Theoretical Insights into Novel *Telluro*-ketones

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Abstract:

Telluroformaldehyde ($H_2C=Te$), silanetellone ($H_2Si=Te$) and germatellone ($H_2Ge=Te$) are novel heavy congeners of formaldehyde commonly known as *telluro*-ketones. Knowledge of the properties of such compounds is significant for a better understanding of the contribution of heavier main group elements in organometallic chemistry, and the ability of such ketones to form complexes of bio-organometallic importance. In 1983, telluroformaldehyde ($H_2C=Te$), was first stabilized by coordination to transition-metal centers but the synthesis and isolation of tellurium containing heavy ketones are still elusive. Following our interest in *telluro*-ketones, we reported the structures and energetics of $X_2E=Te$ and $XYE=Te$ (E=C and Si and X, Y=H, F, Cl, Br, I and CN) molecules, but their stabilities have always been questioned. Thus, in order to diminish the skepticism of experimental communities, thermodynamic and kinetic stabilities of the mentioned *telluro*-ketones have been endeavored using state-of-the-art computations. Moreover, a careful attempt has been made to study the stabilization of the E=Te double bond using bulky substituents such as 2,4,6-triisopropylphenyl (Tip) and the Lewis donor-acceptor ligands. The findings of this research work should serve as a good reference for the scrutinized novel *telluro*-ketones and also assist their synthesis and applications in future.

Keywords: Telluro-ketones, Energetics, Structures and Stabilities

1.0 Introduction

- Molecules containing a double bond between heavier group 14 and chalcogen atoms are commonly known as heavy ketones.

- $R_2C=O$, are important organic molecules in industry and biology, but their homologues, the heavy ketones, $R_2A=E$ (A=C, Si and Ge, E=S, Se and Te), have not yet been isolated as stable monomeric molecules.

- Some of the heavy ketones ($R_2A=E$) with a terminal heavier Group 16 element, have been synthesized [1-9], through the attachment of the bulky 2,4,6-tris(bis(trimethylsilyl)methyl)phenyl and 2,6-bis(bis(trimethylsilyl)methyl)-4-(tris(trimethylsilyl)methyl)phenyl groups to the Group 14 elements.

- Moreover, homologous monomeric heavy ketones with an oxygen atom remained elusive until recently [10,11].

- The unavailability of many $R_2A=E$ species, as monomeric molecules is sometimes ascribed to their strong tendency for intermolecular oligomerization via opening of the A=E double bond or isomerization into singly-bonded molecules or decomposition into simpler entities.

- Might not the isolation of monomeric *telluro*-ketones be encouraged by studying their relative energetics on the pertinent potential energy surfaces (PES)?

2.0 Objectives of this research

The objectives of the research are to study the:

1) nature of the reactants, products and transition states of the unimolecular isomerization and decomposition reactions.
2) structural geometries and the spectroscopic parameters (vibrational frequencies) of different isomers.
3) feasibility of both the1,2-hydrogen shift and 1,1-hydrogen elimination reactions of the H_2A=Te (A=C, Si and Ge) molecules.
4) energetics to determine the most stable ground state.
5) comparison with literature of corresponding lighter chalcogen analogs.
6) optimization of some *telluro*-ketones attached to bulky substituents such as 2,4,6-triisopropylphenyl (Tip) [8] and the Lewis donor-acceptor ligands [11].

3.0 Methodology

The isomerization and decomposition reactions of $H_2A=Te$ and $HFA=Te$ (A=C, Si and Ge) systems have been studied using the second order Møller-Plesset perturbation theory (MP2) [12] in conjunction with the double-ζ basis sets with polarization and diffuse functions, denoted as DZP++, for all atoms except for tellurium, where the LANL2DZdp ECP [13-15] basis sets were employed.

Complex molecules attached to the mentioned bulky substituents are optimized using the density functional theory (DFT) at BP86 [16,17]and the def2-SVP [18] basis sets.

All the molecules were fully optimize independently in the gas phase and vibrational frequency analyses were performed to assess the nature of the stationary points of the optimized structures.

4.0 Results and Discussion

3.1 H_2A=Te (A=C, Si and Ge) Isomerization and Decomposition Reactions

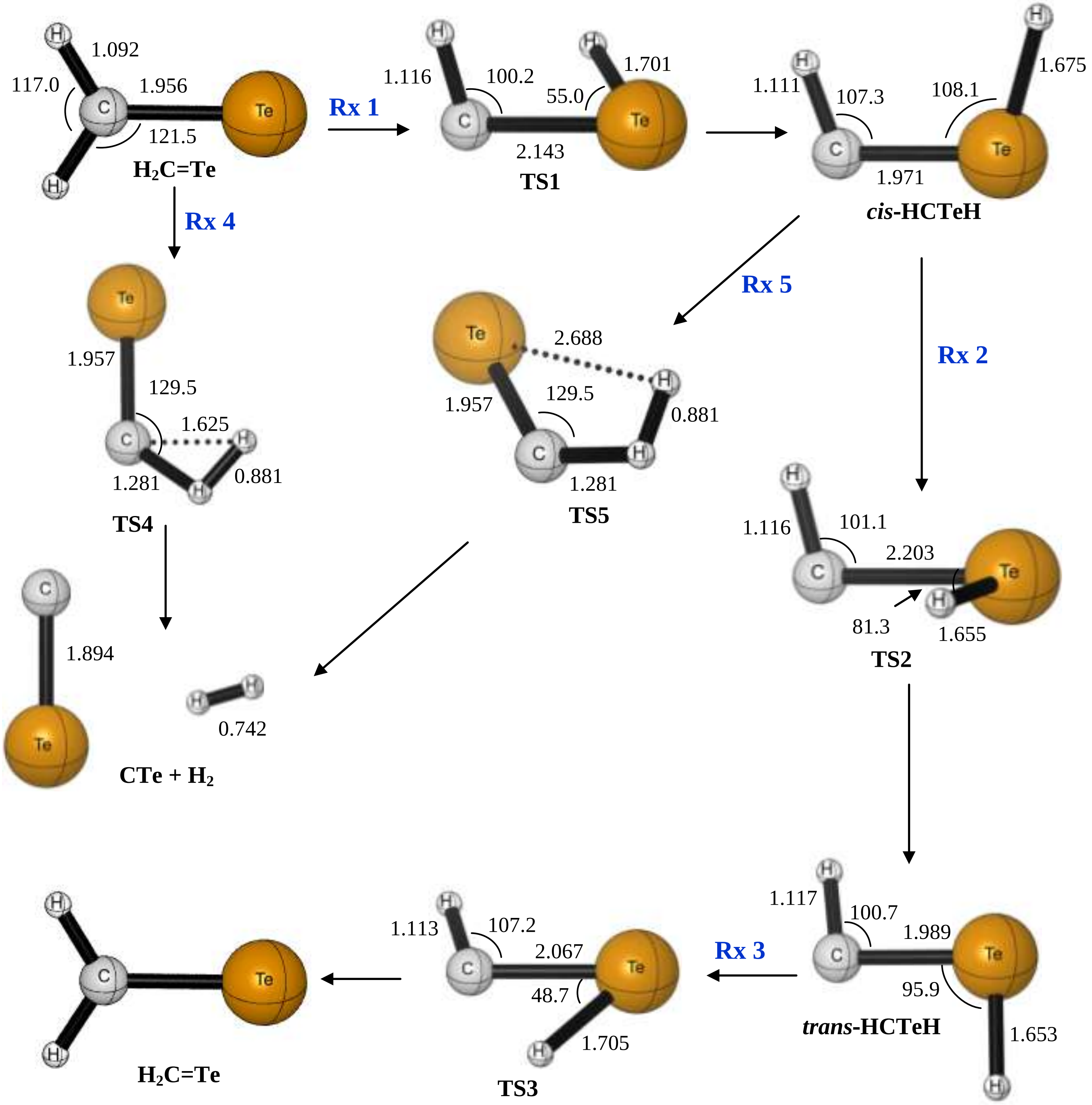


Figure 1: Optimized geometries (bond lengths and bond distances in Å and bond angles in °) of H_2CTe isomers and decomposition products

- 5 different reactions have been considered, namely, **Rx 1**: *keto*- to *cis*-, **Rx 2**: *cis*- to *trans*-, **Rx 3**: *trans*- to *keto*-, **Rx 4**: *keto*- to H_2 + XTe and **Rx 5**: *cis*- to H_2 + ATe.

- The optimized geometries for the H_2C=Te molecule, the intermediates and the transition states of the above mentioned reactions channels are depicted in Figure 1.

- Figures 2-4 illustrate the energies including zero-point corrections relative to the H_2A=Te (A=C, Si and Ge) molecules, for the four minima and the five transition states on the singlet potential energy surface.

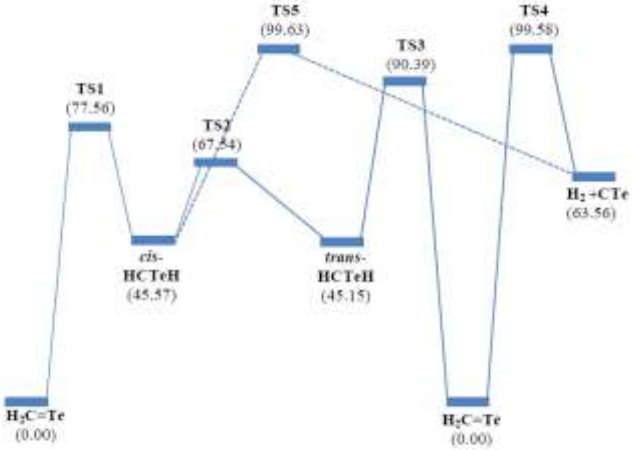


Figure 2: Sketch of the potential energy surface for the unimolecular reactions of H_2C=Te. Relative energies (kcal/mol) are in parentheses.

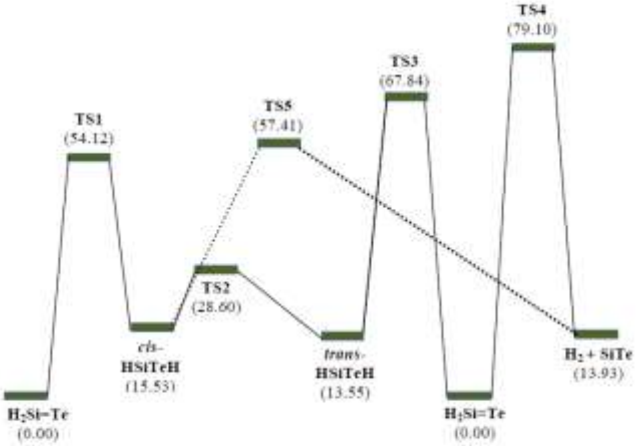


Figure 3: Sketch of the potential energy surface for the unimolecular reactions of H_2Si=Te. Relative energies (kcal/mol) are in parentheses.

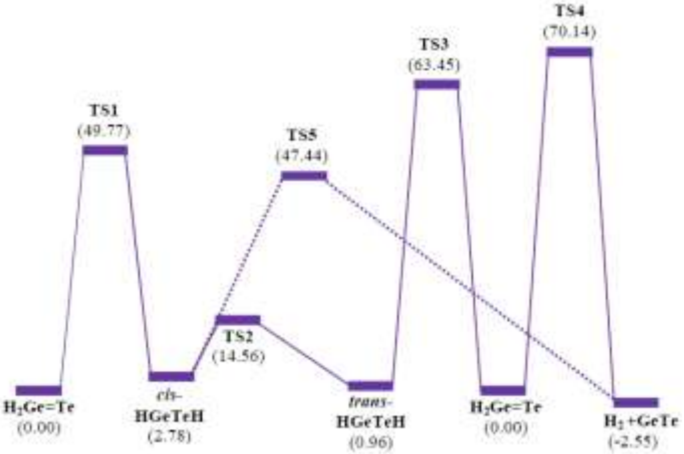
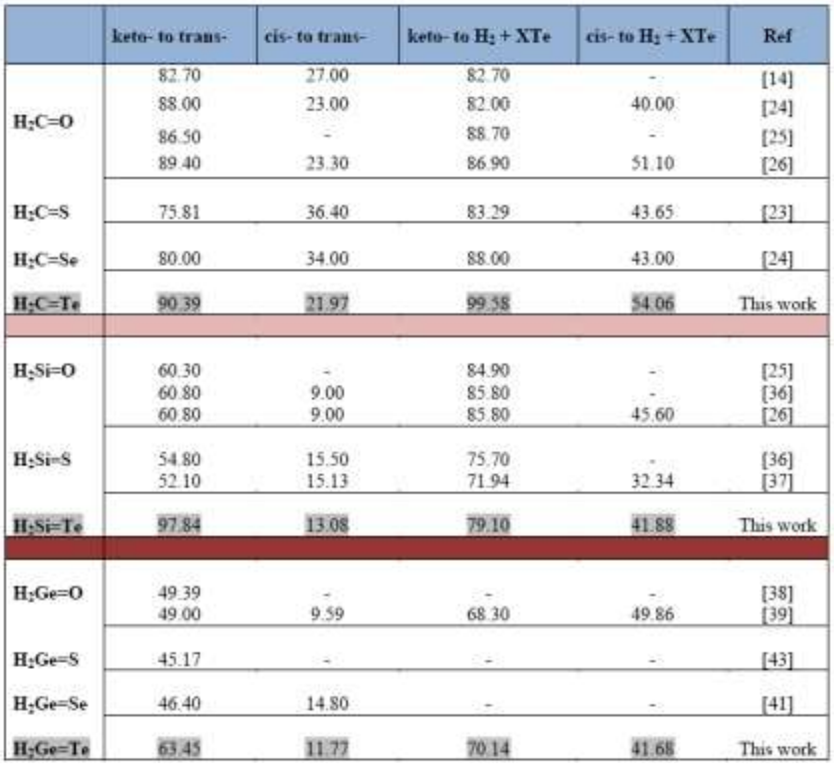


Figure 4: Sketch of the potential energy surface for the unimolecular reactions of $H_2Ge=Te$. Relative energies (kcal/mol) are in parentheses.

- Predicted activation energies (kcal/mol) for the unimolecular reactions of $H_2A=E$ (A=C, Si and Ge, E=O, S, Se and Te) are reported in Table 1.

Table 1: Predicted Activation Energies (kcal/mol) for the Unimolecular Reactions of $H_2A=Te$ (X=C, Si and Ge) and Comparison with the Literature for Some Analogous Compounds.



	keto- to trans-	cis- to trans-	keto- to $H_2 + XTe$	cis- to $H_2 + XTe$	Ref
$H_2C=O$	82.70	27.00	82.70	-	[14]
	88.00	23.00	82.00	40.00	[24]
	86.50	-	88.70	-	[25]
	89.40	23.30	86.90	51.10	[26]
$H_2C=S$	75.81	36.40	83.29	43.65	[23]
$H_2C=Se$	80.00	34.00	88.00	43.00	[24]
$H_2C=Te$	90.39	21.97	99.58	54.06	This work
$H_2Si=O$	60.30	-	84.90	-	[25]
	60.80	9.00	85.80	-	[36]
	60.80	9.00	85.80	45.60	[26]
$H_2Si=S$	54.80	15.50	75.70	-	[36]
	52.10	15.13	71.94	32.34	[37]
$H_2Si=Te$	97.84	13.08	79.10	41.88	This work
$H_2Ge=O$	49.39	-	-	-	[38]
	49.00	9.59	68.30	49.86	[39]
$H_2Ge=S$	45.17	-	-	-	[43]
$H_2Ge=Se$	46.40	14.80	-	-	[41]
$H_2Ge=Te$	63.45	11.77	70.14	41.68	This work

- On going from the A=C to A=Ge, **H_2A=Te** can easily interconvert into the singly-bonded isomers; consistent with the activation energies for the corresponding reactions of H_2A=E (A=C, Si and Ge; E=O, S and Se) reported in Table 1.

- ***Trans*−HATeH** conformer is found to be always energetically preferred to ***cis*−HATeH**, and the relative stability increases steadily from A=C to A=Ge.

- Isomerization into singly-bonded molecules is more favored in the case of the germanium analogs. The factors governing this effect are:
    - Ge can easily accommodate a lone pair to form ***cis*-HGeTeH** and ***trans*-HGeTeH**.
    - Second, the polarity of the A-Te bond in H_2A=Te molecules, increases significantly from A=C to A=Ge as shown by the electrostatic potential maps depicted in Figure 5. Therefore Te is more reluctant to form double bonds with carbon than with germanium.

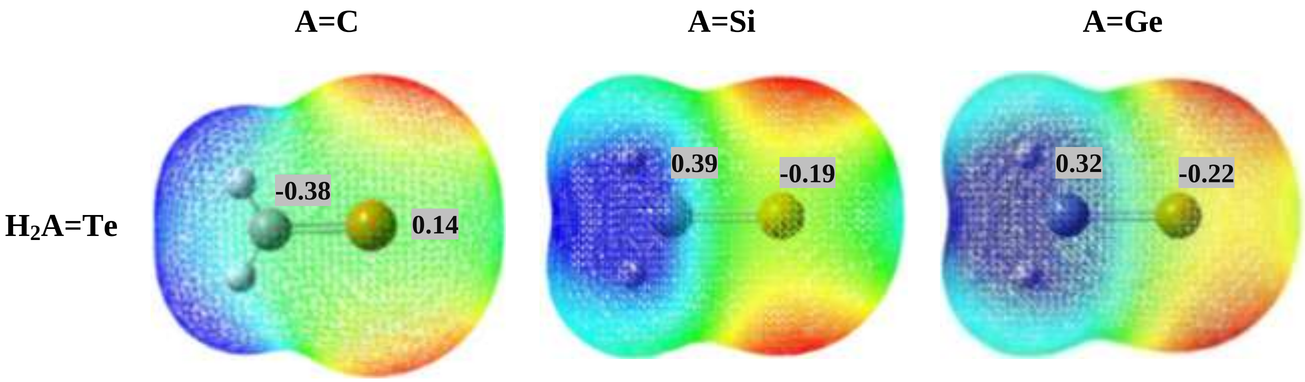


Figure 5: Electrostatic potential maps of H_2A=Te (A=C, Si and Ge). Blue and red regions represent positive and negative potentials, respectively. Mulliken Charges on atoms A and Te are reported.

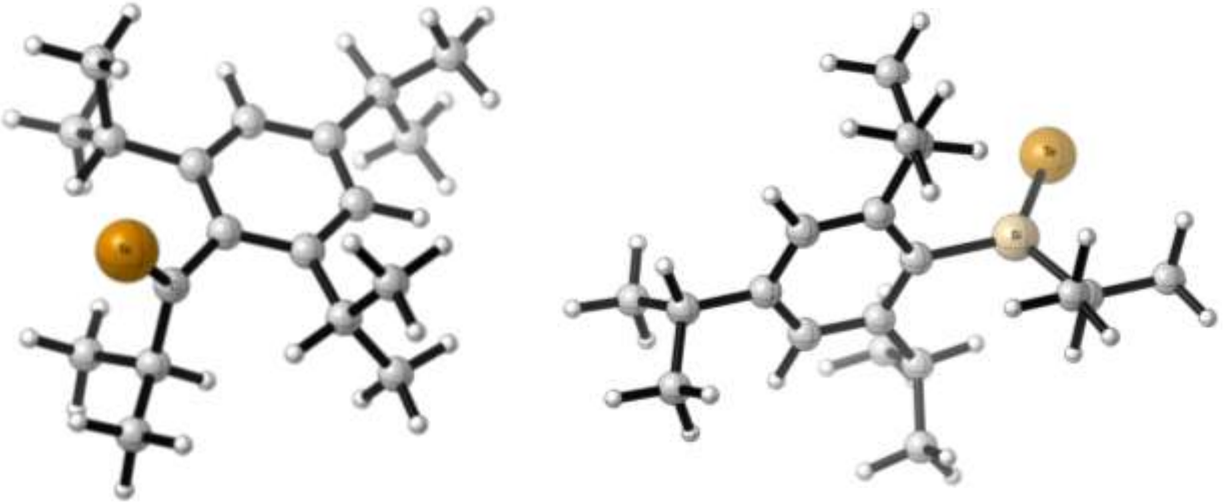
- The feasibility of most of the isomerization and decomposition reactions of the H_2A=Te and HFA=Te molecules follow the trend A=C < A=Si < A=Ge.

- **H_2A=Te** can be classified as viable molecules since they have no imaginary frequencies and their lowest vibrational frequencies is always > 100cm^{-1}.

- Moreover, the high activation energies involved indicate that *telluro*-ketones found more resistant towards the unimolecular reactions than their corresponding lighter chalcogen analogs.

3.2 Optimized Complexes of *Telluro*-ketones.

Monomeric *telluro*-ketones with A=Te double bond (A=C, Si), attached to the bulky substituents namely; 2,4,6-triisopropylphenyl (Tip) and the Lewis donor-acceptor ligands have been successfully optimized. The optimized structures are illustrated in Figures 6



$(CH_3)_2CH(Tip)C{=}Te$

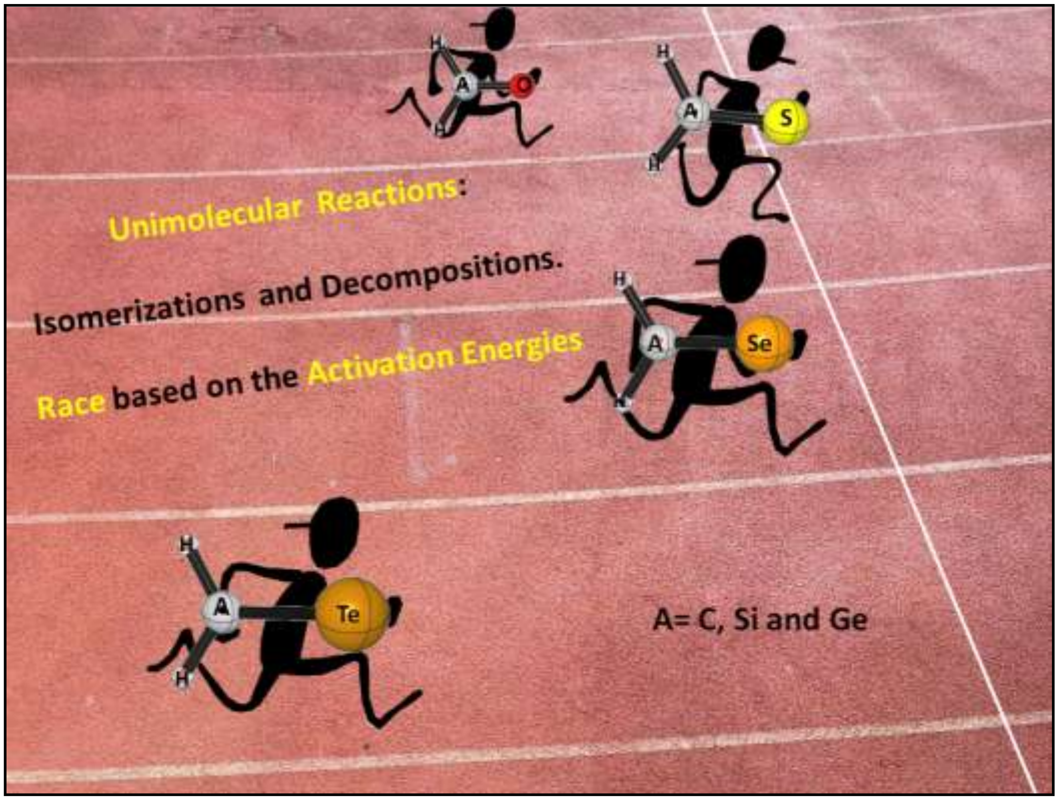
$(CH_3)_2CH(Tip)Si{=}Te$

Figure 6: Optimized structures of $(CH_3)_2CH(Tip)A{=}Te$, A=(C and Si).

4.0 Conclusions

- H_2A=Te (A=C, Si and Ge) can be classified as viable molecules

- *Telluro*-ketones are found to be kinetically and thermodynamically more stable than their corresponding lighter chalcogen analogs.



Future work:

1) Optimisation the monomeric *telluro*-ketones with the even bulkier substituents such as 1,1,3,3,5,5,7,7-octaethyl-s-hydrindacen-4-yl (Eind).
2) Calculating bond dissociation energies to assess the stabilities of $(CH_3)_2CH(Tip)A{=}Te$, $IPr.A(H_2){=}Te.B(C_6F_5)_3$, and $(Eind)_2A{=}Te$, A=(C, Si and Ge) molecules.
3) Analyzing structural and spectroscopic data.
4) Performing NBO analysis.
5) Calculating the HOMO-LUMO gap and studying the Kohn-Sham frontier orbitals.
6) Critical analysis and discussion of the results obtained.

7) Comparison with literature of lighter chalcogen analogs

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5.0 References

1. Tokitoh, N.; Matsumoto, T.; Okazaki, R. *Bull. Chem. Soc. Jpn*. **1999**. *72*, 1665.
2. Okazaki, R.; Tokitoh, N. *Acc. Chem. Res*. **2000**, *33*, 625.
3. Tokitoh, N.; Okazaki, R. The Chemistry of Organic Germanium, Tin and Lead Compounds, **2002** (Wiley), *2* (ed. Rappoport, Z.), 843.
4. Tokitoh, N.; Matsumoto, T.; Manmaru, K.; Okazaki, R. *J. Am. Chem. Soc.* **1993**, *115*, 8855.
5. Suzuki, H.; Tokitoh, N.; Nagase, S.; Okazaki, R. *J. Am. Chem. Soc*. **1994**, *116*, 11578.
6. Saito, M.; Tokitoh, N.; Okazaki, R. *J. Am. Chem. Soc.* **1997**,*119*, 11124.
7. Suzuki, H.; Tokitoh, N.; Okazaki, R.; Nagase, S.; Goto, M. *J. Am. Chem. Soc*. **1998**, *120*, 11096.
8. T. Matsumoto, N. Tokitoh, R. Okazaki, *J. Am. Chem. Soc.*, **1999**, *121*, 8811.
9. Iwamoto, T.; Sato, K.; Ishida, S.; Kabuto, C.; Kira, M. *J. Am. Chem. Soc*. **2006**, *128*, 16914.

10. Li, L.; Fukawa,T.; Matsuo, T.; Hashizume, D.; Fueno, H.; Tanaka, K.; Tamao, K. *Nature Chem.* **2012**, *4*, 361.
11. R. S. Ghadwal, R. Azhakar, H. W. Roesky, K. Pröpper, B. Dittrich, C. Goedecke, G. Frenking, *Chem. Commun*., **2012**, *48*, 8186.
12. Møller, C.; Plesset, M. S. *Phys. Rev*. **1934**, *46*, 618.
13. Hay, P. J.; Wadt, W. R. *J. Chem. Phys*. **1985**, *82*, 270.
14. Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 284.
15. Hay, P. J.; Wadt, W. R. *J. Chem. Phys*. **1985**, *82*, 299.
16. A.D. Becke, *Phys. Rev. A: At., Mol., Opt. Phys*., **1988**, *38*, 3098.
17. J. P. Perdew, *Phys. Rev. B*, **1986**, *33*, 8822.
18. A. Schäfer, H. Horn, R. Ahlrichs, *J. Chem. Phys.,* 1992, **97**, 2571.