

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

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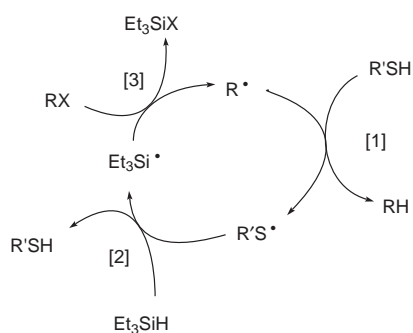
At the highest level of theory in this study (CCSD(T)/aug-cc-pVDZ//MP2/aug-cc-pVDZ), *ab initio* molecular orbital calculations predict that abstraction of hydrogen atom from silane (SiH₄) by methylthiyl radical (CH₃S[•]) proceeds with an energy barrier of 34.0 kJ mol⁻¹ and is endothermic by 18.3 kJ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



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_H) of 10^6 – 10^7 M⁻¹ s⁻¹ as compared with the analogous reactions involving triethylsilane (k_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 Chatgililoglu, 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

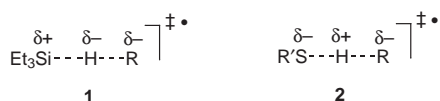


Table 1 Calculated important geometrical features of the transition state **3** involved in the transfer of hydrogen atom from silane (SiH₄) to methylthiyl radical (CH₃S[•])

Method	$r(S-H)/\text{\AA}$	$r(Si-H)/\text{\AA}$	$\theta(S-H-Si)^\circ$
SCF/DZP	1.548	1.831	176.9
SCF/6-311G**	1.548	1.829	176.6
MP2/DZP	1.539	1.759	172.0
MP2/6-311G**	1.534	1.761	172.4
MP2/cc-pVDZ	1.549	1.760	171.7
MP2/aug-cc-pVDZ	1.558	1.748	167.7
B3LYP/DZP	1.501	1.900	177.1
B3LYP/6-311G**	1.505	1.887	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 pseudo-potential (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- ζ correlation consistent (cc-pVDZ, cc-pVTZ, aug-cc-pVDZ, aug-cc-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^\ddagger) and reverse (ΔE_2^\ddagger) 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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