

Reactivity of Tris(trimethylsilyl)silane toward Diarylaminyll Radicals

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Absolute rate constants for the reaction of tri-*tert*-butylphenoxy radical (ArO[•]) with (TMS)₃SiH were measured spectrophotometrically in the temperature range 321–383 K. Rate constants for the hydrogen abstraction from (TMS)₃SiH by diarylaminyll radicals of type (4-X-C₆H₄)₂N[•] were determined by using a method in which the corresponding amines catalyze the reaction of ArO[•] with (TMS)₃SiH. At 364.2 K, rate constants are in the range of 2–50 M⁻¹ s⁻¹ for X = H, CH₃, CH₃O, and Br, whereas the corresponding value for ArO[•] is 3 orders of magnitude lower. A common feature of these reactions is the low preexponential factor [$\log(A/M^{-1} s^{-1})$] of 4.4 and 5.2 for ArO[•] and Ph₂N[•], respectively, which reflects high steric demand in the transition state. A semiempirical approach based on intersecting parabolas suggests that the observed reactivity is mainly related to the enthalpy of the reaction and allowed to estimate activation energies for the reaction of (4-X-C₆H₄)₂N[•] and ArO[•] radicals with a variety of silicon hydrides.

Introduction

The reaction of atoms or radicals with silicon hydrides is the main way of generating silyl radicals (eq 1), which play a strategic role in diverse areas of science, i.e., organic synthesis, polymers, and materials.¹ All available kinetic data for reaction 1 as well as for the analogous reaction of germanium and tin hydrides have recently been collected and critically discussed.²



Polysilanes, whose backbones consist entirely of silicon atoms, have been shown to possess a number of interesting chemical and physical properties, which have enormous potential for technological applications.³ A characteristic of poly(hydrosilane)s is the presence of Si–H moieties in each silicon atom of the backbone. The importance of poly(hydrosilane)s in radical chemistry is manifested in their applications as processing stabilizers for organic polymeric materials subject to oxidative degradation.⁴ The degradation of polyolefins during processing takes place by a widely accepted free radical

mechanism. The ability of poly(hydrosilane)s to stabilize polypropylene during multiple extrusion is believed to be due to the synergism of hydrogen donation to carbon-centered radicals⁵ and its capability to scavenge the traces of oxygen present during the extrusion process.⁶

A large number of substituted phenols and aromatic amines have extensively been explored as autoxidation inhibitors.⁷ All these compounds are known to be excellent traps for peroxy radicals and to give, by hydrogen abstraction from OH or NH groups, persistent phenoxy and aminyl radicals. Sulfur and phosphorus compounds have been used in commercial practice in conjunction with hindered phenolic antioxidants as synergists.⁸ The reactivity of alkylperoxy radicals toward poly(hydrosilane)s is a few orders of magnitude lower than the reaction with ArOH or Ar₂NH.⁹ We thought that the combined action of ArOH or Ar₂NH with poly(hydrosilane)s could be of great importance provided that the hydrogen donor ability of SiH moieties toward the corresponding phenoxy or aminyl radicals is reasonable. Since rate constants for these reactions are lacking,² we

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chosed tris(trimethylsilyl)silane, $(\text{TMS})_3\text{SiH}$,¹⁰ as a reliable model for this purpose. However, it was recently reported that the reaction of phenothiazinyl radical ($\text{Ar}_2\text{N}^\bullet$) with $(\text{TMS})_3\text{SiH}$ does not occur, being endothermic of 20 kJ/mol.¹¹ Herein we report a kinetic study of the reaction of tri-*tert*-butylphenoxy radical (ArO^\bullet) with $(\text{TMS})_3\text{SiH}$ which is 11 kJ/mol endothermic¹² as well as a number of diarylaminy radicals ($\text{Ar}_2\text{N}^\bullet$) with $(\text{TMS})_3\text{SiH}$ which are 0–15 kJ/mol exothermic.¹⁵ We also applied a semi-empirical model of intersecting parabolas for estimating activation energies for the reaction of $\text{Ar}_2\text{N}^\bullet$ with a variety of silicon hydrides.^{7,18}

Results and Discussion

Reaction of 2,4,6-Tri-*tert*-butylphenoxy Radical with $(\text{TMS})_3\text{SiH}$. The reaction of tri-*tert*-butylphenoxy radical (**1**) with $(\text{TMS})_3\text{SiH}$ in chlorobenzene as the solvent under Ar was followed spectrophotometrically either at 400 or 625 nm, where the radical **1** absorbs with extinction coefficients of 2×10^3 and $4 \times 10^2 \text{ M}^{-1} \text{ cm}^{-1}$, respectively.^{19,20a} In all experiments, the kinetic curves of radical **1** disappearance showed a short and fast decay at the initial phase followed by a long and slow process. The later time profile was used for the kinetic investigation.²¹

When a large excess of tris(trimethylsilyl)silane is used, i.e., $[(\text{TMS})_3\text{SiH}] \geq 100 \times [\mathbf{1}]$, the time profile of radical **1** disappearance followed clean first-order kinetics (Figure 1a). The pseudo-first-order rate constants, k_{obs} ,

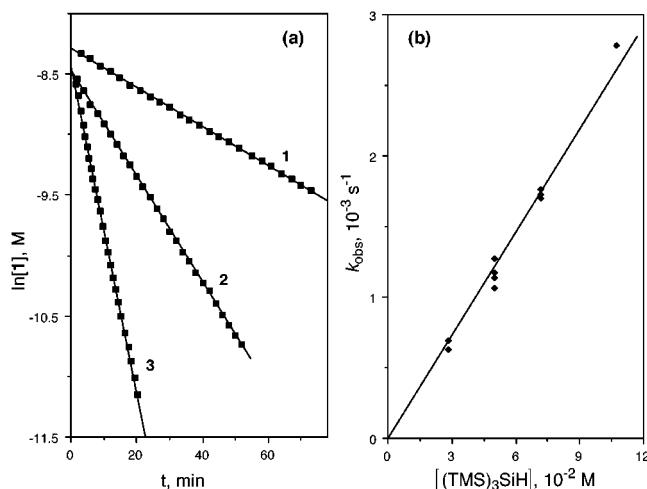
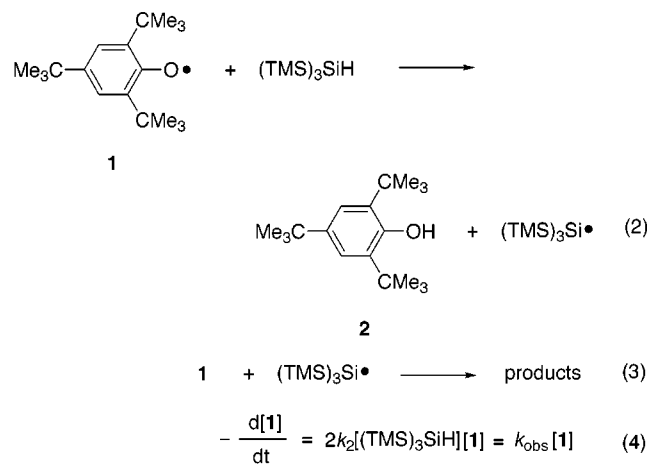


Figure 1. (a) Plot of $\ln[\mathbf{1}]$ vs time: at 321.5 K with 74.4 mM of $(\text{TMS})_3\text{SiH}$ (line 1); at 343.7 K with 72.9 mM of $(\text{TMS})_3\text{SiH}$ (line 2); at 383.2 K with 49.1 mM of $(\text{TMS})_3\text{SiH}$ (line 3). The initial time refers to the beginning of the clean slow decay (see text and ref 21). (b) Dependence of the observed first-order rate constant, k_{obs} , from the concentration of $(\text{TMS})_3\text{SiH}$. Initial concentration of radical **1** in the range of $1.03 \times 10^{-4} - 7.12 \times 10^{-4} \text{ M}$ ($\lambda_{\text{mon}} = 400 \text{ nm}$ for $[\mathbf{1}] \leq 3 \times 10^{-4} \text{ M}$ and $\lambda_{\text{mon}} = 625 \text{ nm}$ for $[\mathbf{1}] > 3 \times 10^{-4} \text{ M}$).

were proportional to $[(\text{TMS})_3\text{SiH}]$ and independent of $[\mathbf{1}]$ (Figure 1b). These results suggest that the hydrogen abstraction from silane by radical **1** is the rate determining step (eq 2). In analogy with the well-known reaction of aryloxy radicals with hydroperoxides and hydrocarbons,²² the silyl radical should react with another radical **1** (eq 3).²³ For $[(\text{TMS})_3\text{SiH}] \gg [\mathbf{1}]$, the kinetic expression describing the consumption of radical **1** is shown in eq 4, where $k_{\text{obs}} = 2k_2[(\text{TMS})_3\text{SiH}]$.



The rate constants obtained from the slope of the linear plot of k_{obs} vs $[(\text{TMS})_3\text{SiH}]_0$ are reported in Table 1. Linear regression analysis of $\log(k_2/\text{M}^{-1} \text{ s}^{-1})$ vs $1/T$ plot yields the Arrhenius parameters given in Table 2.

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(23) The removal of $(\text{TMS})_3\text{Si}^\bullet$ by ArO^\bullet (eq 3) is expected to be faster than the backward reaction 2, i.e., $k_3[\text{ArO}^\bullet] \gg k_{-2}[\text{ArOH}]$. Indeed, k_{-2} can be estimated to be in the range of $0.09\text{--}0.7 \text{ M}^{-1} \text{ s}^{-1}$ at the temperature range 283–322 K from the relation $\Delta H \approx -2.3RT \log K$, where $K = k_2/k_{-2}$. Assuming $k_3 \approx 10^8 \text{ M}^{-1} \text{ s}^{-1}$, it can be calculated that the backward reaction 2 is unimportant under the present experimental conditions.

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(12) Based on the following bond dissociation energies (in kJ/mol): $D^\circ[(\text{TMS})_3\text{SiH}] = 351$,^{1,2,13} and $D^\circ[\text{ArOH}] = 339.9$,¹⁴ where Ar = 2,4,6-*t*-Bu-C₆H₂.

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(15) The $D^\circ[\text{Ar}_2\text{NH}]$ values were determined by an equilibration method using UV–vis detection (see Table 4)¹⁶ or by combination of the equilibrium acidities and the oxidation potentials of their conjugate anions.¹⁷ The two sets of data are similar, the later being slightly higher (1–4 kJ/mol). Values of 359 and 364 kJ/mol for $D^\circ[\text{Ph}_2\text{NH}]$ are also recently reported.^{11,13}

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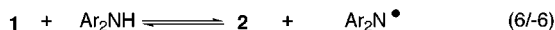
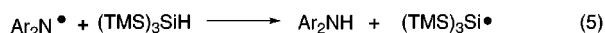
(21) The following observations suggest that the short and fast decay at the initial phase is due to the reaction of **1** with “impurities” present in the stock solution of silane: (i) the consumption of radical **1** at the initial phase is not temperature dependent but increases by increasing silane concentration, (ii) addition of parent phenol in concentration from 10 to 50 times higher than **1** does not influence the reaction decay at the initial phase, and (iii) faster decay of **1** at the initial phase is observed for a prolonged storage of the $(\text{TMS})_3\text{SiH}$ solution in chlorobenzene. To minimize the disappearance of **1** with impurities, we adjusted the concentration of $(\text{TMS})_3\text{SiH}$ so that less than 20% of the starting **1** is consumed by this way.

Table 1. Rate Constants for the Reaction of Radical 1 with (TMS)₃SiH at Various Temperatures^a

T, K	$k_2, M^{-1} s^{-1}$
321.5	$(1.78 \pm 0.01) \times 10^{-3}$
343.7	$(4.97 \pm 0.05) \times 10^{-3}$
364.2	$(1.19 \pm 0.02) \times 10^{-2}$
383.2	$(2.49 \pm 0.05) \times 10^{-2}$

^a Chlorobenzene as the solvent.

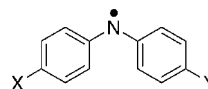
Reactions of Diarylaminy Radical with (TMS)₃SiH. We thought that the rate constants for the reaction of a variety of diarylaminy radicals (Ar₂N•) with (TMS)₃SiH (eq 5) could be determined by using a method in which an amine catalyzes the reaction of radical **1** with (TMS)₃SiH (eq 2). This approach is based on the known methodology used for determining the reactivity of Ar₂N• toward hydroperoxides²⁴ and hydrocarbons.²⁰ We briefly describe the method and the necessary modifications. The reactions of radical **1** with Ar₂NH are relatively fast and reversible (eqs 6/–6). For example, k_6 and k_{-6} are in the range of 10^2 – 10^4 and 10^6 – $10^7 M^{-1} s^{-1}$ at 294 K, respectively, depending on the nature of the aryl moieties²⁵ and, therefore, several orders of magnitude higher than k_2 .



It is possible to reach a quasi-equilibrium regime (eqs 6/–6), if **2** and Ar₂NH are added to the solution of radical **1** and (TMS)₃SiH. The time (τ) to reach the quasi-equilibrium conditions can be estimated from the relation $\tau \approx (k_{-6}[2]_0)^{-1}$. For $[2]_0 = 10^{-3}$ – $10^{-2} M$, a τ value of 10^{-3} – $10^{-5} s$ is calculated, which means that a quasi-equilibrium is reached immediately after mixing the reactants. Under these conditions, some of the radical **1** will be replaced by Ar₂N• radical, i.e., $[Ar_2N\bullet] = K_6[1][Ar_2NH]/[2]$, where $K_6 = k_6/k_{-6}$. Since the rate constants for hydrogen abstraction by Ar₂N• radical are usually much higher than that for the analogous reactions of radical **1** (4–6 orders of magnitude),²⁰ the replacement of **1** by Ar₂N• radical, even at a low extent, suffices for performing the desired measurements.

The amine is regenerated during the reaction 5, and then it returns into the catalytic cycle (eqs 6/–6). The silyl radical formed in reaction 5 should decay by recombination with radical **1** as happens in the absence of the catalyst (eq 3), since the concentration of radical **1** exceeds by several orders of magnitude the overall concentration of all the other radicals. We predicted that the decay of radical **1** in the presence of (TMS)₃SiH should be accelerated by addition of Ar₂NH. In the absence of side reactions, amines behave as the catalyst because they are not consumed and do not affect the composition of the products. To achieve this scenario, the $[Ar_2NH]$ and $[2]$ should be used as higher as possible²⁶ whereas the ratio $[Ar_2NH]/[2]$ should be kept at minimum.²⁷ The $[1]$ and $[(TMS)_3SiH]$ should also be kept relatively low and high, respectively.

Under such experimental conditions, the time profile of radical **1** disappearance in the presence of five amines of type (4-X-C₆H₄)₂NH (cf. structures **3**–**7** for the corresponding aminyl radicals) followed clean first-order kinetics. Two examples are shown in Figure 2a and 2b



- 3** X = Y = H
4 X = Y = CH₃
5 X = H, Y = OCH₃
6 X = Y = OCH₃
7 X = Y = Br

for Ph₂NH and (4-MeO-C₆H₄)PhNH in the absence (line 1) and in the presence (lines 2 and 3) of amine. In the presence of amine, the overall rate of radical **1** disappearance is equal to the sum of “noncatalyzed” and “catalyzed” reaction rates and, consequently, k_{obs} is given by eq 7 which, for practical purposes, can be written as eq 8.

$$k_{obs} = 2k_2[(TMS)_3SiH] + 2k_5K_6 \frac{[Ar_2NH]}{[2]} [(TMS)_3SiH] \quad (7)$$

$$\frac{k_{obs}}{2[(TMS)_3SiH]} = k_2 + k_5K_6 \frac{[Ar_2NH]}{[2]} \quad (8)$$

Table 2. Arrhenius Parameters for the Reaction of (TMS)₃SiH with Some Persistent Radicals

Radical	log (A/M ⁻¹ s ⁻¹)	E, kJ/mol	$k^{298}/M^{-1}s^{-1}$	Ref.
	4.36 ± 0.07	43.8 ± 0.4	4.8 × 10 ⁻⁴	this work
	5.22 ± 0.28	26.1 ± 2.0	4.4	this work
	4.8	18.4	34.4	31

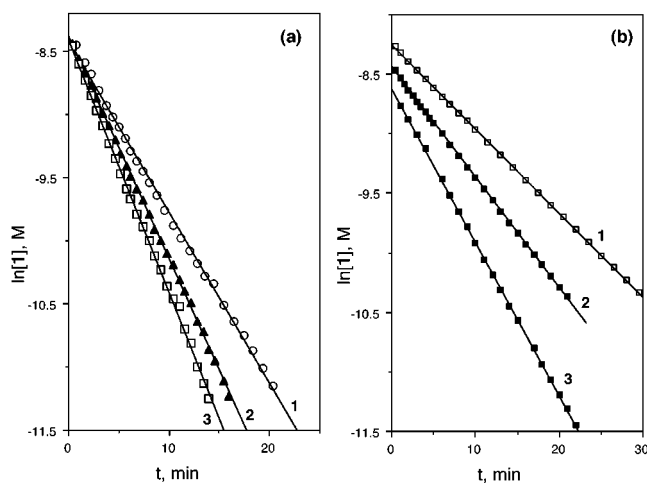


Figure 2. Plot of $\ln[1]$ vs time in the absence and presence of Ar_2NH . The initial time refers to the beginning of the clean slow decay (see text and ref 21). (a) At 383.2 K with 49.1 mM of $(\text{TMS})_3\text{SiH}$. Initial concentration of compounds **2** and Ph_2NH , respectively: 1.5 and 0 mM (line 1); 4 and 1 mM (line 2); 3 and 6 mM (line 3). (b) At 364.2 K with 50.1 mM (line 1 and 2) or 64.4 mM (line 3) of $(\text{TMS})_3\text{SiH}$. Initial concentration of compounds **2** and $(4\text{-MeO-C}_6\text{H}_4)\text{PhNH}$, respectively: 10 and 0 mM (line 1); 6 and 0.47 mM (line 2); 3 and 0.47 mM (line 3).

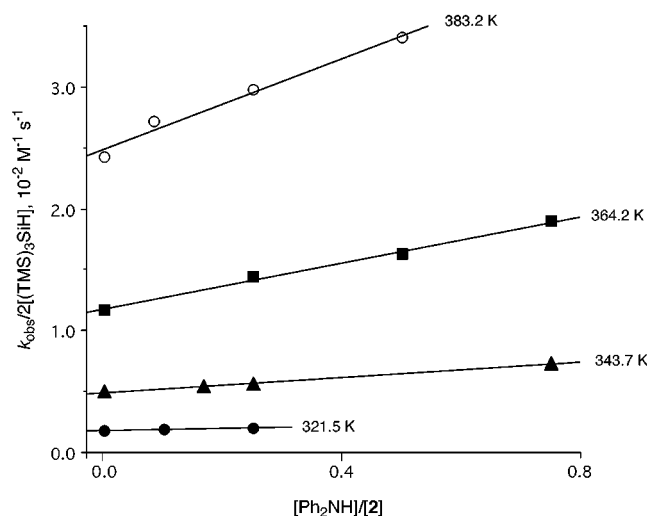


Figure 3. Linear regression analysis of $k_{\text{obs}}/2[(\text{TMS})_3\text{SiH}]$ vs $[\text{Ph}_2\text{NH}]/[\mathbf{2}]$ at different temperatures.

Table 3. k_5K_6 Values for the Reaction of $\text{Ph}_2\text{N}^\bullet$ Radical with $(\text{TMS})_3\text{SiH}$ at Various Temperatures^a

<i>T</i> , K	k_5K_6 , $\text{M}^{-1} \text{s}^{-1}$
321.5	$(9.24 \pm 0.63) \times 10^{-4}$
343.7	$(3.01 \pm 0.14) \times 10^{-3}$
364.2	$(9.46 \pm 0.40) \times 10^{-3}$
383.2	$(1.87 \pm 0.18) \times 10^{-2}$

^a Chlorobenzene as the solvent.

Figure 3 shows the dependence of $k_{\text{obs}}/2[(\text{TMS})_3\text{SiH}]$ on the ratio $[\text{Ph}_2\text{NH}]/[\mathbf{2}]$ according to eq 8 at different temperatures, whose slopes provide the k_5K_6 values for this amine (Table 3). Linear regression analysis of $\log(k_5K_6)$ vs $1/T$ plot yields the relative Arrhenius pa-

rameters given by eq 9, where $\theta = 2.3RT/\text{kJ/mol}$ and the errors correspond to one standard deviation.

$$\log(k_5K_6/\text{M}^{-1} \text{s}^{-1}) = (5.23 \pm 0.28) - (50.8 \pm 1.90)/\theta \quad (9)$$

Combination of the Arrhenius expression for k_5K_6 with the known parameters³⁰ for the equilibrium 6/-6 yields the temperature dependence of k_5 (Table 2). The value of k_5 can be calculated as $4.4 \text{ M}^{-1} \text{s}^{-1}$ at 298 K.

The Arrhenius parameters obtained for the reaction of radical **1** and $\text{Ph}_2\text{N}^\bullet$ with $(\text{TMS})_3\text{SiH}$ and the analogous reaction of 2,2,6,6-tetramethylpiperidiny radical³¹ are reported in Table 2 for comparison. A remarkable feature of the three reactions is the low value of $\log A$ which is normally in the range of 8.5–9.0 for hydrogen abstraction.³² The low value can be explained in terms of the high steric demand for a reaction in which both substrates are sterically hindered.³³ Indeed, the steric constraints in the transition state should manifest both in the entropy of activation and the energy of activation, the former being more pronounced due to the loss of rotational and vibrational degrees of freedom.

Figure 4 shows the dependence of $k_{\text{obs}}/2[(\text{TMS})_3\text{SiH}]$ on the ratio $[\text{Ar}_2\text{NH}]/[\mathbf{2}]$ at 364.2 K for other amines. The k_5K_6 values for these amines including Ph_2NH are reported in Table 4 together with the equilibrium constants and $D^\circ(\text{Ar}_2\text{NH})$ taken from the literature¹⁶ and the calculated absolute k_5 values. The reactivity of $(4\text{-X-C}_6\text{H}_4)_2\text{N}^\bullet$ radicals with $(\text{TMS})_3\text{SiH}$ is increasing with the decrease of the electron-donating properties of substituents X, the rate constants being in the range $2\text{--}46 \text{ M}^{-1} \text{s}^{-1}$ at 364.2 K. A reasonably good linear correlation was found when $\log k_5$ was plotted vs $D^\circ(\text{Ar}_2\text{NH})$ ($r^2 = 0.95$) indicating that the observed effects are primarily caused by the ability of substituent to stabilize the aminyl radical. A plot of $\log k_5$ against the $\Sigma\sigma_p^+$ substituent constants³⁴ also shows a good linear relation with $\rho^+ = 0.73$ ($r^2 = 0.96$), which is not surprising in view of the fact that correlation was also observed when $D^\circ(\text{Ar}_2\text{NH})$ was plotted vs $\Sigma\sigma_p^+$ values, with $\rho^+ = 9.02$ ($r^2 = 0.97$). Therefore, polarized transition states should be unimportant and the reactivity trend simply reflects the

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(26) For a quasi-equilibrium the rates of reactions 6 and -6 should be close to each other and much higher than those of reactions 2 and 5, respectively. Therefore, $[\text{Ar}_2\text{NH}] \gg k_2[(\text{TMS})_3\text{SiH}]/k_6$ and $[\mathbf{2}] \gg k_5[(\text{TMS})_3\text{SiH}]/k_{-6}$.

(27) Since the cross-coupling of $\text{Ar}_2\text{N}^\bullet$ and **1** radicals is unimportant,²⁸ the self-termination of $\text{Ar}_2\text{N}^\bullet$ radicals is the only possible side reaction. Indeed, these rate constants ($2k_t$) are in the range of $10^6\text{--}10^8 \text{ M}^{-1} \text{s}^{-1}$, depending on the nature of substituents.²⁹ Therefore, the rate of the reaction 5 should be much higher than the rate of self-termination of $\text{Ar}_2\text{N}^\bullet$ radicals, i.e., $k_5[(\text{TMS})_3\text{SiH}]/2k_tK_6[\mathbf{1}] \gg [\text{Ar}_2\text{NH}]/[\mathbf{2}]$.

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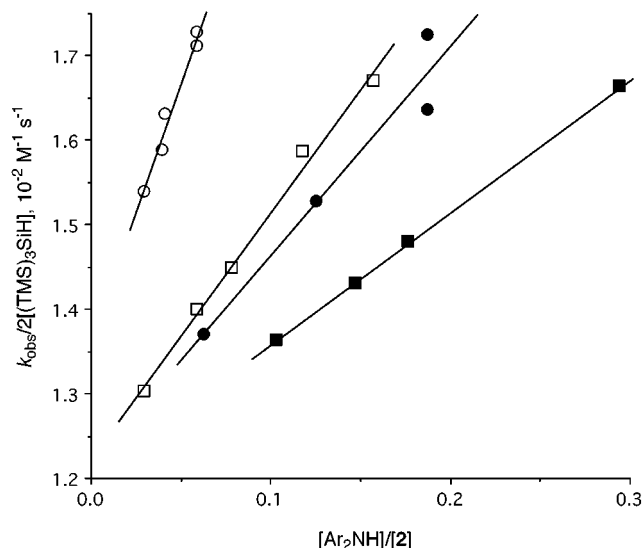


Figure 4. Linear regression analysis of $k_{\text{obs}}/2[(\text{TMS})_3\text{SiH}]$ vs $[\text{Ar}_2\text{NH}]/[2]$ for amines (4-Br- C_6H_4) $_2\text{NH}$ (■), (4-Me- C_6H_4) $_2\text{NH}$ (●), (4-MeO- C_6H_4)PhNH (□), and (4-MeO- C_6H_4) $_2\text{NH}$ (○) at 364.2 K.

Table 4. Kinetic Data for the Reaction of $\text{Ar}_2\text{N}^\bullet$ Radicals with $(\text{TMS})_3\text{SiH}$ at 364.2 K

$\text{Ar}_2\text{N}^\bullet$	$k_5 K_6$, $10^{-2} \text{ M}^{-1} \text{ s}^{-1}$	K_6 , ^a 10^{-3}	k_5 , $\text{M}^{-1} \text{ s}^{-1}$	$D^\circ(\text{Ar}_2\text{NH})$, ^a kJ/mol
3	0.95 ± 0.04	0.283	33.5	364.7
4	2.48 ± 0.43	3.41	7.27	357.5
5	2.93 ± 0.14	5.21	5.63	355.9
6	11.43 ± 0.14	46.6	2.45	348.6
7	1.57 ± 0.01	0.343	45.8	364.2

^a From ref 16.

differences in the bond dissociation energies of amines, $D^\circ(\text{Ar}_2\text{NH})$.³⁵ It is interesting to note that the reactivity of $\text{Ar}_2\text{N}^\bullet$ radicals toward $(\text{TMS})_3\text{SiH}$ is ca. 2 orders of magnitude higher than that in the analogous reaction with PhCMe_2H ,^{20a} whereas the dissociation energies of the corresponding Si-H and C-H bonds are very similar.

Semiempirical Calculations Based on the Parabolic Model. One of us has introduced in recent years a parabolic model for estimating activation energies of hydrogen abstraction reactions.^{7,18} This semiempirical method has also been applied for calculating kinetic parameters of reaction of atoms and radicals with a variety of silicon hydrides and is herein extended to the reactions with $\text{Ar}_2\text{N}^\bullet$ radicals.³⁶ The parabolic model describes the transition state of hydrogen abstraction as the point of intersection between two potential curves (unperturbed) of the stretching vibrations (harmonic) associated with cleaving Si-H and forming N-H bonds (Figure 5). Along with the enthalpy (ΔH_e) and activation energy (E_e) of the reaction, this model uses the coefficients b_i , b_f , and r_e . ΔH_e is the energy difference between the minimum points of the two parabolic curves and is related to the experimental reaction enthalpy ΔH (eq 10). E_e is the difference between the minimum point of the Si-H parabolic curve and the point of intersection of the two curves and is related to experimental activation

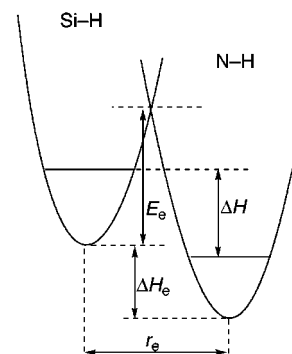


Figure 5. Intersection of Si-H and N-H bond potential curves for the parabolic model.

Table 5. Calculated E_e , ΔH_e , and $b_i r_e$ Values for the Reactions of $\text{Ar}_2\text{N}^\bullet$ Radicals with $(\text{TMS})_3\text{SiH}$

$\text{Ar}_2\text{N}^\bullet$	E , kJ/mol	E_e , kJ/mol	ΔH_e , kJ/mol	$b_i r_e$, (kJ/mol) ^{1/2}
3	26.3 ^a	37.4	-21.1	11.01
4	30.9 ^b	42.0	-13.9	11.27
5	31.7 ^b	42.8	-12.3	11.29
6	34.2 ^b	45.3	-5.0	11.27
7	25.4 ^b	36.5	-20.6	10.88

^a Taken from Table 2. ^b Calculated from the k_5 values reported in Table 4 by assuming $\log(A/\text{M}^{-1} \text{ s}^{-1}) = 5.3$.

energy E (eq 11). The coefficients $b_i = \pi\nu_i(2\mu_i)^{1/2}$ and $b_f = \pi\nu_f(2\mu_f)^{1/2}$ characterize the relationship between the potential energy and the vibration amplitude of the Si-H and N-H bonds, respectively, whereas $2b^2$ is the force constant of a bond.^{37a} The coefficient r_e is the distance between the minimum points of the two potential curves (Figure 5). The relationship between these parameters may be represented as shown in eq 12, where $\alpha = b_i/b_f$.

$$\Delta H_e = \Delta H + 0.5hN_A c(\nu_i - \nu_f) \quad (10)$$

$$E_e = E + 0.5hN_A c\nu_i - 0.5RT \quad (11)$$

$$b_i r_e = \alpha(E_e - \Delta H_e)^{1/2} + E_e^{1/2} \quad (12)$$

For reaction 5, the following parameters were used: $\alpha = b_i/b_f = 0.640$, $b_i = 2.756 \times 10^{11} (\text{kJ/mol})^{1/2} \text{ m}^{-1}$, $0.5hN_A c(\nu_i - \nu_f) = -7.4 \text{ kJ/mol}$, $0.5hN_A c\nu_i - 0.5RT = 11.1 \text{ kJ/mol}$.^{37b} The activation energies (E) were estimated by assuming $\log(A/\text{M}^{-1} \text{ s}^{-1}) = 5.3$, in analogy with the experimental results reported in Table 2. ΔH_e , E_e , and $b_i r_e$ are obtained from eqs 10, 11, and 12, respectively. Table 5 summarizes the calculated data for the five $\text{Ar}_2\text{N}^\bullet$ radicals described in the above section.

The $b_i r_e$ value is a general characteristic of a certain reaction. The $b_i r_e$ values of the five reactions in Table 5

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(37) (a) Zero vibration frequency (ν) and reduce mass (μ) of the bond are expressed in cm^{-1} and g mol^{-1} , respectively. The subscripts i and f refer to the cleaving (Si-H) and the forming (N-H) bonds, respectively. (b) The following parameters are used: $\nu_{\text{Si-H}} = 2100$, $\nu_{\text{N-H}} = 3337$, $\nu_{\text{O-H}} = 3600$, $T = 364.2 \text{ K}$, $h = \text{Planck constant}$, $N_A = \text{Avogadro constant}$, $c = \text{light speed}$.

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Table 6. Calculated Activation Energies (E , kJ/mol) for the Reaction of (4- X - C_6H_4) $_2N^{\bullet}$ (3–7) and ArO^{\bullet} (1) Radicals with a Variety of Silicon Hydrides

silane	$D^{\circ}(Si-H)$, kJ/mol	3	4	5	6	7	1
H ₄ Si	384.1 ± 2.0 ^a	40.0	43.1	43.8	47.2	40.2	57.5
MeSiH ₃	386 ^b	40.8	43.9	44.7	48.1	41.0	58.4
Me ₃ SiH	397.4 ± 2.0 ^c	45.9	49.3	50.0	53.7	46.1	63.8
Et ₃ SiH	398 ^{b,d}	46.1	49.6	50.3	54.0	46.4	64.1
PhSiH ₃	377 ^b	37.0	40.0	40.7	43.9	37.2	54.3
PhMeSiH ₂	382 ^b	39.1	42.2	42.9	46.2	39.3	56.5
Me ₃ SiSi(H)Me ₂	378 ^{b,d}	37.4	40.4	41.1	44.4	37.7	54.7
(TMS) ₃ SiH	351 ^{b,d}	27.4	29.9	30.5	33.2	27.6	43.8
(MeS) ₃ SiH	366 ^{b,d}	32.8	35.5	36.2	39.1	33.0	49.6

^a From ref 38. ^b From ref 1. ^c From ref 39. ^d From ref 13.

are very close to each other indicating that all these reactions belong to one class and the difference in the activation energies is related only to the enthalpy of the reaction. Therefore, the average value of 11.14 ± 0.17 (kJ/mol)^{1/2} can be used to calculate the activation parameters of the radicals 3–7 with a variety of organosilicon hydrides. For practical purposes, eq 11 can be written as eq 13. ΔH_c values, obtained from eq 10 using appropriate bond dissociation energies, allow to calculate the corresponding E_c values, which are transformed into E through eq 11. In Table 6 are reported 45 calculated activation energies for hydrogen abstraction from a variety of silanes by the aminyl radicals 3–7.

$$\sqrt{E_c} = \frac{b_r r_e}{1 - \alpha^2} \left\{ 1 - \alpha \sqrt{1 - \frac{1 - \alpha^2}{(b_r r_e)^2} \Delta H_c} \right\} \quad (13)$$

The above-described parabolic model has also been applied to reaction 2. The following parameters were used: $\alpha = b_r/b_t = 0.590$, $b_t = 2.756 \times 10^{11}$ (kJ/mol)^{1/2} m⁻¹, $0.5hL(\nu_1 - \nu_i) = -8.9$ kJ/mol, $0.5hL\nu_1 - 0.5RT = 11.4$ kJ/mol.^{37a} Taken the activation energy of 43.8 kJ/mol for reaction 2 (Table 2) and using the appropriate bond

dissociation energies,¹² the values of $\Delta H_c = 2.2$ kJ/mol, $E_c = 55.2$ kJ/mol, and $b_r r_e = 11.72$ (kJ/mol)^{1/2} are obtained. Using these values together with the appropriate bond dissociation energies of silanes and applying eqs 10, 13 and 11, the activation energies for hypothetical hydrogen abstraction from a variety of silanes by the radicals 1 can be obtained (Table 6, last column).

Experimental Section

Materials. Tris(trimethylsilyl)silane (Fluka AG) was used as received. Secondary aromatic amines (compounds 3–7) and 2,4,6-tri-*tert*-butylphenol (2) were purified by silica gel column chromatography with UV-detection. Chlorobenzene was passed prior to use in a glass column (inner diameter 3 cm) through the following layers (layers in cm indicated in parentheses): 15 wt % H₂SO₄ on SiO₂ (3); SiO₂ (2); KMnO₄ on Al₂O₃ (5); CaCl₂ (7); KOH (10); Al₂O₃ (40).

Tri-*tert*-butylphenoxy Radical (1). The stable radical 1 was prepared from the corresponding phenol by oxidation. A 0.15 M solution of tri-*tert*-butylphenol in chlorobenzene was slowly (1 drop/min) passed by means of an argon flow through a glass column (length 5 cm, inner diameter 0.8 cm) filled with a mixture of PbO₂ and glass wool in order to increase the permeability. At the outlet of the column, the solution of radical 1 was diluted to 1.5–3 mM under argon and used for the kinetic experiments. The solution was stored under argon immediately prior to use. Such a solution was stable in the dark for several months and a solution of 0.2 mM kept at 383.2 K for 10 min was consumed of $\leq 1\%$.

Kinetic Measurements. The disappearance of radical 1 in the presence of (TMS)₃SiH or (TMS)₃SiH/Ar₂NH was followed spectrophotometrically either at 400 or 625 nm where it absorbs with extinction coefficients of 2×10^3 and 4×10^2 M⁻¹ cm⁻¹, respectively. The real concentration of the reactants was calculated taking into account the thermal expansion of the solvent (0.001 deg⁻¹). The experiments were carried out under Ar in a thermostated 8.5 mL cell-reactor having 2 cm optical path using a Specord UV-vis spectrometer. The temperature (± 0.2 K) was controlled with a standard variable-temperature accessory. In all experiments, the kinetic curves of radical 1 disappearance show a short and fast decay at the initial phase followed by a long and slow process. The later time profile was used for kinetic investigation.²¹

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