CZnCl intermediate. The SN₂ reaction in the product formation stage contributed to the rate-determining step in the whole zinc promoted silylation.

This detailed mechanistic investigation was first reported for the heterogeneous zinc surface reaction, both clarifying the pathway to generate the alkynylsilane product and styrene byproduct. Further efforts will focus on improving the performance of zinc promoted silylation to inhibit terminal alkene by-products and increase the selectivity in polycondensation of diacetylenes and dichlorosilanes according to the mechanism, thus producing silicon-containing arylacetylene (PSA) resins with higher heat-resistant temperature.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This work is sponsored by Shanghaple Pulliang Program (18PJ1402500), and the Open Project of State Key Laboratory of Chemical Engineering (SKL-ChE-18C01) at the East China University of Science and Technology. The authors acknowledge the joint-Ph.D. program supported by China Scholarship Council (CSC) for fellowships.

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