

The mechanism of polarity-reversal catalysis as involved in the radical-chain reduction of alkyl halides using the silane–thiol couple

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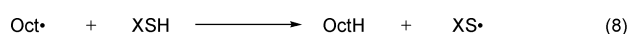
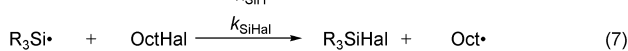
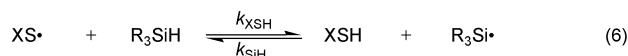
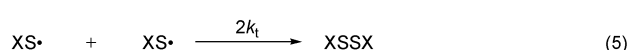
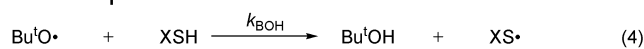
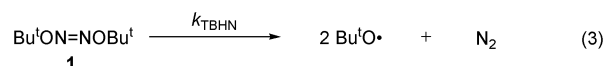
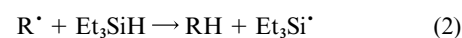
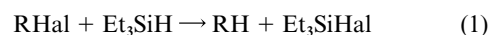
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The mechanism by which thiols promote the radical-chain reduction of alkyl halides by a variety of simple silanes, such as Et_3SiH and Ph_3SiH , has been investigated in detail. Kinetic studies of the thiol-catalysed reduction of 1-bromooctane and of 1-chlorooctane by Et_3SiH in cyclohexane at 60 °C are consistent with a mechanism that involves reversible abstraction of hydrogen by the thiyl radical from the silane, followed by abstraction of halogen from the octyl halide by the resulting triethylsilyl radical and quenching of the derived octyl radical by the thiol to give octane. On the basis of this mechanism, rate constants for abstraction of hydrogen from Et_3SiH by the adamantane-1-thiyl radical (k_{XSH}) and for transfer of hydrogen in the reverse direction (k_{SiH}) were determined as $3.2 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ and $5.2 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$, respectively, at 60 °C. The equilibrium constant $k_{\text{XSH}}/k_{\text{SiH}}$ is thus 6.2×10^{-4} at 60 °C and corresponds to $\Delta_r H \approx \Delta_r G = +20.4 \text{ kJ mol}^{-1}$ for abstraction of hydrogen from Et_3SiH by 1-AdS \cdot , implying that the Si–H bond in the silane is stronger by *ca.* 20 kJ mol $^{-1}$ than the S–H bond in the alkanethiol. The silanethiol $(\text{Bu}^t\text{O})_3\text{SiSH}$ was found to be a more effective catalyst than 1-AdSH, because k_{XSH} is greater ($1.3 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$) while k_{SiH} is very similar ($5.1 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$). The value of $k_{\text{XSH}}/k_{\text{SiH}}$ is now 2.6×10^{-3} at 60 °C and thus the S–H bond in this silanethiol is stronger by *ca.* 4 kJ mol $^{-1}$ than that in 1-AdSH. The proposed mechanism for alkyl halide reduction is strongly supported by kinetic studies of the thiol-catalysed H/D-exchange between $\text{R}_3\text{SiH/D}$ and XSH/D and the thiol-catalysed racemisation of (*S*)- $\text{Bu}^t\text{MePhSiH}$, radical-chain processes that provide independent confirmation of the values of k_{XSH} derived from octyl bromide reduction. The value of $\Delta_r H$ determined in this work indicates that abstraction of hydrogen from Et_3SiH by an alkanethiyl radical in cyclohexane solvent is *ca.* 11 kJ mol $^{-1}$ less endothermic than implied by the difference in the currently-favoured experimental gas-phase dissociation enthalpies for the $\text{Et}_3\text{Si-H}$ and MeS-H bonds.

In 1989, we reported that thiols efficiently catalyse the radical-chain reduction of alkyl halides at 60–80 °C to give the corresponding alkanes, using triethylsilane or triphenylsilane as the stoichiometric reductant [e.g. eqn. (1)].¹ This preliminary work was subsequently extended and described in detail in a full paper² which appeared in 1991 and, over the succeeding 10 years, we demonstrated that simple silanes in combination with a thiol catalyst can often be used as an effective replacement for tributyltin hydride in several types of radical-chain reaction that are of importance in organic synthesis.³ The thiol was viewed as fulfilling the role of a *protic polarity-reversal catalyst*,^{1–3} that acts to promote the overall transfer of an electron-rich hydrogen atom from the silane to the nucleophilic chain-carrying alkyl radical [e.g. eqn. (2)], a reaction that is relatively slow in the absence of a catalyst.⁴ The proposed mechanism for the thiol-catalysed process is illustrated in Scheme 1 for the reduction of a 1-halogenooctane, in the presence of di-*tert*-butyl hyponitrite⁵ (TBHN **1**) as a thermal source of initiating *tert*-butoxyl radicals. † Under such conditions, it is likely that the predominant chain-terminating reaction will be that between pairs of thiyl radicals to give mainly disulfide [eqn. (5)] and the propagation cycle is shown in eqns. (6–8), Scheme 1.

At the time of our initial work,^{1,2} the available experimental values for the $\text{Et}_3\text{Si-H}$ and MeS-H bond dissociation



Scheme 1

enthalpies (BDEs) were 377 and 384 kJ mol $^{-1}$, respectively, implying that the reversible hydrogen-atom transfer reaction (6) will be exothermic by 7 kJ mol $^{-1}$ in the forward direction when X = Me and R = Et. However, since that time these values have been revised and the currently favoured^{8,9} experimental BDEs are $397 \pm 2 \text{ kJ mol}^{-1}$ for $\text{Et}_3\text{Si-H}$ (assumed to be the same as that¹⁰ for $\text{Me}_3\text{Si-H}$) and $366 \pm 2 \text{ kJ mol}^{-1}$ for MeS-H .¹¹ The abstraction of hydrogen from triethylsilane by the methanethiyl radical would then become *endothermic* by $31 \pm 4 \text{ kJ mol}^{-1}$. This more recent value of $\Delta_r H$ for hydrogen-atom transfer from Et_3SiH to MeS^\cdot is in accord with the calculations of Schiesser

† It is possible that overall abstraction of hydrogen by $\text{Bu}^t\text{O}^\cdot$ from the thiol [eqn. (4), Scheme 1] could take place in part, or even in whole, by an addition elimination pathway involving initial formation of an intermediate sulfanyl radical adduct $\text{XS}^\cdot(\text{H})\text{OBu}^t$.^{6,7}

Table 1 Reduction of 1-bromooctane by silanes catalysed by thiols in cyclohexane solvent at 60 °C^a; determination of k_{XSH}

Entry	Silane	Thiol	[OctBr] ₀ /M	[R ₃ SiH] ₀ /M	[XSH] ₀ /M	[TBHN] ₀ /M	$k_{\text{XSH}}^b/M^{-1} s^{-1}$
1	Et ₃ SiH	1-AdSH	0.38	0.50	0.025	0.025	3.5×10^4
2	Et ₃ SiH	1-AdSH	0.38	0.25	0.025	0.025	3.3×10^4
3	Et ₃ SiH	1-AdSH	0.19	0.50	0.025	0.025	3.0×10^4
4	Et ₃ SiH	1-AdSH	0.38	0.50	0.0125	0.025	3.3×10^4
5	Et ₃ SiH	1-AdSH	0.38	0.50	0.025	0.0125	3.0×10^4
6	Et ₃ SiH	<i>t</i> -C ₁₂ H ₂₅ SH	0.38	0.50	0.025	0.0125	3.5×10^4
7	Et ₃ SiH	Ph ₃ SiSH	0.38	0.50	0.025	0.0125	4.3×10^4
8	Et ₃ SiH	Bu ^t MePhSiSH ^c	0.38	0.50	0.025	0.0125	4.1×10^4
9	Et ₃ SiH	(Bu ^t O) ₃ SiSH	0.19	0.125	0.0125	0.0125	1.3×10^5
10	Et ₃ SiH	Pr ¹ SiSH	0.19	0.125	0.0125	0.0125	1.6×10^5
11	Bu ^t MePhSiH ^c	1-AdSH	0.27	0.54	0.0135	0.0135	3.4×10^4
12	Ph ₃ SiH	1-AdSH	0.38	0.50	0.025	0.0125	7.5×10^4
13	Ph ₃ SiH	Ph ₃ SiSH	0.38	0.50	0.025	0.0125	8.8×10^4

^a A subscript 0 indicates a value at $t = 0$. ^b Evaluated using eqn. (15). ^c Racemic compound.

and Skidmore^{12,13} who reported that, at the highest level of theory they applied, abstraction of hydrogen by MeS[•] from the Si–H group of trimethylsilane is endothermic by 30.8 kJ mol⁻¹. The energy barrier associated with this H-atom transfer, which was believed to take place in a single step *via* a transition state of the type [MeS...H...SiMe₃][‡], was calculated to be 41.9 kJ mol⁻¹. Schiesser and Skidmore concluded¹³ that the “equilibrium constant” (*i.e.* $k_{\text{XSH}}/k_{\text{SiH}}$) for reaction (6) would be “in all likelihood too small to sustain the radical chain” depicted in Scheme 1, at least when both X and R are simple alkyl groups. Furthermore, these authors stated that their “computational data have distinct significance and may require that the synthetically useful chemistry developed by Roberts be mechanistically re-examined”. Although Schiesser and Skidmore believed that the *equilibrium constant* for reaction (6) was of critical importance in determining the efficiency of thiol catalysis, they omitted to compare their computed value of $\Delta_r H$ with the difference in the contemporary experimental values of the MeS–H and Me₃Si–H BDEs. Both we³ and Zavitsas¹⁴ have highlighted the mechanistic problem that arises if the Si–H bond in a simple trialkylsilane is indeed stronger by >30 kJ mol⁻¹ than the S–H bond in an alkanethiol, but we have also stressed that if this difference were to be 10–20 kJ mol⁻¹ there would then be no difficulty in accepting the mechanism shown in Scheme 1. We have also noted that mechanistic complications might arise if conversion of an alkanethiol to a silanethiol were to take place under the reaction conditions.³

In the present paper we re-examine the use of thiols to promote the reduction of alkyl halides by simple silanes and explore the detailed mechanism of thiol catalysis. In order to probe reaction (6) in isolation, thiol-catalysed hydrogen-deuterium exchange in the systems R₃SiH + XSD and R₃SiD + XSH has been investigated and the thiol-catalysed radical-chain racemisation of enantiomerically-pure (*S*)-Bu^tMePhSiH has also been examined. The related racemisation of (*R*)-tetrahydrofurfuryl acetate, where a thiol catalyst likewise mediates the transfer of hydrogen between two nucleophilic radicals, has been reported previously.¹⁵

Results and discussion

Reduction of alkyl halides

Thiol-catalysed reduction of 1-halogenooctanes (Hal = Br, Cl, I) by triorganosilanes in cyclohexane at 60 °C was monitored as a function of time by GLC analysis of the reaction mixtures, using nonane as an internal concentration standard; TBHN was used as initiator throughout. All experiments were conducted under an atmosphere of dry argon, using freshly dried solvents and purified reagents, and these precautions proved to be essential in order to obtain reproducible results. The reduction of 1-bromooctane by Et₃SiH or Ph₃SiH was carried out

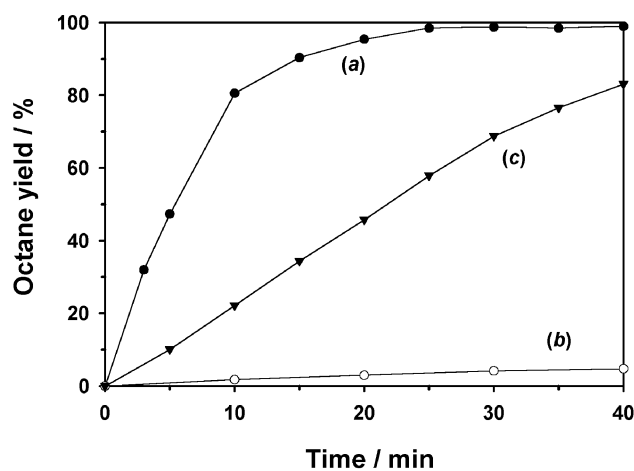


Fig. 1 The reduction of octyl halides by triethylsilane at 60 °C in cyclohexane. The initial reagent concentrations were: (a) [OctBr] 0.38 M, [Et₃SiH] 0.50 M, [TBHN] 0.025 M and [1-AdSH] 0.025 M; (b) as (a) but without thiol; (c) [OctCl] 0.19 M, [Et₃SiH] 1.00 M, [TBHN] 0.025 M and [1-AdSH] 0.050 M. Data points are joined with straight lines.

using different thiol catalysts and the results are summarised in Table 1. Adamantane-1-thiol (1-AdSH) was chosen as the principal alkanethiol catalyst, although *tert*-dodecanethiol[‡] and dodecane-1-thiol were also examined. A number of silanethiols were also quantitatively evaluated as promoters of alkyl halide reduction, because we have previously found qualitative evidence that these compounds are more effective protic polarity-reversal catalysts than the alkanethiols.³ A representative reduction of 1-bromooctane in the presence and absence of thiol is illustrated in Fig. 1 and the experimental evidence for the effectiveness of thiol catalysis is unequivocal. In this experiment at 60 °C, the initial rate of reduction of 1-bromooctane by Et₃SiH was about 50 times greater in the presence of 5 mol% 1-AdSH (based on silane) than in its absence.

The primary alkanethiol dodecane-1-thiol was a less effective catalyst for alkyl halide reduction than adamantane-1-thiol or *tert*-dodecanethiol. With the primary thiol, reaction rates were often irreproducible and the reduction sometimes stopped well short of completion. We believe that this behaviour may be associated with the higher heterolytic reactivity of the less hindered primary thiol, in conjunction with the ease of nucleophilic substitution at silicon in the halogenosilanes formed as reaction products. The influence of adventitious moisture on the success of reductions catalysed by primary

[‡] This compound is an isomeric mixture of tertiary alkanethiols C₁₂H₂₅SH, as obtained from the Aldrich Chemical Company, and is thus less well defined chemically than 1-AdSH. However, *tert*-dodecanethiol serves as a readily available, relatively malodorous, tertiary alkanethiol for use in preparative work.

Table 2 Reduction of 1-chlorooctane by triethylsilane catalysed by thiols in cyclohexane solvent at 60 °C^a; determination of k_{SiH}

Entry	Thiol	[XSH] ₀ /M	{d[OctH]/dt} ₀ /M s ⁻¹	k_{SiH} ^b /M ⁻¹ s ⁻¹
1	1-AdSH	0.050	7.65×10^{-5}	4.9×10^7 ^c
2	1-AdSH	0.060	6.06×10^{-5}	5.2×10^7 ^c
3	1-AdSH	0.075	4.84×10^{-5}	5.3×10^7 ^c
4	1-AdSH	0.100	3.51×10^{-5}	5.5×10^7 ^c
5	(Bu ^t O) ₃ SiSH	0.050	2.20×10^{-4}	7.1×10^7 ^d
6	(Bu ^t O) ₃ SiSH	0.100	1.49×10^{-4}	5.3×10^7 ^d
7	(Bu ^t O) ₃ SiSH	0.200	1.03×10^{-4}	3.8×10^7 ^d
8	(Bu ^t O) ₃ SiSH	0.300	6.11×10^{-5}	4.4×10^7 ^d

^a In all reactions [OctCl]₀ = 0.19 M, [Et₃SiH]₀ = 1.00 M and [TBHN]₀ = 0.025 M; R_i was taken to be 1.75×10^{-5} M s⁻¹ in all experiments. ^b Calculated using eqn. (11), taking $2k_t = 9.0 \times 10^9$ M⁻¹ s⁻¹ and $k_{\text{SiHal}} = 7.4 \times 10^5$ M⁻¹ s⁻¹. ^c Taking $k_{\text{XSH}} = 3.2 \times 10^4$ M⁻¹ s⁻¹. ^d Taking $k_{\text{XSH}} = 1.3 \times 10^5$ M⁻¹ s⁻¹.

thiols also appeared to be much more deleterious than when the reduction was promoted by a more bulky tertiary alkanethiol. However, even using a tertiary alkanethiol as catalyst, the reduction of 1-iodooctane by triethylsilane in cyclohexane at 60 °C was irreproducible, often unexpectedly slow and did not proceed to completion. In addition to the high heterolytic reactivity of iodasilanes, we ascribe these problems to the formation of small amounts of hydrogen iodide and iodine, arising from traces of moisture and oxygen entering the reaction mixture (especially during the sampling procedure), leading to inhibition of the chain process. In support of this explanation, the samples usually developed a very pale yellow–brown coloration soon after the start of the reaction. However, in agreement with our previous report,² we have confirmed that 1-iodooctane is rapidly and completely reduced by triethylsilane in the presence of TBHN and adamantane-1-thiol when the reaction is carried out in refluxing hexane (bp 69 °C) and without the removal of samples to monitor the progress of the reduction. We suggest that this difference arises not only because of the greater rate of initiation at the higher reaction temperature, but also because the refluxing solvent effectively protects the reaction mixture from traces of moisture and oxygen and also drives any iodine out of solution. Because of these difficulties, our quantitative kinetic studies were restricted to the reduction of 1-bromooctane and 1-chlorooctane. In general, alkyl chlorides are reduced less readily than bromides by the silane–thiol couple (see Fig. 1).² The rate of reduction of 1-chlorooctane by triethylsilane, catalysed by 1-AdSH or *tert*-butoxysilanethiol, was followed at 60 °C as a function of thiol concentration and these results are summarised in Table 2.

Kinetic analysis based on Scheme 1

The self- and cross-termination reactions between the various reactive radicals present in the system would be expected to have similar (diffusion-controlled) rate constants.¹⁶ Since k_{SiH} is undoubtedly significantly greater than k_{XSH} (see later), and silyl radicals are also exchanged irreversibly for octyl radicals by their reaction with the alkyl halide [eqn. (7), Scheme 1], it follows that the steady-state concentration of XS[•] will be much greater than that of R₃Si[•]. Because the octyl radical reacts rapidly and irreversibly with XSH, its steady-state concentration will also be very low in relation to [XS[•]] and thus it is safe to conclude that the dominant termination reaction will take place between pairs of thiol radicals [eqn. (5), Scheme 1]. At the steady state, eqn. (9) will hold and the concentration of XS[•] will be given by eqn. (10), where R_i is the rate of production of *tert*-butoxyl radicals (taken as equal to the rate of production of thiol radicals). The rate of formation of octane will then be given by eqn. (11).

$$\frac{d[\text{XS}^{\bullet}]}{dt} = 0 = R_i - 2k_t[\text{XS}^{\bullet}]^2 \quad (9)$$

$$[\text{XS}^{\bullet}] = (R_i/2k_t)^{1/2} \quad (10)$$

$$\frac{d[\text{OctH}]}{dt} = \frac{k_{\text{XSH}}k_{\text{SiHal}}(R_i/2k_t)^{1/2}[\text{OctHal}][\text{R}_3\text{SiH}]}{k_{\text{SiH}}[\text{XSH}] + k_{\text{SiHal}}[\text{OctHal}]} \quad (11)$$

For the rate of octane production to depend in a straightforward way on the magnitude of the equilibrium constant ($k_{\text{XSH}}/k_{\text{SiH}}$) for reaction (6), as suggested by Schiesser and Skidmore,^{12,13} it would be necessary for equilibrium to be established between R₃Si[•] and XS[•]. In fact, if $k_{\text{SiHal}}[\text{OctHal}]$ is much greater than $k_{\text{SiH}}[\text{XSH}]$ then the only fate of the silyl radical will be to abstract halogen from OctHal. Eqn. (11) then reduces to eqn. (12) and the rate of reduction becomes effectively independent of k_{SiH} . Rate constants for abstraction of halogen by triethylsilyl radicals from primary alkyl halides are available from the literature¹⁷ and at 60 °C are approximately 7.4×10^5 , 6.8×10^8 and 5.5×10^9 M⁻¹ s⁻¹ for chlorides, bromides and iodides, respectively. Rate constants for abstraction of hydrogen from thiols by silyl radicals have not been reported in the literature, but the rate constant for hydrogen-atom transfer from Bu^tSH to a primary alkyl radical is reported to be *ca.* 1.1×10^7 M⁻¹ s⁻¹ at 60 °C.¹⁹ Although the corresponding transfer of hydrogen to a triethylsilyl radical will be somewhat less exothermic, polar effects will be more favourable,³ and thus it seems likely that k_{SiH} should be in the range 10^7 – 10^8 M⁻¹ s⁻¹ at 60 °C, as confirmed by the present work (see later). The calculations of Schiesser and Skidmore¹³ suggest that the activation energy for hydrogen-atom transfer from MeSH to Me₃Si[•] is about 11 kJ mol⁻¹, which would imply that k_{SiH} is *ca.* 2×10^7 M⁻¹ s⁻¹ at 60 °C, if an *A*-factor of $10^{9.0}$ M⁻¹ s⁻¹ is assumed. In our experiments, at the start of the reaction, the value of [OctHal]/[XSH] was 8–30 for OctBr and 0.6–4 for OctCl and thus the condition that $k_{\text{SiHal}}[\text{OctHal}] \gg k_{\text{SiH}}[\text{XSH}]$ will be met for the reduction of the bromide, but not for reduction of the chloride. It would be met for iodide reduction under most experimental conditions.

$$\frac{d[\text{OctH}]}{dt} = (R_i/2k_t)^{1/2}k_{\text{XSH}}[\text{R}_3\text{SiH}] \quad (12)$$

Only when $k_{\text{SiHal}}[\text{OctHal}]$ can be neglected in relation to $k_{\text{SiH}}[\text{XSH}]$ does eqn. (11) reduce to eqn. (13) and the rate of octane formation then becomes directly proportional to ($k_{\text{XSH}}/k_{\text{SiH}}$), as implied by Schiesser and Skidmore in the analysis of their computational data.^{12,13} Thus, when $k_{\text{SiHal}}[\text{OctHal}]$ is less than or comparable to $k_{\text{SiH}}[\text{XSH}]$, as will be the situation for the reduction of 1-chlorooctane under our conditions, the value of

$$\frac{d[\text{OctH}]}{dt} = \frac{k_{\text{XSH}}k_{\text{SiHal}}(R_i/2k_t)^{1/2}[\text{OctHal}][\text{R}_3\text{SiH}]}{k_{\text{SiH}}[\text{XSH}]} \quad (13)$$

§ The rate constants reported in ref. 18 for halogen abstraction from 1-chlorobutane and from 1-bromobutane are remarkably consistent with the results obtained by Chatgialiloglu *et al.*¹⁷ for halogen abstraction from other primary alkyl halides.

k_{XSH} derived from the reduction of 1-bromooctane can be used in conjunction with eqn. (11) to obtain an estimate of k_{SiH} .

The rate constants k_{TBHN} for unimolecular decomposition of TBHN [eqn. (3), Scheme 1] have been measured by Kiefer and Traylor^{5a} over a range of temperatures in isooctane and values of 1.3×10^{-5} , 5.4×10^{-5} and $2.1 \times 10^{-4} \text{ s}^{-1}$ at 40, 50 and 60 °C, respectively, can be calculated from their data. This decomposition yields mainly free *tert*-butoxyl radicals, although there is reportedly a small amount of geminate cage combination to give Bu'OOBu'.^{5a} The operational values of k_{TBHN} adopted here (which refer to the rate of production of initiating *tert*-butoxyl radicals) are those determined by direct NMR spectroscopic measurement of the rate of formation of Bu'OH during the decomposition of TBHN in the presence of a thiol and a silane, as described below, using eqn. (14). ¶ The average values of k_{TBHN} determined in this way were 1.6×10^{-5} , 7.8×10^{-5} and $3.5 \times 10^{-4} \text{ s}^{-1}$ at 40, 50 and 60 °C, respectively, in very satisfactory agreement with the values obtained from the data of Kiefer and Traylor, considering the different conditions and the widely differing experimental methods employed.

$$\frac{d[\text{Bu}'\text{OH}]}{dt} = R_i = 2k_{\text{TBHN}}[\text{TBHN}] \quad (14)$$

Treatment of kinetic data

By considering only the initial stages of the reductions, it may be assumed that the rate of initiation is effectively constant. With the further assumption that $[\text{R}_3\text{SiH}] = [\text{R}_3\text{SiH}]_0 - [\text{OctH}]$, where $[\text{R}_3\text{SiH}]_0$ is the initial concentration of silane, integration of eqn. (12) gives eqn. (15). Thus, k_{XSH} may be determined from the initial slope of a plot of $\ln\{1 - [\text{OctH}]/[\text{R}_3\text{SiH}]_0\}$ against time. In order to apply eqn. (11) to the reduction of 1-chlorooctane, initial reaction rates obtained by manually drawing tangents to concentration *versus* time curves (e.g. Fig. 1c) at $t = 0$ were used in order to simplify the kinetic treatment. In some experiments, short induction periods were observed and the 'initial' rate measurements then refer to those made immediately after the onset of uninhibited reduction.

$$\ln\{1 - [\text{OctH}]/[\text{R}_3\text{SiH}]_0\} = -(R_i/2k_t)^{1/2}k_{\text{XSH}}t \quad (15)$$

The absolute values of the rate constants k_{XSH} and k_{SiH} determined using eqns. (11) and (15) obviously depend on the choice of $2k_t$ for the self-reaction of the relevant thiyl radical. This type of radical-radical reaction is expected to occur at close-to the diffusion-controlled rate in solution,^{16,23–25} with a rate constant that is essentially independent of the nature of the radical, and thus it is reasonable to assume that $2k_t$ is the same for all the thiyl radicals studied. Furthermore, the absolute values of k_{XSH} and k_{SiH} depend only on the *square root* of $2k_t$ and are thus relatively insensitive to changes in the value of this termination rate constant. The value of $2k_t$ for PhS' in cyclohexane has been recently determined to be $5.9 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ at

¶ It is possible that *tert*-butoxyl radicals will abstract hydrogen competitively from the silane^{20,21} and the thiol, rather than exclusively from the latter. The rate constant for hydrogen-atom transfer to Bu'O' from triethylsilane (extrapolated to 60 °C) is $9.1 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ and abstraction takes place mainly (ca. 80%) from the Si–H group.²¹ The rate constant for hydrogen abstraction from triphenylsilane²¹ is similar (ca. $1.4 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ at 60 °C) and presumably reaction now takes place exclusively at the Si–H group. Rate constants for the abstraction of hydrogen from thiols by Bu'O' have not been determined. Although, as noted previously, this reaction could proceed *via* an intermediate sulfonyl radical adduct, overall H-atom transfer is likely to be extremely rapid. The rate constant for overall transfer of hydrogen from Bu'SH to a dialkylaminy radical is reported to be ca. $10^7 \text{ M}^{-1} \text{ s}^{-1}$ at 60 °C,²² and abstraction by Bu'O' will be much more exothermic. In any case, provided termination takes place essentially only by self-reaction of thiyl radicals, any competing reaction of Bu'O' with the silane is not kinetically significant and eqn. (10) remains valid, since radicals derived from the silane will be subsequently converted to XS' in the presence of thiol.

25 °C.²⁴ Scaling this to 60 °C, using an Arrhenius *A*-factor of $10^{11.69} \text{ M}^{-1} \text{ s}^{-1}$ as determined by Schuh and Fischer²⁵ for the diffusion-controlled self-reaction of *tert*-butyl radicals in heptane, gives $2k_t(\text{PhS}') = 9.4 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$. The Arrhenius function for the self-reaction of *tert*-butyl radicals gives $2k_t(\text{Bu}'\text{t}') = 1.3 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ at 60 °C in heptane and thus it is reasonable to assume a termination rate constant of $9.0 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ at 60 °C for all the thiyl radicals studied in the present work; the corresponding rate constants at 40 and 50 °C are taken to be 7.0×10^9 and $8.0 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$, respectively.

For the adamantanethiol-catalysed reduction of 1-bromooctane by Et₃SiH, the five values of k_{XSH} (Table 1, entries 1–5) obtained using eqn. (15) are all in close agreement, supporting the kinetic treatment used. The average values of k_{XSH} for this and other reducing silane-thiol couples are gathered in Table 3. At 60 °C, the rate constant for abstraction of hydrogen from Et₃SiH by a tertiary alkanethiyl radical is ca. $3.3 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ which would correspond to an activation energy of ca. 29 kJ mol⁻¹ if an Arrhenius *A*-factor of $10^{9.0} \text{ M}^{-1} \text{ s}^{-1}$ is assumed. The silanethiyl radicals Ph₃SiS' and Bu'MePhSiS' abstract hydrogen from Et₃SiH slightly more rapidly than the alkanethiyl radicals (Table 3, entries 1–5), but (Bu'O)₃SiS' and Pr₃SiS' are significantly more reactive in this regard (entries 6 and 7), with k_{XSH} in the region of $1.5 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$. The latter rate constant translates into an activation energy of ca. 25 kJ mol⁻¹. The presence of one or more phenyl substituents at silicon appears to decrease the H-abstrating ability of a silanethiyl radical, although the results obtained with Ph₃SiSH and Bu'MePhSiSH as catalysts may be rather less reliable than those obtained with (Bu'O)₃SiSH and Pr₃SiSH, because of the greater heterolytic reactivity of the former silanethiols by way of nucleophilic attack at silicon. As expected in view of the weakening of the Si–H bond caused by the *Si*-phenyl substituents,⁸ Ph₃SiH is a more reactive hydrogen-atom donor than Et₃SiH towards both alkane- and silanethiyl radicals (Table 3, entries 16 and 17).

The results obtained for the reduction of 1-chlorooctane by Et₃SiH catalysed by 1-AdSH or (Bu'O)₃SiSH (Table 2) allow k_{SiH} to be extracted by applying eqn. (11). As required by this relationship, when other variables are kept constant, the initial rate of reduction decreases as the thiol concentration increases and the close similarity of the values of k_{SiH} obtained for a particular thiol gives confidence in the approach adopted. The mean values of k_{SiH} obtained (Table 3), $5.2 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ for abstraction of hydrogen by Et₃Si' from 1-AdSH and $5.1 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ for abstraction from (Bu'O)₃SiSH, are very reasonable when compared with the rate constant for abstraction of hydrogen from Bu'SH by a primary alkyl radical ($1.1 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ at 60 °C),¹⁹ bearing in mind the favourable kinetic polar effects that arise from charge transfer in the transition state for abstraction of electron-deficient hydrogen from the thiol by a strongly nucleophilic silyl radical.³

Assuming that the entropy change associated with the reversible reaction (6) is zero, the equilibrium constants ($k_{\text{XSH}}/k_{\text{SiH}}$) translate into $\Delta_r H = +20.4 \text{ kJ mol}^{-1}$ for abstraction of hydrogen from Et₃SiH by 1-AdS' and $+16.5 \text{ kJ mol}^{-1}$ for abstraction by (Bu'O)₃SiS'. These results imply that the S–H bond in (Bu'O)₃SiSH is ca. 4 kJ mol⁻¹ stronger than that in 1-AdSH and we have proposed previously that the generally greater effectiveness of silanethiols, compared to alkanethiols, as protic polarity-reversal catalysts is partly a result of the greater strength of the S–H bonds in the silanethiols, although polar effects are probably also important.^{2,3}

|| *Ab initio* molecular orbital calculations were carried out at the G2 level²⁶ to estimate the difference in strengths of the S–H bonds in H₃CS–H and H₃SiS–H. The G2 enthalpies at 298 K for H₃CSH, H₃CS', H₃SiSH and H₃SiS' are -438.143896 , -437.507108 , -689.193211 and -688.522408 hartree, respectively. These results indicate that the S–H bond in silanethiol is stronger by 10.5 kJ mol⁻¹ than that in methanethiol, identical with our previous estimate at a different level of theory.²

Table 3 Averaged scaled values of k_{XSH} and k_{SiH} at 60 °C obtained using different experimental methods

Entry	Silane	Thiol	Octyl halide reduction			H/D exchange		Racemisation of (S)-Bu ^t MePhSiH $k_{\text{XSH}}/\text{M}^{-1} \text{s}^{-1}$
			$k_{\text{XSH}}/\text{M}^{-1} \text{s}^{-1}$	$k_{\text{SiH}}/\text{M}^{-1} \text{s}^{-1}$	$(k_{\text{XSH}}/k_{\text{SiH}})$	$(k_{\text{XSH}}/k_{\text{XSD}})$ at 50 °C ^a	$k_{\text{XSH}}^b/\text{M}^{-1} \text{s}^{-1}$	
1	Et ₃ SiH	1-AdSH	3.2×10^4	5.2×10^7	6.2×10^{-4}	(4.0)	1.5×10^4	—
2	Et ₃ SiH	<i>tert</i> -C ₁₂ H ₂₅ SH	3.5×10^4	—	—	—	—	—
3	Et ₃ SiH	<i>n</i> -C ₁₂ H ₂₅ SH	—	—	—	4.4	1.3×10^4	—
4	Et ₃ SiH	Ph ₃ SiSH	4.3×10^4	—	—	(3.5)	1.6×10^4	—
5	Et ₃ SiH	Bu ^t MePhSiSH ^c	4.1×10^4	—	—	(3.5)	1.8×10^4	—
6	Et ₃ SiH	(Bu ^t O) ₃ SiSH	1.3×10^5	5.1×10^7	2.6×10^{-3}	3.0	1.9×10^5	—
7	Et ₃ SiH	Pr ⁱ ₃ SiSH	1.6×10^5	—	—	2.5	2.2×10^5	—
8	Me ₂ PhSiH	Ph ₃ SiSH	—	—	—	(3.5)	1.9×10^4	—
9	Bu ^t MePhSiH	1-AdSH	3.4×10^4	—	—	(4.0)	2.2×10^4	3.5×10^4
10	Bu ^t MePhSiH	<i>n</i> -C ₁₂ H ₂₅ SH	—	—	—	(4.0)	1.3×10^4	1.6×10^4
11	Bu ^t MePhSiH	Ph ₃ SiSH	—	—	—	(3.5)	2.2×10^4	5.6×10^4
12	Bu ^t MePhSiH	Bu ^t MePhSiSH ^c	—	—	—	(3.5)	2.3×10^4	5.5×10^4
13	Bu ^t MePhSiH	(Bu ^t O) ₃ SiSH	—	—	—	(3.0)	1.5×10^5	2.6×10^5
14	Bu ^t MePhSiH	Pr ⁱ ₃ SiSH	—	—	—	(2.5)	1.5×10^5	2.5×10^5
15	MePh ₂ SiH	Ph ₃ SiSH	—	—	—	(3.5)	3.4×10^4	—
16	Ph ₃ SiH	1-AdSH	7.5×10^4	—	—	—	—	—
17	Ph ₃ SiH	Ph ₃ SiSH	8.8×10^4	—	—	(3.5)	5.3×10^4	—

^a Values in parentheses are estimated by comparison with experimentally-determined values for related thiols. Values are assumed to be the same at 40 °C. ^b Assuming $A_{\text{XSH}} = 10^{9.0} \text{M}^{-1} \text{s}^{-1}$. ^c Racemic thiol.

H/D exchange between R₃SiH/D and XSH/D

It might be argued that the presence of Lewis-acidic silyl halides or Brønsted-acidic hydrogen halides (produced by hydrolysis of the former) could increase the reactivity of a thiol radical by protonation or by attachment of the Lewis-acidic silicon to the sulfur atom. Therefore, in order to estimate rate constants for the abstraction of hydrogen from silanes by thiol radicals in the absence of alkyl halides or of any products derived from them, the radical-chain isotopic exchange between R₃SiH and XSD and between R₃SiD and XSH was examined. We consider first the exchange of H for D in the Si-deuteriated silane R₃SiD (≥ 98 atom% D) upon treatment with an isotopically normal thiol XSH in the presence of TBHN as initiator. The solvent was perdeuteriocyclohexane and hexamethyldisiloxane (Me₃SiOSiMe₃) was present as an internal concentration standard. Reactions were carried out under argon at 40 or 50 °C in the thermostatted probe of an ¹H NMR spectrometer, operating at 400 MHz, and spectra were monitored at 1 minute intervals after raising the probe temperature. The concentrations of Bu^tOH, TBHN, R₃SiH and (where possible) of XSH and XSD were determined as a function of time, by integration of appropriate peaks in the spectra (see Fig. 2). The SiH resonances of the silanes and the *tert*-butyl singlets for TBHN (δ 1.29) and Bu^tOH/D (δ 1.17) were used to monitor concentrations; the rate of production of *tert*-butyl alcohol was always essentially twice the rate of removal of TBHN. Silanethiols were monitored *via* the SiSH resonances but, because of peak overlap, the concentration of dodecane-1-thiol could be followed only *via* the C₁₁H₂₃CH₂SH/D resonances.

Following its generation from TBHN [eqn. (3), Scheme 1], the *tert*-butoxyl radical is assumed to abstract hydrogen rapidly from the protiated thiol to give *tert*-butyl alcohol [eqn. (4), Scheme 1]. Competitive abstraction of deuterium from silicon or from the solvent, if it occurs at all, is assumed to be kinetically insignificant. As discussed above, the rate of production of thiol radicals XS[•] (R_i) is taken as equal to the rate of production of Bu^tOH as measured by ¹H NMR spectroscopy [eqn. (14)]. Since the only significant termination reaction will take place between pairs of thiol radicals [eqn. (5), Scheme 1], the stationary-state concentration of thiol radicals is again given by eqn. (10).

The general mechanism for H/D exchange between R₃SiH/D and XSH/D is shown in Scheme 2. However, for exchange between completely deuteriated R₃SiD and XSH, the only

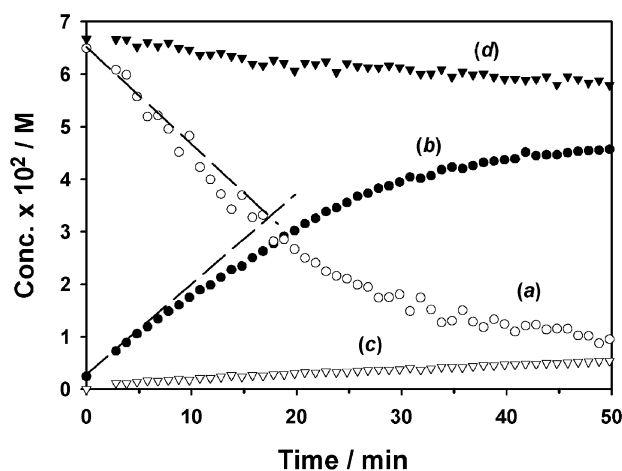
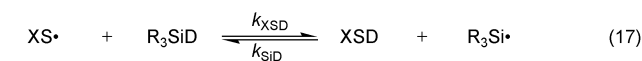
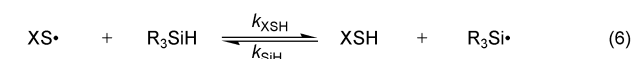
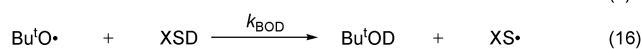
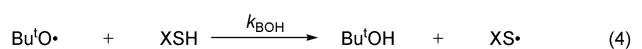


Fig. 2 Isotopic exchange between Et₃SiD and Ph₃SiSH at 50 °C in perdeuteriocyclohexane. The initial reagent concentrations were: [Et₃SiD] 0.48 M, [Ph₃SiSH] 0.065 M and [TBHN] 0.013 M; (a) [Ph₃SiSH], (b) [Et₃SiH], (c) [Bu^tOH]. Curve (d) shows [Ph₃SiSH] for a similar experiment in the absence of Et₃SiD. The dashed lines (tangents at $t = 0$) indicate the estimated initial rates of H/D exchange.



Scheme 2

reaction of consequence open to the thiol radical at $t = 0$ is to abstract deuterium from R₃SiD [eqn. (17), Scheme 2]. If abstraction of hydrogen from the Si-alkyl group or of deuterium from the solvent were to take place, the fate of the derived carbon radicals would be to abstract hydrogen rapidly from XSH, leading to regeneration of R₃SiD and to the formation of C₆D₁₁H, respectively. Both these reactions also regenerate XS[•] and their occurrence should not complicate the determination of the rate constant k_{XSD} for the forward reaction (17). At $t = 0$, the fate of the silyl radical R₃Si[•] formed in the latter reaction will

Table 4 Isotopic exchange between R₃SiH/D and XSH/D in perdeuteriocyclohexane solvent

Entry	Silane	Thiol	Temp./ °C	[R ₃ SiD/H] ₀ ^{a/} M	[XSH/D] ₀ ^{a/} M	[TBHN] ₀ ^{a/} /M	R _f /M s ⁻¹	{d[R ₃ SiH]/dt} ₀ ^{d/} M s ⁻¹	k _{XSD/H} ^{b/c/} M ⁻¹ s ⁻¹
1	Et ₃ SiD	Ph ₃ SiSH	50	0.48	0.065	0.013	2.06 × 10 ⁻⁶	2.66 × 10 ⁻⁵	3.5 × 10 ³
2	Et ₃ SiD	Ph ₃ SiSH	50	0.21	0.051	0.010	1.73 × 10 ⁻⁶	9.01 × 10 ⁻⁶	2.9 × 10 ³
3	Et ₃ SiD	Ph ₃ SiSH	50	0.48	0.065	0.020	3.13 × 10 ⁻⁶	2.79 × 10 ⁻⁵	2.9 × 10 ³
4	Et ₃ SiD	Ph ₃ SiSH	50	0.48	0.035	0.012	2.01 × 10 ⁻⁶	2.89 × 10 ⁻⁵	3.7 × 10 ³
5	Et ₃ SiD	Bu ^t MePhSiSH ^d	50	0.42	0.052	0.013	2.00 × 10 ⁻⁶	2.41 × 10 ⁻⁵	3.7 × 10 ³
6	Et ₃ SiD	(Bu ^t O) ₃ SiSH	40	0.58	0.061	0.0095	2.92 × 10 ⁻⁷	1.39 × 10 ⁻⁴	3.7 × 10 ⁴
7	Et ₃ SiH	(Bu ^t O) ₃ SiSD	40	0.385	0.073	0.0092	3.17 × 10 ⁻⁷	2.39 × 10 ^{-4ef}	1.1 × 10 ⁵
8	Et ₃ SiD	1-AdSH	50	0.55	0.057	0.015	2.33 × 10 ⁻⁶	2.37 × 10 ⁻⁵	2.5 × 10 ³
9	Et ₃ SiD	<i>n</i> -C ₁₂ H ₂₅ SH	50	1.15	0.120	0.016	2.40 × 10 ⁻⁶	3.89 × 10 ⁻⁵	2.0 × 10 ³
10	Et ₃ SiH	<i>n</i> -C ₁₂ H ₂₅ SD	50	0.94	0.092	0.011	1.87 × 10 ⁻⁶	1.03 × 10 ^{-4eg}	8.8 × 10 ³
11	Et ₃ SiD	Pr ⁱ ₃ SiSH	40	0.51	0.062	0.0097	3.10 × 10 ⁻⁷	1.67 × 10 ⁻⁴	5.0 × 10 ⁴
12	Et ₃ SiH	Pr ⁱ ₃ SiSD	40	0.275	0.069	0.0085	2.71 × 10 ⁻⁷	1.82 × 10 ^{-4eg}	1.3 × 10 ⁵
13	Me ₂ PhSiD	Ph ₃ SiSH	50	0.48	0.055	0.012	1.89 × 10 ⁻⁶	2.81 × 10 ⁻⁵	3.8 × 10 ³
14	Bu ^t MePhSiD ^d	Ph ₃ SiSH	50	0.48	0.059	0.010	1.70 × 10 ⁻⁶	3.23 × 10 ⁻⁵	4.6 × 10 ³
15	Bu ^t MePhSiD ^d	Bu ^t MePhSiSH ^d	50	0.48	0.061	0.011	1.70 × 10 ⁻⁶	3.28 × 10 ⁻⁵	4.7 × 10 ³
16	Bu ^t MePhSiD ^d	(Bu ^t O) ₃ SiSH	40	0.41	0.063	0.0096	3.06 × 10 ⁻⁷	7.52 × 10 ⁻⁵	2.8 × 10 ⁴
17	Bu ^t MePhSiD ^d	Pr ⁱ ₃ SiSH	40	0.43	0.055	0.0091	2.92 × 10 ⁻⁷	9.26 × 10 ⁻⁵	3.4 × 10 ⁴
18	Bu ^t MePhSiD ^d	1-AdSH	50	0.53	0.044	0.019	3.20 × 10 ⁻⁶	4.20 × 10 ⁻⁵	4.0 × 10 ³
19	Bu ^t MePhSiD ^d	<i>n</i> -C ₁₂ H ₂₅ SH	50	0.54	0.067	0.018	2.62 × 10 ⁻⁶	2.17 × 10 ⁻⁵	2.2 × 10 ³
20	MePh ₂ SiD	Ph ₃ SiSH	50	0.48	0.058	0.0091	1.29 × 10 ⁻⁶	4.33 × 10 ⁻⁵	7.1 × 10 ³
21	Ph ₃ SiD	Ph ₃ SiSH	50	0.51	0.060	0.0095	1.29 × 10 ⁻⁶	6.67 × 10 ⁻⁵	1.1 × 10 ⁴

^a Concentrations in the reaction mixture were determined by integration of the ¹H NMR spectrum using hexamethyldisiloxane as an internal reference. ^b The value of k_{XSD} was calculated using eqn. (18). ^c The value of k_{XSH} was calculated using eqn. (19) taking I₁ = 1.5 and I₂ = 3.0. ^d Racemic compound. ^e {d[XSH]/dt}₀ is given. ^f Taking r = 0.064. ^g Taking r = 0.075.

also be to abstract hydrogen from XSH [eqn. (6), Scheme 2], leading to the production of R₃SiH with a rate constant k_{SiH} such that the *initial* rate of production of *Si*-protiated silane will be given by eqn. (18). Values of {d[R₃SiH]/dt}₀ were obtained by drawing tangents to concentration *versus* time curves at t = 0, when the concentrations of R₃SiH and XSD are effectively zero and the concentrations of R₃SiD and XSH are known exactly. The results are summarised in Table 4 and the course of a representative exchange experiment involving Et₃SiD and Ph₃SiSH is shown in Fig. 2. No exchange of protium into the deuterated silane took place if the TBHN was omitted from the reaction mixture. In the presence of TBHN but without any silane, H/D exchange between Ph₃SiSH and the solvent C₆D₁₂ was very slow (see Fig. 2). No exchange of deuterium into the ethyl groups of Et₃SiD was detectable by ¹H NMR spectroscopy.

$$\left\{ \frac{d[R_3SiH]}{dt} \right\}_{t=0} = k_{XSD}[XS^*][R_3SiD] = (R_f/2k_t)^{1/2} k_{XSD}[R_3SiD] \quad (18)$$

In principle, the rate constant k_{XSH} can be obtained directly from the kinetics of isotopic exchange between R₃SiH and XSD. However, in practice these experiments proved to be more difficult and less accurate for technical reasons. First, it was difficult to achieve very high levels of *S*-deuteration of the thiols, which undergo rapid exchange with protic compounds, especially atmospheric moisture, and these problems are compounded by the relatively low concentrations of XSD used in the exchange experiments. Second, using ¹H NMR spectroscopy, the rate of production of R₃SiD could not be determined satisfactorily in the presence of excess R₃SiH and the exchange had to be followed by measuring the rate of production of XSH. This could be accomplished for three of the thiols, by monitoring the C₁₁H₂₃CH₂SH resonance of dodecane-1-thiol and the SiSH resonances of (Bu^tO)₃SiSH and Prⁱ₃SiSH.

Experiments were carried out using *S*-deuterated dodecane-1-thiol, tri-*tert*-butoxysilanethiol and triisopropylsilanethiol containing *ca.* 96, 98 and 96 atom% D, respectively, in bulk, figures that reduced to *ca.* 93%, 94% and 93% in reaction mixtures immediately after preparation. Because the thiols were not completely deuterated and XSH will be a more reactive

hydrogen-atom donor than XSD, the H/D exchange kinetics become more complex than for the R₃SiD/XSH system, even when initial rates of exchange are considered. Since both XSD and XSH are present at t = 0, reactions of both thiols must be included, leading to eqn. (19) for the rate of formation of XSH. In this equation, the derivation of which assumes that Bu^tO[•] reacts only with XSH/D, r = [XSH]/[XSD], I₁ = k_{BOH}/k_{BOD} and I₂ = k_{SiH}/k_{SiD}. The term R_i{rI₁/(rI₁ + 1)} represents the loss of XSH as XSSX and it seems likely that the Bu^tOH formed as a result of this process will exchange reversibly with XSD to partially regenerate XSH. However, because the kinetic chains are relatively long under the extant conditions, this term proved to be very small with respect to d[XSH]/dt and its effect on the determination of k_{XSH} was fortunately negligible.

$$\left\{ \frac{d[XSH]}{dt} \right\}_{t=0} = (R_f/2k_t)^{1/2} k_{XSH}[R_3SiH] \{ 1/(rI_2 + 1) \} - R_i \{ rI_1/(rI_1 + 1) \} \quad (19)$$

As discussed before, the abstraction of hydrogen from XSH/D by Bu^tO[•] is undoubtedly a very fast reaction and, irrespective of its detailed mechanism,^{6,7} the kinetic isotope effect I₁ would be expected to be small and, rather arbitrarily, it was taken to be 1.5 at 50 °C. However, again because of the relatively small size of the term in I₁ in eqn. (19), the value of this isotope effect is unimportant. The rate constants k_{SiH} obtained in this work for the abstraction of hydrogen from alkane- and silanethiols by Et₃Si[•] are similar to those for the analogous abstraction by alkyl radicals (see above) and thus it is reasonable to assume that the kinetic isotope effects will be similar for the two types of reaction. On this basis, we estimate I₂ = 3.0 at 50 °C, by comparison with the values reported^{27a} for the reactions of a variety of simple alkyl radicals with Bu^tSH.

The results of the H/D exchange experiments are gathered in Table 4 and the first four entries refer to the abstraction of deuterium from Et₃SiD by Ph₃SiS[•] when the concentrations of silane, thiol and TBHN were varied in turn. The closely similar values of k_{XSD} obtained by applying eqn. (18) lend confidence to the approach adopted. Several other combinations of silane and thiol were investigated at 50 °C, but exchanges catalysed by (Bu^tO)₃SiSH/D or Prⁱ₃SiSH/D proved to be very rapid at this temperature and were more accurately monitored at 40 °C

under the same conditions except that bromotriethylsilane was also present initially in the same concentration as the thiol, the rate of racemisation was unchanged (Table 5, entry 5). This result confirms that in the reduction of alkyl halides by the silane–thiol couple, the halogenosilane product (or hydrogen halide formed by its adventitious hydrolysis) does not influence the reactivity of XS^{\cdot} or XSH . In agreement with the results obtained using the other two methods for determining k_{XSH} , the silanethiyl radicals $(\text{Bu}^{\text{t}}\text{O})_3\text{SiS}^{\cdot}$ and $\text{Pr}^{\text{t}}_3\text{SiS}^{\cdot}$ abstract hydrogen more rapidly from $\text{Bu}^{\text{t}}\text{MePhSiH}$ than do alkanethiyl radicals.

A possible complicating factor with all these experiments is the extent to which an alkanethiol catalyst XSH is subject to $\text{S}_{\text{H}2}$ attack at sulfur by the silyl radical $\text{R}_3\text{Si}^{\cdot}$, leading to displacement of X^{\cdot} and to the formation of XH together with R_3SiSH , which could then also function as a catalyst.^{29,30} In the racemisation experiments, this reaction would result in the formation of $\text{Bu}^{\text{t}}\text{MePhSiSH}$. However, by making quantitative measurements only during the initial stages of the racemisation any possible interference from silanethiol formation will be eliminated. Furthermore, $\text{Bu}^{\text{t}}\text{MePhSiSH}$ was one of the thiols investigated as a catalyst for the racemisation (Table 5, entry 7) and it turns out to be only about as effective as 1-AdSH. Furthermore, for the reduction of 1-bromooctane by several silane–adamantanethiol couples, it was confirmed by GLC analysis that negligible amounts of adamantane were formed until all the alkyl bromide had been reduced, concordant with the known greater reactivity of 1-bromobutane compared with dibutyl sulfide towards attack by triethylsilyl radicals.¹⁸ It was also shown by GLC that most of the 1-AdSH catalyst survived until the end of the reduction. Evidently, silanethiol formation does not complicate the mechanistic interpretation of the alkanethiol-catalysed reduction of alkyl bromides by silanes.

The values of k_{XSH} for hydrogen abstraction from $\text{Bu}^{\text{t}}\text{MePhSiH}$ by $\text{Ph}_3\text{SiS}^{\cdot}$ or $\text{Bu}^{\text{t}}\text{MePhSiS}^{\cdot}$ obtained from the racemisation studies were about 2.5 times larger than those determined by H/D exchange (Table 3, entries 11 and 12). However, agreement between the two methods was better when the more heterolytically stable silanethiols $(\text{Bu}^{\text{t}}\text{O})_3\text{SiSH}$ and $\text{Pr}^{\text{t}}_3\text{SiSH}$ were used as catalysts (Table 3, entries 13 and 14) and, in common with their reactions with other silanes, the radicals $(\text{Bu}^{\text{t}}\text{O})_3\text{SiS}^{\cdot}$ and $\text{Pr}^{\text{t}}_3\text{SiS}^{\cdot}$ abstract hydrogen particularly rapidly from $\text{Bu}^{\text{t}}\text{MePhSiH}$. Considering the very different experimental techniques employed and the various approximations involved, the general level of agreement between the various methods is considered to be satisfactory.††

Summarising remarks and conclusion

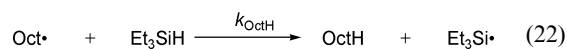
Both alkane- and silane-thiols efficiently catalyse the reduction of alkyl halides by simple silanes, such as Et_3SiH and Ph_3SiH . The kinetic studies described in this paper for the reduction of octyl bromide and octyl chloride are entirely consistent with the radical-chain mechanism depicted in Scheme 1 and originally proposed in 1989.¹ The kinetic analysis indicates that, for reduction by Et_3SiH catalysed by 1-AdSH at 60 °C, $k_{\text{XSH}} = 3.2 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ and $k_{\text{SiH}} = 5.2 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ for the reversible reaction (6), corresponding to an equilibrium constant of 6.2×10^{-4} and $\Delta_r H \approx \Delta_r G = +20.4 \text{ kJ mol}^{-1}$ for abstraction of hydrogen

from Et_3SiH by 1-AdS $^{\cdot}$. The H/D exchange and racemisation experiments provide strong supporting evidence for the mechanism shown in Scheme 1 and for the values of k_{XSH} and k_{SiH} obtained from the kinetic analysis that assumes its validity.

We conclude that the enthalpy change associated with abstraction of hydrogen from Et_3SiH by an alkanethiyl radical is smaller by *ca.* 11 kJ mol^{-1} than the value computed by Schiesser and Skidmore¹³ for the reaction between MeS^{\cdot} and Me_3SiH , which is the same as that implied by the currently favoured values of $DH(\text{MeS-H})$ and $DH(\text{Me}_3\text{Si-H})$. If an *A*-factor of $10^{9.0} \text{ M}^{-1} \text{ s}^{-1}$ is assumed, the value of k_{XSH} at 60 °C determined in the present work for abstraction of hydrogen from Et_3SiH by an alkanethiyl radical corresponds to an activation energy of *ca.* 29 kJ mol^{-1} , some 13 kJ mol^{-1} less than that computed by Schiesser and Skidmore for the abstraction of hydrogen from Me_3SiH by MeS^{\cdot} .¹³ Admittedly, both the computations and the experimental BDEs refer to the gas phase, while our experiments were conducted in cyclohexane solution. However, solvent effects seem unlikely to be entirely responsible for the differences observed. It is tempting to suggest that the more recent experimental determinations of $DH(\text{Me}_3\text{Si-H})$ may be too high and/or perhaps $DH(\text{MeS-H})$ is too low. For example, if $DH(\text{Me}_3\text{Si-H})$ were to be *ca.* 391 kJ mol^{-1} and $DH(\text{MeS-H})$ were *ca.* 371 kJ mol^{-1} , the consequent value of $\Delta_r H$ for the abstraction of hydrogen from Me_3SiH by MeS^{\cdot} would fall into line with our results in solution. It is important not to lose sight of the fact that, because of the logarithmic dependence of rate and equilibrium constants on free-energy differences, relatively small changes in the latter can have large and mechanistically significant effects on the former.

In the present context, we note that the determination of $DH(\text{Me}_3\text{Si-H})$ involved a kinetic study of the abstraction of hydrogen from HBr by $\text{Me}_3\text{Si}^{\cdot}$, a process for which the rate constant was found to decrease as the temperature increased.¹⁰ The negative apparent activation energies for this and related halogen-atom transfer processes have been the subject of controversy³¹ and other problems associated with the quantitative thermochemistry of $\text{Me}_3\text{Si}^{\cdot}$ have been discussed by Walsh.³² We note that bromine and sulfur are diagonally related in the Periodic Table and, if the negative apparent activation energy for the $\text{Me}_3\text{Si}^{\cdot} + \text{HBr}$ reaction were to be a consequence of the initial formation of a loosely bound hypervalent 9-Br-2 adduct $\text{Me}_3\text{SiBr}^{\cdot}\text{H}$, this could suggest the formation of a similar 9-S-3 sulfuranyl radical adduct $\text{Me}_3\text{SiS}^{\cdot}(\text{H})\text{X}$ *en route* to the overall abstraction of hydrogen from a thiol by a silyl radical.

The reduction of 1-bromooctane by Et_3SiH is about 50 times faster at 60 °C in the presence of 5 mol% 1-AdSH than in its absence (compare Fig. 1a and b). In the absence of a thiol, the silane itself can function as the effective hydrogen-atom donor towards the octyl radical [eqn. (22)], although abstraction of hydrogen from the cyclohexane solvent will also take place. Although the chain length is very short, if we assume that termination now takes place between two octyl radicals, the rate of reduction will be given approximately by eqn. (23). For two experiments with and without thiol under otherwise similar conditions (Fig. 1), comparison of eqns. (12) and (23) indicates that $k_{\text{OctH}} \approx k_{\text{XSH}}/50$, *i.e.* *ca.* $7 \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$ at 60 °C. The rate constant for abstraction of hydrogen from Et_3SiH by $\text{PhC-Me}_2\text{CH}_2^{\cdot}$ is reported to be *ca.* $2.7 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ at 60 °C,⁴ although this abstraction takes place from both the ethyl and SiH groups. Nevertheless, the order-of-magnitude agreement between this rate constant and the estimate of k_{OctH} based on the mechanism shown in Scheme 1 is further confirmation of this pathway for the reduction of alkyl halides by the silane–thiol couple.



$$\frac{d[\text{OctH}]}{dt} \approx (R_i/2k_t)^{1/2} k_{\text{OctH}} [\text{Et}_3\text{SiH}] \quad (23)$$

†† The discussion in ref. 29 concerning the enantioselectivity of the reaction between (S) - $\text{Bu}^{\text{t}}\text{MePhSiH}$ and *tert*-dodecanethiol or triphenylphosphine sulfide to give $\text{Bu}^{\text{t}}\text{MePhSiSH}$ is confused by an unfortunate error at the end of the relevant paragraph on page 4583. The last sentence of this paragraph should conclude with 'and abstraction of hydrogen from the silane by the thiyl radical is also likely to be reversible under the reaction conditions (Scheme 2)'. The point being made is that if (S) - $\text{Bu}^{\text{t}}\text{MePhSi}^{\cdot}$ abstracts hydrogen from the thiol in competition with its reaction at sulfur in the thiol to displace a *tert*-dodecyl radical, then the starting silane will be subject to racemisation, as described in the present paper, in competition with its conversion to (S) - $\text{Bu}^{\text{t}}\text{MePhSiSH}$.

Table 6 Computational modelling of the thiol-catalysed reduction of 1-chlorooctane by triethylsilane^a

Entry ^b	Thiol	[XSH] ₀ /M	$k_{\text{XSH}}/\text{M}^{-1}\text{s}^{-1}$	$k_{\text{SiH}}/\text{M}^{-1}\text{s}^{-1}$	$\{d[\text{OctH}]/dt\}_0/\text{M s}^{-1}$	Computed values ^c				
						$\{d[\text{OctH}]/dt\}_0/\text{M s}^{-1}$	[XS*] _{ss} ^d /M	[Et ₃ Si*] _{ss} /M	[Oct*] _{ss} /M	[Bu'O*] _{ss} /M
1	1-AdSH	0.050	3.2×10^4	4.9×10^7	7.7×10^{-5}	7.5×10^{-5}	4.3×10^{-8}	5.4×10^{-10}	1.4×10^{-10}	3.5×10^{-12}
2	1-AdSH	0.060	3.2×10^4	5.2×10^7	6.1×10^{-5}	6.0×10^{-5}	4.4×10^{-8}	4.3×10^{-10}	9.1×10^{-11}	2.9×10^{-12}
3	1-AdSH	0.075	3.2×10^4	5.3×10^7	4.8×10^{-5}	4.7×10^{-5}	4.4×10^{-8}	3.4×10^{-10}	5.8×10^{-11}	2.3×10^{-12}
4	1-AdSH	0.100	3.2×10^4	5.5×10^7	3.5×10^{-5}	3.5×10^{-5}	4.4×10^{-8}	2.5×10^{-10}	3.2×10^{-11}	1.8×10^{-12}
5	(Bu'O) ₃ SiSH	0.050	1.3×10^5	7.1×10^7	2.2×10^{-4}	2.0×10^{-4}	4.2×10^{-8}	1.5×10^{-9}	3.8×10^{-10}	3.5×10^{-12}
6	(Bu'O) ₃ SiSH	0.100	1.3×10^5	5.3×10^7	1.5×10^{-4}	1.4×10^{-4}	4.3×10^{-8}	1.0×10^{-9}	1.3×10^{-10}	1.8×10^{-12}
7	(Bu'O) ₃ SiSH	0.200	1.3×10^5	3.8×10^7	1.0×10^{-4}	1.0×10^{-4}	4.3×10^{-8}	7.3×10^{-10}	4.6×10^{-11}	8.7×10^{-13}
8	(Bu'O) ₃ SiSH	0.300	1.3×10^5	4.4×10^7	6.1×10^{-5}	5.9×10^{-5}	4.4×10^{-8}	4.2×10^{-10}	1.8×10^{-11}	5.8×10^{-13}

^a Concentrations [OctCl]₀ = 0.19 M, [Et₃SiH]₀ = 1.00 M and [TBHN]₀ = 0.025 M, as in Table 2. All possible termination reactions between XS*, Et₃Si* and Oct* are included, all with the same rate constant of $9.0 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$. The values of k_{TBHN} , k_{SiCl} , the rate constant for abstraction of hydrogen from the thiol by Oct* and that for transfer of hydrogen from the thiol to Bu'O* were taken to be $3.5 \times 10^{-4} \text{ s}^{-1}$, $7.4 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$, $1.1 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ and (somewhat arbitrarily) $1.0 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$, respectively. ^b The entries correspond to those in Table 2. ^c The steady-state radical concentrations are those present after the first 10 s of reaction. The rate of octane formation is the effectively-linear rate over the first minute of reaction. ^d $(R_i/2k_t)^{1/2} = 4.4 \times 10^{-8} \text{ M}^{-1} \text{ s}^{-1}$.

In order to support the kinetic approximations used to determine k_{XSH} and k_{SiH} , the composition of each of the Et₃SiH–OctCl–XSH–TBHN reaction mixtures listed in Table 2 was modelled as a function of time using a numerical integration computer program written by Professor J. H. Ridd of this department.³³ This program is based on the modified Euler method³⁴ and the use of numerical integration means that it is unnecessary to make explicitly the steady-state approximation or make any simplifying assumptions regarding the relative magnitudes of terms in the differential equations; the reaction mechanism, the starting reagent concentrations and the rate constants are the only input data required to model the time evolution of the system. A time interval starting at $2 \times 10^{-10} \text{ s}$, but increasing rapidly to $5 - 20 \times 10^{-8} \text{ s}$, was used in conjunction with $12 - 3 \times 10^8$ steps, so as to correspond to the first minute of each reduction; the results are summarised in Table 6. The close agreement between the observed and computed initial reduction rates gives us confidence in the approach used to determine k_{XSH} and k_{SiH} and provides further justification for the assumptions made. In particular, the 'stationary-state' concentrations of the thiyl radicals [XS*]_{ss} are close to $(R_i/2k_t)^{1/2}$ and are far greater than those of both the silyl radical and the octyl radical, confirming the conclusion that the only significant termination reaction will be that between two thiyl radicals. These steady-state radical concentrations are established within the first 10^{-2} s and do not vary by more than 1% over the first minute of reaction.

Finally, since 1989, we have described several other types of reaction in which the overall transfer of hydrogen from an electron-rich Si–H or C–H group to a nucleophilic carbon- or silicon-centred radical is mediated by a thiol acting as a protic polarity-reversal catalyst.^{3,35,36} We note in particular the thiol-catalysed radical-chain hydrosilylation of electron-rich alkenes,^{30,37} where no halogen-containing compounds are present and where modification of the reactivity of XS* or XSH by complexation seems very unlikely. Nevertheless, thiol catalysis of the addition of the Si–H group across the double bond is extremely efficient and independent evidence for the thiol as the hydrogen-atom donor towards the chain-carrying β-silylalkyl radical is provided by the fact that high degrees of asymmetric induction (up to 96% ee in the product) can result if an enantiomerically-pure thiol is used to promote the hydrosilylation of a prochiral alkene.^{30,38}

Experimental

NMR spectra were recorded using a Bruker AMX400 instrument (400 MHz for ¹H). Quoted NMR data refer to cyclohexane-*d*₁₂ solvent and chemical shifts are reported relative to internal Me₄Si; *J* values are given in Hz.

GLC analysis to monitor octyl halide reduction was carried out using an HP 6890 Series instrument (Agilent Technologies) in conjunction with a flame-ionisation detector and a capillary column (25 m × 0.32 mm id) coated with BPX5 (non-polar, 0.32 μm film) and obtained from SGE International Ltd. The enantiomeric composition of Bu'MePhSiH was determined using a beta-DEX 120 column (Supelco Inc.). The carrier gas was helium for both applications.

All kinetic runs and manipulations reagents were carried out using oven-dried apparatus and under an atmosphere of dry argon. Syringes, stirrer bars and septa were all stored in a desiccator over P₂O₅.

Materials

Cyclohexane and cyclohexane-*d*₁₂ (Aldrich 99.6 atom% D) were distilled from NaH and LiAlD₄, respectively, and stored under argon. All the isotopically normal silanes and hexamethyldisiloxane were commercial products (Aldrich) which were distilled from CaH₂ and stored under argon. Nonane was stored over activated 4A molecular sieves. 1-Bromooctane, 1-chlorooctane and 1-iodooctane (all Aldrich) were dried over P₂O₅, then distilled under reduced pressure (*ca.* 10 mmHg) and stored (for short periods only) under argon. *Si*-Deuteriated silanes were prepared by reduction of the corresponding chlorosilanes with LiAlD₄ (nominally 98 atom% D) in diethyl ether according to standard procedures³⁹ and were shown by ¹H NMR analysis to contain ≥ 98 atom%D after final distillation from a small amount of LiAlD₄. Di-*tert*-butyl hyponitrite was prepared from sodium hyponitrite and *tert*-butyl bromide in the presence of ZnCl₂, following the method of Mendenhall.^{5b} (*S*)-*tert*-Butyl(methyl)phenylsilane,²⁸ adamantane-1-thiol,⁴⁰ *tert*-butyl(methyl)phenylsilanethiol,²⁹ tri-*tert*-butoxysilanethiol^{35,41} and triisopropylsilanethiol⁴² were prepared by published methods. Other thiols were commercial materials (Aldrich) and were used as received.

Preparation of *S*-deuteriated thiols

Dodecane-1-thiol (10 cm³), dry benzene (25 cm³) and deuterium oxide (99.9 atom% D; 5 cm³) were introduced into a dry, argon-filled 50 cm³ two-necked round-bottomed flask containing a magnetic stirrer bar and fitted with a Dean–Stark water trap filled with dry benzene and carrying a condenser, through which a slow downward flow of argon was maintained. After addition of the reagents, the side neck was closed with a stopper and the mixture was stirred and heated under reflux. After all the water had been removed by azeotropic distillation, the exchange was repeated five more times with fresh D₂O (5 × 5 cm³). Finally, the benzene was removed by distillation at

atmospheric pressure and the residual thiol was distilled under reduced pressure from a small amount of LiAlD₄ to give a colourless oil (bp 134–136 °C, 10 mmHg). ¹H-NMR spectroscopic analysis showed that the *S*-deuteriated dodecane-1-thiol contained ca. 96 atom% D by comparison of the C₁₁H₂₃CH₂SD resonance (δ_{H} 2.41, tt, ³J_{HH} 7.1, ³J_{HD} 1.1) with the C₁₁H₂₃CH₂SH resonance (δ_{H} 2.42, apparent q, ³J_{HH} > 7.3).

S-Deuteriated tri-*tert*-butoxysilanethiol and triisopropylsilanethiol were prepared by the same method and were shown to contain ca. 98% and 96% atom% D, respectively, by integration of the residual SiSH singlets at δ -0.01 and δ -0.77, respectively, against other peaks in the spectra. Bearing in mind the sensitivity to hydrolysis of Ph₃SiSH, the relative stability of (Bu^tO)₃SiSH/D and Pr₃SiSH/D towards D₂O at ca. 80 °C is remarkable.

Representative procedure for reduction of octyl halides

The response of the flame-ionisation detector was calibrated using mixtures of known amounts of authentic compounds and nonane as reference.

Admantane-1-thiol (8.4 mg, 0.05 mmol), triethylsilane (116 mg, 1.0 mmol), bromo-1-octane (147 mg, 0.76 mmol), nonane (90 μ l, added using a calibrated microsyringe) were successively introduced into an argon-filled 10 cm³ two-necked round-bottomed flask, containing a dry magnetic stirrer bar, and fitted with a condenser through which a very slow downward flow of argon was maintained. Cyclohexane (1.42 cm³) was then added so that, after addition of the initiator, the total volume of the reaction mixture would be 2.00 cm³ (assuming ideal mixing and neglecting thermal expansion of the solution). The side arm was closed with a self-sealing silicone rubber septum (Aldrich) and the flask was immersed in a thermostatically-controlled oil bath pre-heated to 60 °C. The mixture was stirred for 5 min to allow thermal equilibration to take place, before a 0.25 M solution of TBHN in cyclohexane (200 μ l, 0.05 mmol) was added to the mixture *via* the septum; this addition defined *t* = 0. Samples of the reaction mixture (10 μ l) were removed at 3–5 min intervals and quenched by dilution with ice-cold dry hexane (100 μ l) in a small sample tube closed with a septum. These solutions were then analysed by GLC to give the results listed in Table 1.

Representative procedure for H/D exchange experiments

Triphenylsilanethiol (ca. 12.3 mg, 0.042 mmol), Et₃SiD (ca. 36.6 mg, 0.312 mmol), hexamethyldisiloxane (ca. 5 μ l) and TBHN (ca. 42.5 μ l of a 0.20 M solution in cyclohexane-*d*₁₂, 0.0085 mmol) were successively introduced at room temperature into a dry, argon-filled NMR tube closed with a self-sealing rubber cap. Cyclohexane-*d*₁₂ (ca. 550 μ l) was then added to make the total volume up to a 650 μ l calibration mark on the NMR tube. The rubber cap was replaced with a dry standard polypropylene cap, the solution was mixed thoroughly by shaking and an NMR spectrum was recorded at 25 °C, allowing the initial concentrations of the reagents to be determined accurately by integration of appropriate peaks using the silane as the primary standard. The probe temperature was then increased to 50 °C, without removing the sample from the spectrometer in order to reduce the time needed for re-shimming; we estimate that the sample temperature would reach 50 °C within 2–3 min. The progress of the reaction was then monitored every minute and the results are given in Table 4. Similar experiments at 40–60 °C were also used to determine the effective rate of initiation by thermal decomposition of TBHN (see Results section).

Representative procedure for racemisation of (*S*)-Bu^tMePhSiH

Admantane-1-thiol (6.7 mg, 0.040 mmol), (*S*)-Bu^tMePhSiH (142 mg, 167 μ l, 0.80 mmol) and cyclohexane (1.67 cm³) were successively introduced into an argon-filled 10 cm³ two-necked round-bottomed flask, containing a dry magnetic stirrer bar,

and fitted with a condenser through which a very slow downward flow of argon was maintained. The side arm was closed with a self-sealing silicone rubber septum and the flask was immersed in a thermostatically-controlled oil bath pre-heated to 60 °C. The mixture was stirred for 5 min to allow thermal equilibration to take place, before a 0.25 M solution of TBHN in cyclohexane (160 μ l, 0.04 mmol) was added to the mixture *via* the septum; this addition defined *t* = 0. Samples of the reaction mixture (10 μ l) were removed at 3 min intervals and quenched by dilution with ice-cold dry hexane (100 μ l) in a small sample tube closed with a septum. These solutions were then analysed by GLC to give the results listed in Table 5.

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