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Rate constants for the reaction of cumylperoxyl radicals with group 14 hydrides

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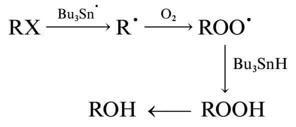
Rate constants for the reaction of a cumylperoxyl radical with a variety of group 14 hydrides were measured by using inhibited hydrocarbon oxidation methodologies. In the silane series the rate constants at 345.5 K are in the range 0.10–0.90 M^{-1} s^{-1} for t-$BuSiHMe_2$, $PhSiH_3$, $PhSiHMe_2$, Ph_2SiH_2, Ph_2SiHMe and Ph_3SiH, whereas the rate constant for $(TMS)_3SiH$ is 2–3 orders of magnitude higher. The rate constants for Bu_3GeH and Bu_3SnH are 19.4 and 1.8 × 10^3 M^{-1} s^{-1}, respectively, at 345.5 K. The trends in reactivity for these reactions are similar to those observed for other radicals with group 14 hydrides although the reactions are several orders of magnitude slower.

Introduction

The reaction of peroxyl radicals with organic substrates is one of the most important classes of reactions in chemistry[1] since it is the key step of several processes, *e.g.*, autoxidation of synthetic polymers, lipid peroxidation, DNA damage and chemical synthesis. Aerobic oxygenation of organic compounds in the presence of a reducing agent has attracted considerable attention.[2] In this context, the conversion of halides to alcohols has recently been approached using tin hydride.[3,4] The reaction sequence that has been suggested is shown in Scheme 1.



Scheme 1

Examples in which the alkyl radical rearranges itself prior to reaction with molecular oxygen are reported,[3] although in some cases the reaction is sluggish and gives undesired products.[5] Nakamura and co-workers were able to run these experiments under conditions where hydroperoxides were isolated in good yields.[6] In one case, the $(TMS)_3SiH$-mediated halide-to-alcohol transformation was reported to give a moderate yield.[6] In all these transformations, the reaction of a peroxyl radical with a tin or silicon hydride is crucial. Although the reactivity of peroxyl radicals with a variety of substrates is well documented by a large number of kinetic data,[7] studies on the reaction of peroxyl radicals with group 14 hydrides are extremely scarce. For a synthetically useful radical chain reaction the intermediates must be *disciplined*.[8] The majority of such chain processes have been carried out by using Bu_3SnH or $(TMS)_3SiH$, which are the most widely used reagents under reduction conditions.[9,10] The concept of discipline in free radical reactions is strictly connected with the kinetic information of each individual step although, upon first consideration, the importance of the kinetic knowledge might be less apparent in planning a synthetic strategy.

In their recent mechanistic studies on model DNA damage, Greenberg and co-workers[11] assumed the rate constant for the $ROO^•$ radical with Bu_3SnH to be 5 × 10^3 M^{-1} s^{-1} at 55 °C in THF. This number was chosen based on the knowledge that the rate constant of alkylperoxyl radicals with PhSH is 5 × 10^3 M^{-1} s^{-1} at 30 °C in isopentane[12] and that the rate constants of the peroxyl radicals of polyuridylic acid and polyadenylic acid with a variety of water soluble thiols were found to be in the range 8 × 10^3–1.3 × 10^5 M^{-1} s^{-1}.[13]

Following these considerations, the knowledge of the rate constants for the reaction of peroxyl radicals with group 14 hydrides turns out to be necessary for better synthetic planning as well as a reference reaction for mechanistic studies. With the exception of our preliminary results on the reaction of cumylperoxyl radicals with Bu_3SnH and $(TMS)_3SiH$,[14] only a rate constant of 0.004 M^{-1} s^{-1} at 303 K for the reaction of t-$BuOO^•$ radical with $PhSiHMe_2$ has been reported by Howard in a review article[15] without any experimental details, and to our knowledge this is the only value available in the literature.† Herein, we describe our detailed kinetic studies of cumylperoxyl radicals with a variety of group 14 hydrides.

Results

The oxidation rates of cumene in the presence or absence of group 14 hydrides were measured by the oxygen uptake. Reactions were carried out in a thermostatic glass reactor equipped with shake stirrer and attached to a manometric device. All reactions were carried out under oxygen pressure at 1.0 × 10^5 Pa and at a temperature of 345.5 ± 0.1 K. After the addition of a known volume of the solution, the reactor was evacuated and flushed with oxygen several times to ensure that complete required atmosphere was attained in the reaction cell. Sufficient time was given for the solution to attain equilibrium. The experimental error of the rate of oxygen absorption at the

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† Doba and Ingold, in their kinetic study on the $(CF_3)_2NO^•$ radical, presented a figure that correlates the rate constants of hydrogen abstraction for the $(CF_3)_2NO^•$ and t-$BuOO^•$ radicals with a variety of substrates.[16] However, in this figure they reported rate constants of *ca.* 0.1 and 10 M^{-1} s^{-1} for the reaction of t-$BuOO^•$ radicals with Et_3SiH and Ph_3GeH, respectively, referring to J. A. Howard as a private communication. To our knowledge the original source of these rate constants has never been published.

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Table 1 Rates of oxidation of cumene in the presence of a variety of substrates[a]

Substrate	$(-d[O_2]/dt)/$ 10^{-5} M s^{-1}	$[Substrate]_0$/M
t-BuSi(H)Me_2[b]	3.97	0.112
	3.81	0.141
	3.78	0.215
	3.56	0.287
PhSi(H)Me_2[b]	3.78	0.097
	3.17	0.147
	3.09	0.219
	3.09	0.299
	2.53	0.381
	2.45	0.472
$PhSiH_3$[b]	3.16	0.037
	2.74	0.058
	2.33	0.092
	1.99	0.121
	1.78	0.181
Ph_2SiH_2[c]	3.44	0.022
	3.00	0.037
	2.48	0.090
	2.18	0.120
	1.78	0.182
$Ph_2Si(H)Me$[c]	3.80	0.040
	3.64	0.078
	3.02	0.142
	2.85	0.174
Ph_3SiH[b]	3.85	1.32×10^{-2}
	3.75	2.80×10^{-2}
	3.51	3.95×10^{-2}
	3.33	5.75×10^{-2}
	3.22	6.60×10^{-2}
5,10-Dihydrosilanthrene[c]	3.56	2.53×10^{-3}
	3.06	4.94×10^{-3}
	2.93	7.77×10^{-3}
	2.47	11.8×10^{-3}
Poly(phenylsilane)[b]	3.72	0.94×10^{-3}
	3.77	1.89×10^{-3}
	3.63	2.83×10^{-3}
	2.85	3.80×10^{-3}
	1.85	5.67×10^{-3}
	1.33	10.4×10^{-3}
	1.18	14.1×10^{-3}
$(TMS)_3SiH$[b]	3.94	1.84×10^{-4}
	3.83	2.45×10^{-4}
	3.70	3.68×10^{-4}
	3.49	4.91×10^{-4}
	3.40	6.13×10^{-4}
n-Bu_3GeH[d]	3.50	1.84×10^{-3}
	3.19	2.41×10^{-3}
	3.03	3.78×10^{-3}
	2.47	5.66×10^{-3}
	1.94	7.55×10^{-3}
	1.75	9.44×10^{-3}

[a] [AIBN] = 0.021 M, $R_i = 1.09 \times 10^{-6}$ M s^{-1} at 345.5 K. [b] $(-d[O_2]/dt)_0 = 4.33 \times 10^{-5}$ M s^{-1}. [c] $(-d[O_2]/dt)_0 = 3.95 \times 10^{-5}$ M s^{-1}. [d] $(-d[O_2]/dt)_0 = 3.80 \times 10^{-5}$ M s^{-1}.

manometric apparatus with automatic pressure control was ±1.0%, and the error in the reproducibility of the experiments was 3%. The oxidation rates (in M s^{-1}) were measured by the oxygen uptake and calculated by eqn. (1), where 6.82×10^{-4}

$$(-d[O_2]/dt) = 6.82 \times 10^{-4} \frac{V(O_2)}{Vt} \qquad (1)$$

was the coefficient constant of the manometric apparatus, $V(O_2)$ the volume in ml of oxygen uptake, t the time of oxygen uptake in min and V the sample volume in ml. In particular, two different kinetic approaches were used for a variety of group 14 hydrides, depending on the absence or presence of an induction period when they were used as antioxidants (methods A and B, respectively).

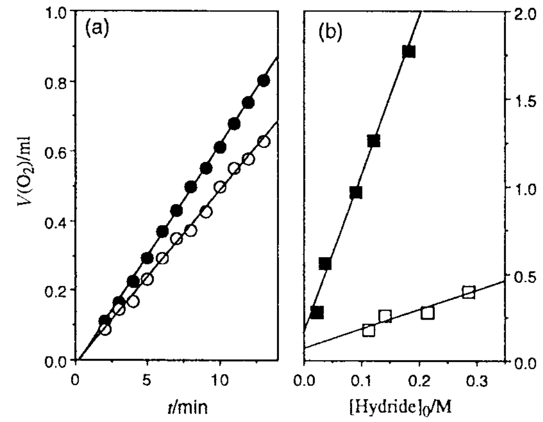


Fig. 1 (a) Oxygen consumption during the AIBN-initiated (0.021 M) oxidation of cumene in the absence (●) and presence of 6.13×10^{-4} M of $(TMS)_3SiH$ (○) at 345.5 K. (b) Linear regression analysis of $(-d[O_2]/dt)_0/(-d[O_2]/dt) - (-d[O_2]/dt)/(-d[O_2]/dt)_0$ *vs.* [t-BuSi(H)Me_2] (□) and [Ph_2SiH_2] (■); [AIBN] = 0.021 M at 345.5 K.

Method A

The oxidation of pure cumene was thermally initiated (0.021 M of AIBN at 345.5 K) and the volume of oxygen uptake, $V(O_2)$, was measured over time at different concentrations of a silane or n-Bu_3GeH. For example, Fig. 1(a) shows the linear dependence of $V(O_2)$ *vs.* time in the absence and in the presence of 6.13×10^{-4} M of $(TMS)_3SiH$ without an induction period. From the slopes of the linear plots the oxidation rates were calculated by using eqn. (1). Table 1 shows that the oxidation rate decreases with increasing the concentration of the substrate.

Scheme 2 shows the reaction mechanism that describes the oxidation of cumene in the presence of a silane or n-Bu_3GeH which agrees with the following observations:

(i) Fate of $R'_3M^\bullet$ radical. Based on available kinetic data,[17,18] under our experimental conditions, $R'_3M^\bullet$ radicals should either add to the molecular oxygen or to the cumene to give the radical adducts **1** or **2**, respectively (Scheme 2). The reaction of

Initiation

Production of $R^\bullet$ at a rate = R_i

Propagation

$$R^\bullet + O_2 \xrightarrow{\text{fast}} ROO^\bullet$$

$$ROO^\bullet + RH \xrightarrow{k_p} ROOH + R^\bullet$$

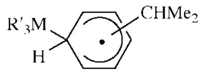
Termination

$$2\ ROO^\bullet \xrightarrow{2k_t} \text{non-radical products}$$

$$ROO^\bullet + R'_3MH \xrightarrow{k_H} ROOH + R'_3M^\bullet$$

$$R'_3M^\bullet + O_2 \xrightarrow{\text{fast}} \underset{\mathbf{1}}{R'_3MOO^\bullet}$$

$$R'_3M^\bullet + RH \xrightarrow{\text{fast}}$$



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$$(f-1)\ ROO^\bullet + \mathbf{1}\ \text{or}\ \mathbf{2} \xrightarrow{\text{fast}} \text{non-radical products}$$

R = $PhCMe_2$

Scheme 2

the cumyl peroxyl radical with these two radicals is much faster than its self-termination. Howard and co-workers have shown by EPR studies that $Ph_3SiOO^\bullet$ radicals decay by bimolecular rate

Table 2 Kinetic data for the reaction of cumylperoxyl radical with a variety of group 14 hydrides at 345.5 K

Substrate	$[2k_H/(2k_tR_i)^{\frac{1}{2}}]/M^{-1}$ [a]	$k_H/M^{-1}\ s^{-1}$
t-BuSi(H)Me$_2$	1.09 ± 0.26	0.10
PhSi(H)Me$_2$	2.28 ± 0.40	0.21
PhSiH$_3$	9.68 ± 1.20	0.90
Ph$_2$SiH$_2$	9.00 ± 0.48	0.84
Ph$_2$Si(H)Me	4.66 ± 0.48	0.43
Ph$_3$SiH	7.15 ± 0.58	0.67
5,10-Dihydrosilanthrene	77.7 ± 11.0	7.26
Poly(phenylsilane)	$(2.65 \pm 0.27) \times 10^2$ [b]	24.7 [b]
(TMS)$_3$SiH	$(7.10 \pm 0.47) \times 10^2$	66.3
n-Bu$_3$GeH	$(2.08 \pm 0.13) \times 10^2$	19.4
(TMS)$_3$GeH		4×10^3 [c]
n-Bu$_3$SnH		1.8×10^3 [c]
Ph$_3$SnH		4×10^3 [c]

[a] Obtained using method A. [b] Referring to each SiH moiety. [c] Obtained using method B.

constants of $1 \times 10^7\ M^{-1}\ s^{-1}$ (at 167 K) and $4.3 \times 10^7\ M^{-1}\ s^{-1}$ (at 218 K), respectively.[19] At 345.5 K, the cross-termination rate constant between the cumyl peroxyl and Ph$_3$SiOO$^•$ radicals is calculated[20] to be about two orders of magnitude larger than the self-termination of cumyl peroxyl radicals ($2k_t = 3.2 \times 10^4\ M^{-1}\ s^{-1}$).[21]

(ii) Formation of hydroperoxides. Thin layer chromatography (TLC: Kiesegal 60 F$_{254}$, Merck. Eluent: 1 : 1 toluene–ethyl acetate) of the reaction mixtures reveals the presence of Me$_2$C(OOH)CN ($R_f = 0.52$) and PhC(OOH)Me$_2$ ($R_f = 0.73$) as the only peroxide products. Since silyl peroxides are known to be stable products, we synthesised t-BuSi(OOH)Me$_2$ ($R_f = 0.66$) and PhSi(OOH)Me$_2$ ($R_f = 0.44$) by following the method of Dannley and Jalics[22] and used as a reference compounds in the TLC analysis. No detectable amounts (less than 0.001 M) of these hydroperoxides were observed in the corresponding oxidation runs we conclude that reaction (2) is not relevant in our

$$\mathrm{R'_3MOO^{\bullet} + PhCHMe_2 \longrightarrow R'_3MOOH + Ph\dot{C}Me_2} \quad (2)$$

experiments which is in agreement with the few data available in the literature on the reactivity of group 14 peroxyl radicals at temperatures above 233 K.[19,23]

The rate constant for H-atom abstraction from the various substrates by a cumylperoxyl radical can be determined by using the inhibited hydrocarbon oxidation methodology developed by Denisov.[24] Eqn. (3) shows the kinetic expression

$$\frac{(-\mathrm{d}[\mathrm{O_2}]/\mathrm{d}t)_0}{(-\mathrm{d}[\mathrm{O_2}]/\mathrm{d}t)} - \frac{(-\mathrm{d}[\mathrm{O_2}]/\mathrm{d}t)}{(-\mathrm{d}[\mathrm{O_2}]/\mathrm{d}t)_0} = \frac{fk_H[\mathrm{(TMS)_3SiH}]_0}{(2k_tR_i)^{1/2}} \quad (3)$$

for such reactions, where $(-\mathrm{d}[\mathrm{O_2}]/\mathrm{d}t)$ and $(-\mathrm{d}[\mathrm{O_2}]/\mathrm{d}t)_0$ represent the initial oxidation rate of cumene with or without a substrate. This relation can be used when the initial oxidation rate and the initiation rate remain essentially constant under the experimental conditions. The stoichiometric factor f which is the number of cumylperoxyl radicals trapped by each molecule of silane, is assumed to be equal to 2. This is possible if the termination reactions in Scheme 2 dominate in the systems and if the products of these reactions are not active towards initiation.

Fig. 1(b) shows the linear regression analysis of eqn. (3) for t-BuMe$_2$SiH and Ph$_2$SiH$_2$ whose slopes provide $2k_H/(2k_tR_i)^{1/2}$ to be (1.09 ± 0.26) and (9.00 ± 0.48) M^{-1}, respectively. In Table 2 the $2k_H/(2k_tR_i)^{1/2}$ values at 345.5 K are reported for all experiments. Since the rate of radical production[25] and the termination for cumylperoxyl radicals[21] are $R_i = 1.09 \times 10^{-6}\ M\ s^{-1}$ and $2k_t = 3.2 \times 10^4\ M^{-1}\ s^{-1}$, respectively, the rate constants k_H can be calculated. The results are also reported in Table 2.

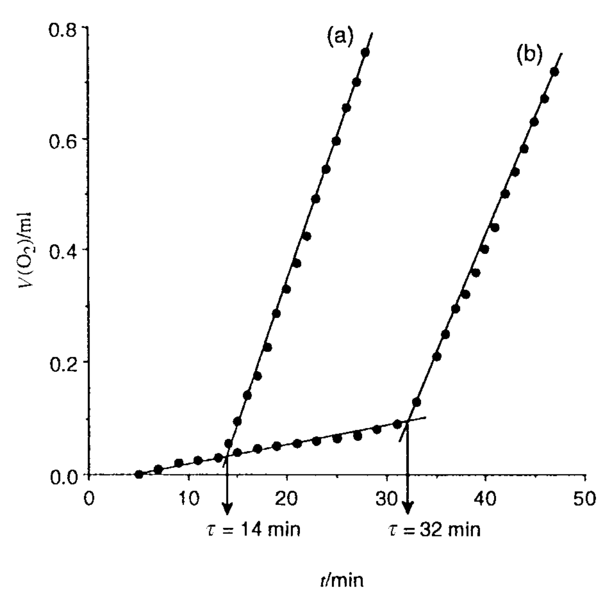


Fig. 2 Oxygen consumption during the AIBN-initiated (0.0179 M) oxidation of cumene in the presence of 1.07×10^{-3} M (a) and 6.40×10^{-3} M (b) of n-Bu$_3$SnH at 345.5 K.

Method B

The approach will be illustrated by the case of n-Bu$_3$SnH. The oxidation of pure cumene was thermally initiated (0.0172 M of AIBN at 345.5 K) and the volume of oxygen uptake, V(O$_2$), was measured over time in the presence of n-Bu$_3$SnH (concentration range of 1.07×10^{-3} to 6.40×10^{-3} M). In all cases the time profile exhibited an induction period (τ). Fig. 2 shows the dependence of V(O$_2$) *vs.* time in the presence of 1.64×10^{-3} and 6.40×10^{-3} M of n-Bu$_3$SnH.

Scheme 3 describes reasonably well the inhibition mechanism. The rate constant for the reaction of n-Bu$_3$Sn$^•$ with O$_2$ is reported to be $7.5 \times 10^9\ M^{-1}\ s^{-1}$ at 300 K.[18] The resulting adduct was shown by EPR spectroscopy to have an unusual structure with two magnetically equivalent oxygen atoms.[19] Howard and co-workers showed that the reactivity of stannyl peroxyl radicals is quite different from typical alkyl peroxyl radicals,[19] *i.e.*, they react more slowly in hydrogen abstraction and much faster in self-termination. Their results suggest that (i) the $2k_t$ for the cross-termination of cumyl and stannyl peroxyl radicals is about two orders of magnitude higher than the self-termination of cumyl peroxyl radicals and (ii) the reaction of stannyl peroxyl radicals with cumene is much slower than the analogous reaction of cumyl peroxyl radicals.

Initiation

Production of R$^•$ at a rate = R_i

Propagation

$$\mathrm{R^{\bullet} + O_2 \xrightarrow{fast} ROO^{\bullet}}$$

$$\mathrm{ROO^{\bullet} + RH \xrightarrow{k_p} ROOH + R^{\bullet}}$$

Termination

$$\mathrm{ROO^{\bullet} + R'_3SnH \xrightarrow{k_H} ROOH + R'_3Sn^{\bullet}}$$

$$\mathrm{R'_3Sn^{\bullet} + O_2 \xrightarrow{fast} R'_3SnOO^{\bullet}}$$

$$(f-1)\ \mathrm{ROO^{\bullet} + R'_3SnOO^{\bullet} \xrightarrow{fast}}\ \text{non-radical products}$$

R = PhCMe$_2$

Scheme 3

Table 3 Kinetic data for the oxidation of cumene in the presence of n-Bu_3SnH[a]

$(-d[O_2]/dt)^b$/ 10^{-6} M s^{-1}	[n-$Bu_3SnH]_0$/ 10^{-3} M	v	τ/min	f
10.94	1.07	11.8	10	0.52
7.01	1.64	7.5	14	0.48
3.15	2.64	3.4	21	0.44
4.67	3.20	5.0	20	0.35
1.74	6.40	1.9	32	0.28

[a] [AiBN) = 0.0179 M, $R_i = 0.93 \times 10^{-6}$ M s^{-1} at 345.5 K. [b] $(-d[O_2]/dt) = (-d[O_2]/dt)_{exp} - R_i$; see text.

Based on the mechanism in Scheme 3, the initial rate of oxidation (before exiting from the induction period), is given by eqn. (4) where the [n-$Bu_3SnH]_0$ is the initial concentration and

$$(-d[O_2]/dt) = \frac{k_p[RH]_0R_i}{fk_H[n\text{-}Bu_3SnH]_0} \qquad (4)$$

f is the number of peroxyl radicals trapped by each molecule of n-Bu_3SnH.[26] The use of Boozer *et al.*'s induction period method[27] of which two examples are illustrated in Fig. 2 (*i.e.* suppression of the oxygen uptake by the presence of n-Bu_3SnH) allows the determination of the τ values. The stoichiometric factor f can then be obtained from $f = R_i\tau/[n\text{-}Bu_3SnH]_0$.[24,26] Since the chain length of oxidation (*i.e.* $v = (-d[O_2]/dt)_{exp}/R_i$) is less than 12, the initial rate of oxidation is corrected for oxygen absorption by the initiator, and nitrogen evolution from the initiator, *i.e.* $(-d[O_2]/dt) = (-d[O_2]/dt)_{exp} - R_i$, where the $(-d[O_2]/dt)_{exp}$ is the experimental initial rate of cumene oxidation. All the data are summarized in Table 3.

From the slope of the plot $(-d[O_2]/dt)$ *vs.* $1/[n\text{-}Bu_3SnH]_0$, $k_p[RH]_0R_i/fk_H = (11.6 \pm 1.5) \times 10^{-9}$ M^2 s^{-1} according to eqn. (4). Taking $k_p = 1.3$ M^{-1} s^{-1},[21] $[RH]_0 = 7.188$ M, $R_i = 0.93 \times 10^{-6}$ Ms^{-1},[25] and an average of $f = 0.42$, we calculated $k_H = 1.8 \times 10^3$ M^{-1} s^{-1} at 345.5 K.‡ Alternatively, the rate constant (k_H) can be calculated for each entry of Table 4 using eqn. (4) and the corresponding f value. The average of the five different experiments gave $k_H = (1.98 \pm 0.56) \times 10^3$ M^{-1} s^{-1}.

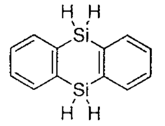
Similar experiments were performed for Ph_3SnH and $(TMS)_3GeH$. However, the experiments for these compounds were limited due to the low observed chain length ($v \leq 4$) even at a low hydride concentration. Therefore, the average rate constants of 4×10^3 M^{-1} s^{-1} calculated for both Ph_3SnH and $(TMS)_3GeH$ should be considered approximate values.

Discussion

The difference of the two methods described above (Schemes 2 and 3, respectively) is based on the rapidity of hydrogen abstraction from the group 14 hydrides by cumylperoxyl radicals. In method A the hydrogen abstraction step is in competition with the termination of cumylperoxyl radicals whereas in Method B this latter reaction is unimportant due to the presence of a better hydrogen donor.

The rate constants for the reaction of cumylperoxyl radicals with group 14 hydrides are reported in Table 2. The previous data available from Howard† for Et_3SiH and Ph_3GeH with t-$BuOO^•$ are of the same order of magnitude although not directly comparable. The trends in reactivity are similar to those observed for other radicals with group 14 hydrides, although the reactions are several orders of magnitude slower.

Specifically, in the silane series, the rate constant increases two times with the substitution of an alkyl group by a phenyl group. The rate constants also increase along the series $PhSi(H)Me_2 < Ph_2Si(H)Me < Ph_3SiH$ and $PhSiH_3 < Ph_2SiH_2 < Ph_3SiH$ when taking into account the statistical number of reactive hydrogen. The rate constant increases about 1 order of magnitude in comparing Ph_2SiH_2 to 5,10-dihydrosilanthrene (**3**). Similar trends were also observed for the reaction of primary and secondary alkyl radicals.[17] The enhancement in the reactivity of silanthrene **3** was previously attributed to the stabilization of the silyl radical induced either by a transannular interaction of the vicinal Si substituent or by the quasiplanar arrangement of the radical center.[28] Moreover, the rate constant increases substantially with substitution of methyl by silyl groups at the SiH function. In comparing $PhSi(H)Me_2$ to each SiH moiety of poly(phenylsilane) (**4**) and t-$BuSi(H)Me_2$ with $(TMS)_3SiH$, an increase of 2–3 orders of magnitude is observed. A similar increase in reactivity is observed in the germanium series upon substitution of n-Bu by silyl groups. Comparison of reactivity of group 14 hydrides, shows that the rate constant increases along the series t-$BuSi(H)Me_2 < n$-$Bu_3GeH < (TMS)_3SiH < n$-Bu_3SnH, the relative rate constants being 1:194:663:18000. The trends just outlined can be entirely attributed to more favorable thermodynamic factors along the series. In fact, the bond dissociation energies of Et_3Si–H, n-Bu_3Ge–H, $(TMS)_3Si$–H and n-Bu_3Sn–H are 95.1, 88.6, 84.0 and 78.6 kcal mol^{-1}, respectively.[29,39]



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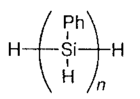

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The reactivity of the $PhC(Me_2)OO^•$ radical is compared with the reactivity of three other radicals in Table 4. For the $(CF_3)_2NO^•$ and $RCH_2^•$ radicals the rate constants are given at the same temperature whereas for the $Me_3CO^•$ radical the temperature is given at *ca.* 300 K. The bond dissociation energies associated with these radicals are $D[CH_3OO$–$H] = 88.5 \pm 1.0$,[40] $D[(CF_3)_2NO$–$H] = 85.3 \pm 3.0$,[16] $D[RCH_2$–$H] = 101.1 \pm 1.0$,[41] $D[Me_3CO$–$H] = 105.1 \pm 1.0$ kcal mol^{-1}.[42] The similar reactivity of $(CF_3)_2NO^•$ and the peroxyl radicals towards a large variety of substrates was previously observed and attributed to rather similar thermochemistries and spin distributions for these two radicals.[16] Table 4 shows that this similarity is extended to group 14 hydrides. With the $RCH_2^•$ and $Me_3CO^•$ radicals the reactions become more exothermic and about 4 and 7 orders of magnitude faster, respectively, although the trends in reactivities are similar. Furthermore, the anticipated decrease in the difference of the rate constants for the group 14 hydrides as the reaction becomes faster is also observed. For example, the $PhC(Me_2)OO^•$, $RC(^•)O$,[43] $RCH_2^•$ and $Me_3CO^•$ radicals abstract hydrogen from the $(TMS)_3SiH$ respectively 27, 16, 5 and 2 times slower than from the Bu_3SnH mainly due to the *ca.* 5 kcal mol^{-1} difference in bond dissociation energies.

Experimental

Materials

All the group 14 hydrides were commercially available from Fluka or Aldrich and used as received, with the exception of dimethylphenylsilane, which was purified from the phenol (*ca.* 1 mM content) by dissolving it in diethyl ether, followed by treatment with 1 M NaOH, drying over anhydrous sodium sulfate and distillation. t-$BuSi(OOH)Me_2$,[22] $PhSi(OOH)Me_2$,[22] 5,10-dihydrosilanthrane[28] and poly(phenylsilane)[44] were pre-

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‡ Based on Scheme 3, the stoichiometric factor f should be equal to 2 (the number of cumyl peroxyl radicals trapped). The difference is probably due to the presence of secondary processes. In similar situations, some authors assume $f = 2$ for calculating the rate constant. This analysis will give a rate constant five time slower.

Table 4 Comparison of rate constants for hydrogen abstraction from a variety of group 14 hydrides by some radicals

	k/M^{-1} s^{-1}			
Hydride	PhC(Me$_2$)OO$^{\bullet}$ at 345.5 K [a]	(CF$_3$)$_2$NO$^{\bullet}$ at 345.5 K [b]	RCH$_2^{\bullet}$ at 345.5 K	Me$_3$CO$^{\bullet}$ at ~300 K
(Alkyl)$_3$SiH	0.10	4.3	2.5×10^{3} [c,d]	4.6×10^{6} [c,e]
Ph$_3$SiH	0.67	—	4.6×10^{4} [f]	1.1×10^{7} [g]
(TMS)$_3$SiH	66.3	—	1.1×10^{6} [h]	1.1×10^{8} [i]
n-Bu$_3$GeH	19.4	2.5×10^{2}	2.6×10^{5} [j]	9.2×10^{7} [e]
(TMS)$_3$GeH	4×10^{3}	—	1.9×10^{7} [k]	—
n-Bu$_3$SnH	1.8×10^{3}	1.5×10^{3}	5.4×10^{6} [l]	2.0×10^{8} [g]
Ph$_3$SnH	4×10^{3}	—	1.6×10^{7} [m]	4.2×10^{8} [g]

[a] This work. [b] From ref. 16. [c] Corrected value referring to attack at the SiH moiety. [d] From ref. 30. [e] From ref. 31. [f] At 383 K; from ref. 32. [g] From ref. 33. [h] From ref. 34. [i] From ref. 35. [j] From ref. 36. [k] At 323 K; from ref. 37. [l] From ref. 38. [m] From ref. 39.

pared according to literature methods. GPC analysis of the poly(phenylsilane) showed a typical bimodal distribution with 15% low molecular weight and 85% high molecular weight peaks ($M_w = 2010$, $M_w/M_n = 1.85$ against a polystyrene standard).[45] Cumene was purified by successive washings with 95% aq. H_2SO_4 (10:1, v/v; several times), water, 10% aq. NaOH, water, 0.1 M $KMnO_4$, water, followed by anhydrification over calcium chloride and distillation.

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