On the Stability of Trivalent Chalcogen Radicals—A Pseudopotential Study of Homolytic Substitution by a Methyl Radical at Methanethiol, Methaneselenol and Methanetellurol

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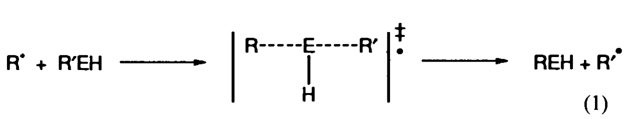
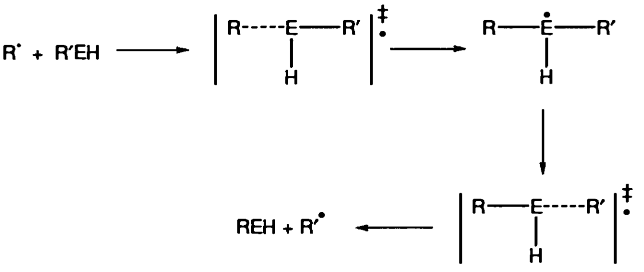
Ab initio molecular orbital theory using pseudopotential basis sets and electron correlation predict that homolytic substitution by a methyl radical at sulfur and selenium proceeds *via* symmetrical transition states with barriers of 87.9 and 63.1 kJ mol^{-1} respectively; the similar reaction at tellurium is predicted to proceed *via* a symmetrical intermediate which lies 23.5 kJ mol^{-1} above reactants.

Homolytic substitution by carbon centred radicals at sulfur and selenium atoms in alkyl sulfides and selenides is a topic of current interest to both synthetic[1-11] and theoretical[1,12-15] chemists. Although this technique offers an effective entry point into a variety of selenium and sulfur containing heterocycles, there is still some uncertainty concerning the reaction mechanism. It is generally agreed that the reaction at both sulfur and selenium proceeds *via* either a T-shaped transition structure [eqn. (1)] or a transient intermediate [eqn. (2)] in which



(1)



(2)

the attacking and leaving groups adopt a near collinear arrangement.[10,16]

Until recently it was believed that intermediates are formed only when radical stabilising groups are attached to the central chalcogen;[5,6] however, recent high-level calculations performed in our group[17] on λ^4-sulfanyl (SH_3), λ^4-selanyl (SeH_3) and λ^4-tellanyl (TeH_3) radicals indicate that all three of these molecules form stable intermediates in contrast to earlier less rigorous studies by both ourselves and other researchers.[1,12,13,15] Our recent study showed that basis sets of triple-ζ quality and very high levels of theory such as QCI methods are often necessary to determine conclusively the nature of stationary points[17] bringing into question the results of a large number of earlier theoretical calculations on related systems using basis sets of double-ζ quality at the MP2 level of theory.

Calculations using rigorous all-electron methods for all but the smallest of these systems are beyond the resources of most research groups; however, pseudopotential basis sets offer an effective alternative with an associated reduction in processor time and disk requirements while providing results which have been found to be at least as reliable as triple-ζ basis sets for both chalcogen trihydrides as well as for a large number of organo-group 16 compounds.[17,18] For this reason and in light of our unexpected results for the EH_3 species,[17] we chose to examine further the nature of the potential energy surfaces of the dimethyl-λ^4-chalcogenyl radicals $(CH_3)_2EH$ (where E = S, Se and Te) with the aim of providing insight into the mechanism of homolytic substitution chemistry.

Table 1 Calculated energies of the structures in this study

Structure	Energy[a] SCF	MP2	QCISD
CH_3	−39.571 764	−39.697 165	−39.718 834
CH_3SH	−50.117 133	−50.394 184	−50.429 439
CH_3SeH	−49.227 174	−49.493 656	−49.526 939
CH_3TeH	−48.047 440	−48.299 297	−48.331 808
1	−89.640 425	−90.057 880	−90.114 342
2	−88.762 027	−89.166 790	−89.221 798
3	−87.593 162	−87.986 818	−88.039 633
4	—	−87.985 140	−88.040 269

[a] Energy in Hartree (E_h) (1 E_h = 2626 kJ mol^{-1}).

Calculations were performed on a Cray Y-MP supercomputer and Sun Sparcstation 10/512 using the Gaussian 92 program.[19] All calculations were performed using the pseudopotential basis set of Hay and Wadt[20-22] for the chalcogens and the DZ basis set of Dunning and Huzinaga for carbon and hydrogen.[23] A single set of d-type polarisation functions was added to the basis set for S, Se, Te and C (exponents 0.60, 0.38, 0.30 and 0.75 respectively) while the H basis set was supplemented with a set of p-type polarisation functions (exponent 1.00). Spin contamination does not appear to be a problem since values for $\langle S^2 \rangle$ never exceeded 0.82 before annihilation of quartet contamination. Ground and transition states were fully optimised at both the SCF and MP2 levels of theory. Vibrational frequencies were calculated numerically from analytical first derivatives at the same levels of theory. Further energy refinements were carried out as single point calculations using the MP2 optimised geometries at the QCISD level of theory. Molecular energies are reported in Table 1.

At the SCF level of theory dimethyl-λ^4-sulfanyl (**1**) was found to be of C_{2v} symmetry in agreement with our earlier work using all-electron basis sets at the same level of theory.[14] Structure **1** was found to lie 127.3 kJ mol^{-1} (see Table 2) above methanethiol and methyl radical, vibrational frequency calculations showed that **1** is a transition state on the C_2H_7S potential energy surface (the asymmetric S–C stretching frequency was calculated to be 684i cm^{-1}) which collapses to methanethiol and methyl radical. At the MP2 level of theory **1** bends to a structure of C_s symmetry (see Fig. 1) with a dihedral angle of 158.0°. As was found at the SCF level of theory, a single imaginary frequency (430i cm^{-1}), indicative of a transition state, was predicted using MP2 theory.

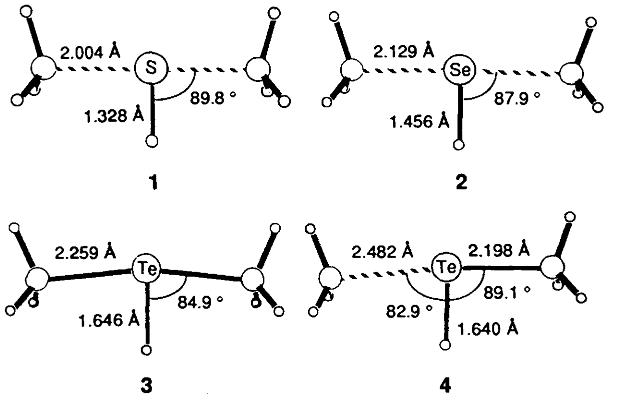


Fig. 1 Calculated transition states and intermediates involved in the homolytic substitution of a methyl radical at methanethiol, methaneselenol and methanetellurol

Table 2 MP2 Calculated differences in energy (ΔE) between reactants and the symmetrical dimethyl-λ^4-chalcogenyl species (**1**–**3**) involved in homolytic substitution of a methyl radical at methanethiol, methaneselenol and methanetellurol and the asymmetric stretching frequency (ω) of the dimethyl-λ^4-chalcogenyl species

	SCF		MP2		QCISD
Molecule	ΔE	ω	ΔE	ω	ΔE
1	127.3	684i	87.9	430i	89.1
2	96.9	491i	63.1	257i	63.0
3	68.4	395i	25.3	115	27.2

[a] Energy difference in kJ mol^{-1}, vibrational frequencies in cm^{-1}.

It is of some note that the difference between the SCF and MP2 skeletal asymmetric stretching frequencies is much smaller than was observed for SH_3[17] suggesting that vibrational frequencies for this structure are far less sensitive to changes in the level of theory. The energy barrier for homolytic substitution was found to be 87.9 kJ mol^{-1} at the MP2 level of theory compared to 81.2 kJ mol^{-1} from our earlier work using MP2/6-31G**;[14] further increasing the level of theory to QCISD (at the MP2 geometry) has little effect on this value (89.1 kJ mol^{-1}).

Dimethyl-λ^4-selanyl (**2**) was also found to be of C_{2v} symmetry at the SCF level of theory which is again in agreement with our earlier calculations using all-electron basis sets at the same level of theory.[13] Vibrational frequency calculations showed that this species, like its sulfur counterpart, is a transition state for the homolytic substitution of a methyl radical at methaneselenol with expulsion of a methyl radical. Structure **2** was found to lie 96.9 kJ mol^{-1} above the reactants at the SCF level of theory. At the MP2 level of theory **2** was found to be of C_s symmetry. The asymmetric skeletal stretching frequency became less imaginary at the higher level of theory (257i cm^{-1}). QCISD single point calculations reduce the barrier to 63.0 kJ mol^{-1} at the QCISD level of theory. This value is to be compared with the predicted barrier of 67.8 kJ mol^{-1} from our earlier work[13] using an all-electron basis set at the MP4 level of theory.

At the SCF level of theory dimethyl-λ^4-tellanyl (**3**) is found to behave in a similar manner to its group 16 counterparts; it is of C_{2v} symmetry and has a single imaginary vibrational frequency (395i cm^{-1}). When MP2 is included **3** is again found to bend to a structure of C_s symmetry. In this case however vibrational analysis shows this molecule to be a local minimum (*i.e.* the vibrational frequencies are all real) on the potential energy surface, this species lies only 25.3 kJ mol^{-1} above methanetellurol and the methyl radical. At the QCISD level of theory this value is increased slightly to 27.2 kJ mol^{-1}.

Since **3** is predicted to be a stable compound at the MP2 level of theory the transition state to its formation was located. This structure (**4**) was found to be of C_1 symmetry (imaginary frequency at 265i cm^{-1}) and to lie 29.7 kJ mol^{-1} above reactants and 4.4 kJ mol^{-1} above **3**. QCISD single point calculations using the MP2 optimised geometry predict that **4** is of lower energy than the ground state by some 1.2 kJ mol^{-1}. Since the transition state geometry for the EH_3 series of structures is known to change substantially when the level of theory is improved,[17] it is likely that the geometry of **3** and **4** need to be optimised using QCISD for reliable data to be obtained at this level of theory. Unfortunately this is a task beyond our current resources.

In summary, high-level calculations using pseudopotential basis sets predict that unlike the parent λ^4-chalcogenyl radicals (EH_3), dimethyl-λ^4-sulfanyl (**1**) and dimethyl-λ^4-selanyl (**2**) radicals are transition states on the reaction pathway for homolytic substitution of the methyl radical at methanethiol and methaneselenol, while dimethyl -λ^4-tellanyl (**3**) is found to correspond to a transient intermediate. These data support the conclusions arrived at in earlier less rigorous calculations and serve to clarify mechanistic details of homolytic substitution chemistry. Further calculated and experimental data will be presented in due course.

Acknowledgements

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