On the mechanism of "polarity reversal catalysis"—an *ab initio* study of hydrogen atom transfer between silane and methylthiyl radicals



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At the highest level of theory in this study (CCSD(T)/augcc-pVDZ//MP2/aug-cc-pVDZ), *ab initio* molecular orbital calculations predict that abstraction of hydrogen atom from silane (SiH₄) by methylthiyl radical (CH₃S[•]) proceeds with an energy barrier of 34.0 kJ mol⁻¹ and is endothermic by 18.3 kJ mol⁻¹.

It is some ten years since Roberts first reported that thiols effectively catalyse the reduction of a variety of alkyl halides by triethylsilane.¹ Since this first report, further work has demonstrated that thiol–silane mixtures are effective for the reduction of a variety of radical precursors² and some stereoselectivity has been observed through the use of chiral thiols.³ More recently, this methodology has been extended by Crich to include the use of selenol–stannane mixtures which can be generated *in situ* through the use of diphenyl diselenide.⁴

There has been some debate concerning the mechanistic details surrounding the thiol-silane "polarity reversal" mechanistic scheme. On the one hand Roberts has suggested that the inclusion of a thiol replaces a poor chain-propagating step involving silane [eqn. (1)] with a more efficient one involving

$$\mathbf{R}^{\bullet} + \mathbf{E}\mathbf{t}_{3}\mathbf{S}\mathbf{i}\mathbf{H} \longrightarrow \mathbf{R}\mathbf{H} + \mathbf{E}\mathbf{t}_{3}\mathbf{S}\mathbf{i}^{\bullet} \tag{1}$$

thiol (step 1, Scheme 1). The significantly greater efficiency



Scheme 1

demonstrated by thiols as hydrogen donors in alkyl radical reductions, with rate constants ($k_{\rm H}$) of 10⁶–10⁷ M⁻¹ s⁻¹ as compared with the analogous reactions involving triethylsilane ($k_{\rm H}$ *ca.* 600 M⁻¹ s⁻¹),^{5,6} has been attributed to favourable polar effects in the "polarity reversal" transition state **2** over the less favourable transition state **1**.² Zavitsas and Chatgilialoglu, on the other hand, suggest that the "concept of polarity reversal does not appear necessary" to explain the relative effectiveness of thiols on the basis of computer modelling studies.⁷

Regardless of the mechanistic origin of the rate constants for

$$\begin{bmatrix} \delta + & \delta - & \delta - \\ Et_3Si - - H - - R \end{bmatrix}^{\ddagger \bullet} \begin{bmatrix} \delta - & \delta + & \delta - \\ R'S - - H - - R \end{bmatrix}^{\ddagger \bullet}$$

$$1 \qquad 2$$

Table 1 Calculated important geometrical features of the transition state **3** involved in the transfer of hydrogen atom from silane (SiH_4) to methylthiyl radical (CH_3S')

SCF/DZP1.5481.831SCF/6-311G**1.5481.829	
MP2/DZP 1.539 1.759 MP2/6-311G** 1.534 1.761 MP2/cc-pVDZ 1.549 1.760 MP2/aug-cc-pVDZ 1.558 1.748 B3LYP/DZP 1.501 1.900 B3LYP/6-311G** 1.505 1.887	176.9 176.6 172.0 172.4 171.7 167.7 177.1 176.9

the transfer of hydrogen atom to carbon-centred radicals from thiols and silanes, the overall chain mechanism as first proposed² relies on the ability of thiyl radicals to abstract hydrogen atom from silanes (step 2, Scheme 1) in order to provide chain propagation. Roberts acknowledges that this reaction "could be thermoneutral or even slightly endothermic" and relies on favourable polar effects in the transition state to provide for a rapid exchange of hydrogen atom.³

The ability of thiyl radicals to abstract hydrogen atom from silanes to give silyl radicals rapidly enough and in sufficient concentration to ensure chain propagation was not clear to us. In order to provide insight into the mechanistic details surrounding "polarity reversal catalysis" in thiol–silane radical reductions, we began to explore the reaction of methylthiyl radical (CH₃S[•]) with silane (SiH₄) through the use of *ab initio* molecular orbital calculations.

Calculations were performed using the Gaussian 94 program⁸ using a previously published (valence) double-ζ pseudopotential (DZP) basis set supplemented with an additional set of polarisation functions,⁹ the 6-311G** basis set as well as the augmented and unaugmented polarisation double- and triple-ξ correlation consistent (cc-pVDZ, cc-pVTZ, aug-cc-pVDZ, augcc-pVTZ) bases reported recently by Dunning.¹⁰ Uncorrelated (SCF) as well as MP2, QCISD and CCSD(T) correlation methods were used in conjunction with the above-mentioned basis sets. Density functional (B3LYP)¹¹ are included for comparison. All structures were confirmed as either ground or transition state through vibrational frequency analysis.

The important geometric features of transition state **3** (Fig. 1, Scheme 2) are summarised in Table 1 while the calculated energy barriers for the forward (ΔE_1^{\dagger}) and reverse (ΔE_2^{\dagger}) reactions (Scheme 2) are listed in Table 2 together with the calculated enthalpy of reaction (ΔH) and the (imaginary) frequency associated with the reaction coordinate.

Inspection of Table 1 reveals that as the basis set is improved at the MP2 level of theory, the transition state **3** becomes "earlier" in the direction indicated in Scheme 2; the S–H_{TS} separation varies from about 1.54 Å (MP2/DZP) to 1.56 Å (MP2/ aug-cc-pVDZ), while the corresponding Si–H_{TS} distance is predicted to change from 1.83 Å to 1.75 Å as the basis set quality is improved. SCF and B3LYP calculations performed with the DZP and 6-311G** bases predict a significantly "later" struc-

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Table 2 Calculated energy barriers $(\Delta E_1^{\dagger}, \Delta E_2^{\dagger})$, ^{*a*} enthalpy $(\Delta H)^a$ for the reaction of silane (SiH₄) and methylthiyl radical (CH₃S'), and (imaginary) frequency $(v)^b$ associated with the reaction coordinate in transition state **3**

Method	ΔE_1^{\ddagger}	$\Delta E_1^{\ddagger} + ZPE^c$	ΔE_2^{\ddagger}	$\Delta E_2^{\ddagger} + ZPE^c$	ΔH	$\Delta H + ZPE^{c}$	ν
SCF/DZP	107.0	101.0	62.2	52.7	44.8	48.3	1836i
SCF/6-311G**	102.1	96.6	58.9	52.5	43.2	44.1	1824i
MP2/DZP	57.0	51.5	34.0	27.3	23.0	24.1	1427i
MP2/6-311G**	48.6	42.6	18.7	24.5	29.9	18.1	1334i
MP2/cc-pVDZ	46.6	40.2	30.1	22.7	16.5	17.5	1307i
MP2/aug-cc-pVDZ	32.1	26.3	21.2	14.3	26.3	10.9	1224i
MP2/cc-pVTZ//MP2/cc-pVDZ	31.2	(25.4)	20.6	(13.7)	10.6	(11.7)	
MP2/aug-cc-pVTZ//MP2/aug-cc-pVDZ	31.1	(25.2)	20.4	(13.5)	10.6	(11.7)	
QCISD/DZP//MP2/DZP	63.4	(57.9)	31.5	(24.8)	31.9	(33.1)	
QCISD/6-311G**//MP2/6-311G**	55.3	(49.3)	30.0	(35.8)	25.4	(13.6)	
CCSD(T)/DZP//MP2/DZP	57.5	(52.0)	29.5	(22.8)	28.0	(29.1)	
CCSD(T)/6-311G**//MP2/6-311G**	48.4	(42.4)	25.5	(31.3)	22.9	(11.1)	
QCISD/cc-pDVZ//MP2/cc-pVDZ	54.9	(48.5)	29.7	(22.3)	25.2	(26.2)	
CCSD(T)/cc-pDVZ//MP2/cc-pVDZ	48.0	(41.6)	25.5	(18.1)	22.5	(22.3)	
QCISD/aug-cc-pDVZ//MP2/aug-cc-pVDZ	42.3	(36.4)	20.9	(14.0)	21.4	(22.4)	
CCSD(T)/aug-cc-pDVZ//MP2/aug-cc-pVDZ	34.0	(28.1)	15.7	(8.7)	18.3	(19.4)	
B3LYP/DZP	41.5	36.0	8.6	2.3	32.9	33.7	590i
B3LYP/6-311G**	35.1	30.0	9.2	2.9	25.9	27.2	590i

^{*a*} Energies in kJ mol⁻¹. ^{*b*} Frequencies in cm⁻¹. ^{*c*} Zero-point vibrational energy correction. Values in parentheses are estimates based on ZPE corrections at the lower (optimised) level of theory.



Fig. 1 MP2/aug-cc-pVDZ optimised structure of transition state 3.



Scheme 2

ture for **3** consistent with the significant endothermicities $(\Delta H = 25.9-44.8 \text{ kJ mol}^{-1})$ predicted at these levels of theory.

Inspection of Table 2 reveals that the SCF calculations in this study, with forward and reverse energy barriers ($\Delta E_1^{\dagger}, \Delta E_2^{\dagger}$) of about 100 and 60 kJ mol⁻¹ respectively not only predict a reaction which lies substantially toward starting materials but are also kinetically unlikely in the direction required to sustain the "polarity reversal" mechanism depicted in Scheme 1. Interestingly, significant reductions in both ΔE_1^{\dagger} and ΔE_2^{\dagger} are observed upon inclusion of electron correlation and improvement in basis set quality. Forward barriers are between 25.2 (MP2/aug-cc-pVTZ//MP2/aug-cc-pVDZ + ZPE) and 51.5 kJ mol⁻¹ (MP2/DZP + ZPE), with reverse barriers lying in the range 8.7 (CCSD(T)/aug-cc-pVDZ//MP2/aug-cc-pVDZ + ZPE) to 34.0 kJ mol⁻¹ (MP2/DZP).

Importantly, at the highest level of theory (CCSD(T)/aug-ccpDVZ//MP2/aug-cc-pVDZ + ZPE), the transfer of hydrogen atom from silane to methylthiyl is predicted to be rapid ($\Delta E_1^{\ddagger} = 28.1 \text{ kJ mol}^{-1}$) and endothermic by 19.4 kJ mol⁻¹, while the smallest value of ΔH (10.6 kJ mol⁻¹) is predicted at the MP2/aug-cc-pVTZ//MP2/aug-cc-pVDZ level of theory. Given similar entropy terms for both forward and reverse reactions depicted in Scheme 2, these endothermicities translate into equilibrium constants of about 0.001 and 0.03 respectively.

In order to sustain the chain reaction depicted in Scheme 1, sufficient chain carrying silyl radicals need to be generated through abstraction of hydrogen atom by methylthiyl radical from silane. It is well established that trialkylsilyl radicals abstract halogen atom from alkyl halides with rate constants approximately two orders of magnitude greater than the corresponding reactions involving trialkylstannyl radicals; 12 chain reactions involving silanes should therefore be approximately as efficient as those involving stannanes with about 100 times less silyl radical present in solution. Given that thiols deliver hydrogen atom to alkyl radicals with rate constants at least as large as the analogous reactions involving trialkylstannanes,⁵ it seems reasonable to suggest that an equilibrium constant for the reaction depicted in Scheme 2 of somewhere between 0.01 and 0.001 or greater will lead to a sustainable chain reaction, especially under high silane concentrations; at the highest level of theory in this study, calculations predict that these conditions are indeed met.

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