Homolytic Substitution at Sulfides and Sulfoxides: An *Ab Initio* Molecular Orbital Study

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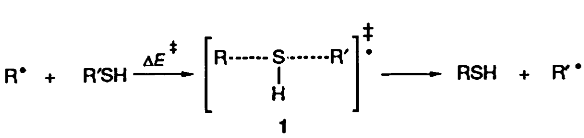
Ab initio molecular orbital calculations at the MP2/6-31G** level of theory predict that homolytic substitution by hydrogen atom and methyl radical at the sulfur atom in alkyl sulfides proceeds *via* T-shaped transition structures and in sulfoxides *via* hypervalent (9-S-3) radical intermediates.

Homolytic substitution by carbon-centred radicals at the sulfur and selenium atoms in alkyl sulfides and selenides is a topic of current interest to both synthetic[1] and theoretical[2,3] chemists. While this technique offers an effective entry point into a variety of sulfur- and selenium-containing heterocycles, there is still uncertainty concerning the reaction mechanism. It is generally agreed[4] that the reaction at sulfur proceeds *via* either a T-shaped transition structure or a radical intermediate in which the attacking and leaving groups adopt a co-linear arrangement.

Sulfuranyl radicals have been observed in EPR experiments,[5] but only when radical stabilizing groups are present on sulfur, and have been implicated in some radical rearrangement reactions.[6] Experiments using chiral sulfoxides have necessitated the inclusion of a single transition state or a transient intermediate in the reaction mechanism in order to explain the strict inversion of configuration observed.[7] *Ab initio* theoretical studies using moderate basis sets have, to date, failed to locate intermediates for homolytic substitution by alkyl radicals at alkyl sulfides[2] and selenides.†[3]



$$\mathrm{R}^{\bullet} + \mathrm{R'SH} \xrightarrow{\Delta E^{\ddagger}} \left[\mathrm{R}\cdots\cdots\underset{\mathrm{H}}{\underset{|}{\mathrm{S}}}\cdots\cdots\mathrm{R'}\right]^{\ddagger\,\bullet} \longrightarrow \mathrm{RSH} + \mathrm{R'}^{\bullet} \quad (1)$$

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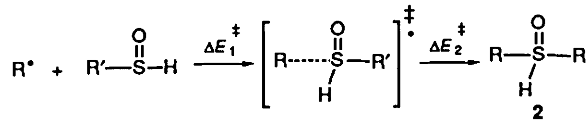

$$\mathrm{R}^{\bullet} + \mathrm{R'}\text{—}\overset{\mathrm{O}}{\overset{\|}{\mathrm{S}}}\text{—H} \xrightarrow{\Delta E_1^{\ddagger}} \left[\mathrm{R}\cdots\cdots\underset{\mathrm{H}}{\underset{/}{\overset{\mathrm{O}}{\overset{\|}{\mathrm{S}}}}}\text{—}\mathrm{R'}\right]^{\ddagger\,\bullet} \xrightarrow{\Delta E_2^{\ddagger}} \mathrm{R}\text{—}\underset{\mathrm{H}}{\underset{/}{\overset{\mathrm{O}}{\overset{\|}{\mathrm{S}}}}}\text{—}\mathrm{R'} \quad (2)$$

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In order to increase our understanding of homolytic substitution processes, we have examined the reaction of hydrogen atom and methyl radical with hydrogen sulfide, methanethiol, dihydrogen sulfoxide and hydrogen methyl sulfoxide using *ab initio* molecular orbital theory.

Ground and transition states were fully optimized in the usual way[9] using the 6-31G** basis set with the inclusion of electron correlation at the MP2 level[10] (MP2/6-31G**) within the GAUSSIAN 90 system of programs.[11] T-Shaped transition structures (**1**) were located for the homolytic substitution reactions involving sulfides [eqn. (1)], while hypervalent intermediates (**2**) were located for sulfoxides [eqn. (2)], and are displayed in Fig. 1. The evaluation of the complete set of harmonic frequencies in each case, except **8** which was a task beyond our current resources, proved that these structures do indeed correspond to the correct stationary point. It is interesting to note that **6**, **7** and **8** are transition structures in the absence of electron correlation, reinforcing the importance of the inclusion of correlation in this study. The MP2/6-31G**-calculated activation energies for the reactions involving sulfides are listed in Table 1, while similar data for sulfoxides are listed in Table 2.

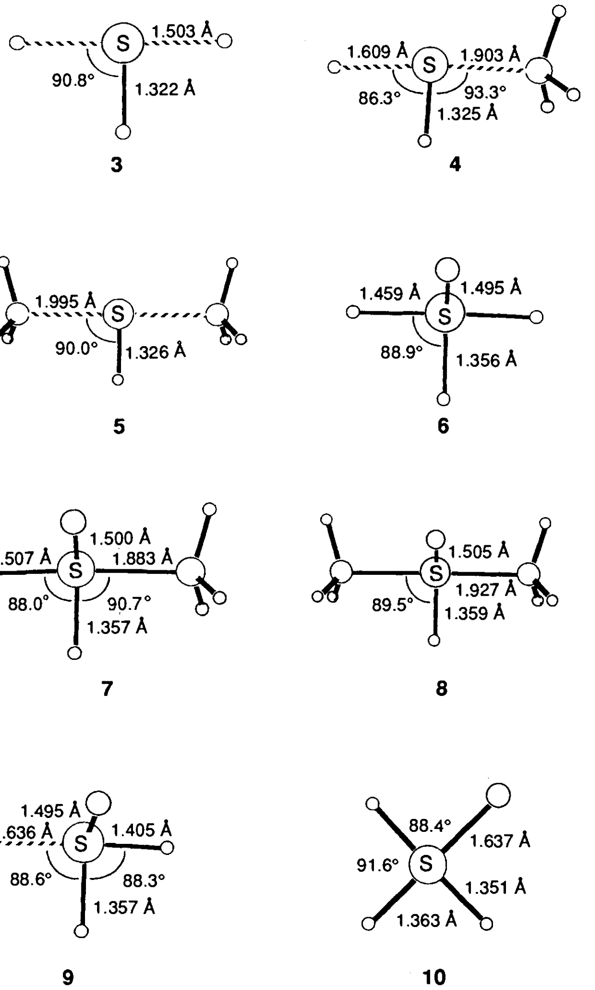

Fig. 1 MP2/6-31G**-calculated structures involved in homolytic substitution at sulfides and sulfoxides

Inspection of Fig. 1 reveals that the transition structures **3**–**5** are indeed T-shaped as expected and correspond favourably with the 4-31G* data of Ferris and Franz.[2] The calculated activation energies ($\Delta E^{\ddagger}$) (Table 1) are approximately 5–10 kJ mol^{-1} higher than for the corresponding attack at alkylselenides[3] and, as expected, depend on the nature of both the attacking and leaving radicals.

Our calculations predict that attack by hydrogen atom at the sulfur atom in dihydrogen sulfoxide leads to the formation

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† An intermediate has been located[8] at the MP2/3-21G(*) level of theory for the reaction of hydrogen atom with aminoselenol (NH_2SeH).

Table 1 MP2/6-31G**-calculated activation energies ($\Delta E^{\ddagger}$)[a] for homolytic substitution at alkyl sulfides [eqn. (1)]

Substituent			
R	R′	Transition structure	$\Delta E^{\ddagger}$/kJ mol^{-1}
H	H	**3**	64.9
H	CH_3	**4**	52.7
CH_3	H	**4**	95.8
CH_3	CH_3	**5**	81.2

[a] MP2/6-31G** energy of transition structure less MP2/6-31G** ground state energies.

Table 2 MP2/6-31G**-calculated reaction profiles[a] for the formation of the radicals **6**–**8** in this study [eqn. (2)]

Substituent				
R	R′	Intermediate	$\Delta E_1^{\ddagger}$/kJ mol^{-1}	$\Delta E_2^{\ddagger}$/kJ mol^{-1}
H	H	**6**	59.8	−2.5
H	CH_3	**7**	58.6	−0.3
CH_3	H	**7**	57.7	−4.5
CH_3	CH_3	**8**	61.9	−0.8

[a] MP2/6-31G** energy of transition structure less MP2/6-31G** ground state energies.

of the radical intermediate **6**. Extensive searching of the MP2/6-31G**-calculated H_3SO potential energy surface failed to locate any radical intermediate other than **6**. Fig. 1 reveals that **6** is trigonal bipyramidal in which the attacking and leaving groups occupy axial positions and the hydrogen, oxygen and unpaired electron occupy the equatorial positions. The activation energy ($\Delta E_1^{\ddagger}$) (Table 2) for the formation of **6** is calculated to be 59.8 kJ mol^{-1}. Single point MP4/6-31G**//MP2/6-31G** correction reduces this barrier to 54.8 kJ mol^{-1}. The transition state (**9**) for the formation of **6** is calculated to be product-like with axial sulfur–hydrogen separations of 1.405 and 1.636 Å; the remaining distances and angles are very similar to those in **6**.

Interestingly, **6** is calculated to lie in a very shallow energy well, being only 2.5 kJ mol^{-1} ($\Delta E_2^{\ddagger}$) below the transition state for its formation. Indeed, single point MP4/6-31G**//MP2/6-31G** calculations provide further support for the existence of a shallow well. At this level of theory **6** is calculated to lie 2.9 kJ mol^{-1} below the transition state **9**.

Having established that permutational isomerism of **6** is unlikely at the MP2/6-31G** level of theory, the transition state **10** for inversion of the sulfur centre was located. This process corresponds to racemization when chiral sulfoxides are used in homolytic substitution. As expected, Fig. 1 reveals that **10** is square planar. The energy barrier for inversion of **6** is calculated to be 64.1 and 43.5 kJ mol^{-1} at the MP2/6-31G** and MP4/6-31G**//MP2/6-31-G** levels respectively. Clearly then, **6** is unlikely to undergo inversion prior to dissociation.

Fig. 1 also indicates that the remaining structures in this study (**7**, **8**) are also trigonal bipyramidal in nature. The MP2/6-31G**-calculated activation energies for the formation of the intermediates in this study are all calculated to lie in the range 57–62 kJ mol^{-1}. Our data suggest that **7** and **8** also lie in shallow energy wells, the deepest being only 0.8 kJ mol^{-1} below the transition state for its formation.

When zero-point vibrational energies are taken into account within the MP2/6-31G** framework, structure **6** is predicted to lie 4.3 kJ mol^{-1} *above* the energy of **9**, while transition structure **7** is calculated to be contained within a shallow well with energy barriers of 0.2 and 4.4 kJ mol^{-1} for dissociation with loss of methyl radical and hydrogen atom respectively. Clearly then, the intermediates **6**–**8** are likely to behave much more like transition structures than intermediates, especially at room temperature. It is unlikely, therefore, that chiral sulfoxides involved in homolytic substitution would undergo racemization, a prediction in keeping with experimental observation.[7]

We are currently investigating other homolytic substitution processes by molecular orbital theory.

Acknowledgements

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