SUPPORTING INFORMATION

In the Chalcogenoxide Elimination Panorama:
Systematic Insight into a Key Reaction

Andrea Madabeni, Simone Zucchelli, Pablo A. Nogara, João B. T. Rocha, Laura Orian

a Dipartimento di Scienze Chimiche, Università degli Studi di Padova, Via Marzolo 1, 35131 Padova, Italy.
b Departamento de Bioquímica e Biologia Molecular, Universidade Federal de Santa Maria (UFSM), Santa Maria, 97105-900, RS, Brazil.

*Author to whom correspondence should be addressed, laura.orian@unipd.it
Tables of Contents

Additional Computational Details..............................................................................................................S3
Extended Benchmark Discussion..............................................................................................................S4
Table S1. Activation and reaction electronic energies (kcal mol\(^{-1}\)) for the \(\beta\)-elimination reaction of chalcogenoxides (OS 0), chalcogeninic acids (OS +2) and chalcogenonic acids (OS +4). Level of theory: ZORA-OPBE/TZP-ae; TZ2P(-ae); QZ4P-ae. ..................................................................................................................S7
Table S2. Activation and reaction electronic energies (kcal mol\(^{-1}\)) for the \(\beta\)-elimination reaction of chalcogenoxides (minimal model) in OS 0, +2, +4. Level of theory: ZORA-xc/TZ2P(-ae)......................................................................................S8
Table S3. Activation and reaction electronic energies (kcal mol\(^{-1}\)) for the \(\beta\)-elimination reaction of chalcogenoxides (OS 0), chalcogeninic acids (OS +2) and chalcogenonic acids (OS +4). Level of theory: xc // OPBE. .....................................................................................................................S8
Table S4. Activation (\(\Delta E^a\)) and reaction (\(\Delta E_r\)) energies (kcal mol\(^{-1}\)) for the \(\beta\)-elimination reaction of chalcogenoxides (OS 0), chalcogeninic acids (OS +2) and chalcogenonic acids (OS +4). ..................................................S10
Table S5. Electronic energies (kcal mol\(^{-1}\)) for the cysteine, selenocysteine and tellurocysteine chalcogenoxide elimination in OS 0, +2, +4. Level of theory: M06 // OPBE. ..........................................................S11
Table S6. Activation and reaction Gibbs free energies (kcal mol\(^{-1}\)) for the minimal model reactions. Level of theory: M06 // OPBE. ......................................................................................................................S12
Table S7: Activation Gibbs free energies (kcal mol\(^{-1}\)) relative to the direct elimination mechanism of PhXEt (\(\Delta G_{elm} \ddagger\)), to the elimination mechanism of their hydrates (\(\Delta G_{hyd}, elm \ddagger\)), and reaction energies for the hydrates formation (\(\Delta G_{grhyd}\)). Level of theory: M06 // OPBE. ..........................................................S12
Table S8: Hirshfeld partial charges (a.u.) on the X = O oxygen atom of chalcogenoxides in different oxidation states. ..........................................................................................................................S12
Table S9: Cartesian coordinates (Å), energies (a.u.) and imaginary frequencies (cm\(^{-1}\)) of the optimized structures (minimal model). Level of theory: ZORA-M06-2X/TZ2P-ae. .............................................................S13
Table S10: Cartesian coordinates (Å), energies (a.u.) and imaginary frequencies (cm\(^{-1}\)) of the optimized structures of the minimal model. Level of theory: ZORA-OPBE/TZ2P. ...............................................................................S19
Table S11: Cartesian coordinates (Å), energies (a.u.) and imaginary frequencies (cm\(^{-1}\)) of the optimized structures of the minimal model. Level of theory: ZORA-OLYP/TZ2P .................................................................................S25
Table S12: Cartesian coordinates (Å), energies (a.u.) and imaginary frequencies (cm\(^{-1}\)) of the optimized structures of the minimal model. Level of theory: ZORA-B3LYP/TZ2P-ae. .............................................................S31
Table S13: Cartesian coordinates (Å), energies (a.u.) and imaginary frequencies (cm\(^{-1}\)) of the optimized structures of the minimal model. Level of theory: ZORA-BLYP-D3(BJ)/TZ2P. ..........................................................S37
Table S14: Cartesian coordinates (Å), energies (a.u.) and imaginary frequencies (cm\(^{-1}\)) of the optimized structures of the amino acid model. Level of theory: ZORA-OPBE/TZ2P. ..........................................................S43
Table S15: Cartesian coordinates (Å), energies (a.u.) and imaginary frequencies (cm\(^{-1}\)) of the optimized structures for the phenyl alkyl model. Level of theory: ZORA-OPBE/TZ2P. ..........................................................S53
Additional References ............................................................................................................................S56
Additional Computational Details

For the benchmark, a total of five functionals (xc), i.e., two GGAs, OLYP\textsuperscript{1–3} and OPBE;\textsuperscript{4} one dispersion-corrected GGA, BLYP-D3(BJ);\textsuperscript{1–3,5–8} one hybrid, B3LYP\textsuperscript{9,10} and one meta-hybrid M06-2X\textsuperscript{11,12}, were preliminarily tested for the geometry optimization and energy calculations. The Slater type TZ2P basis set was used for all calculations. This basis set is of triple-\(\zeta\) quality and augmented with two sets of polarization functions on each atom. For the three GGA, the small frozen core approximation was used, while for the hybrid and the metahybrid, all-electron calculations were performed since frozen core approximation is not implemented in ADF for these functionals. The role of the basis set (TZP, TZ2P and QZ4P) and of frozen core approximation (no frozen core and small core approximation) was tested for the OPBE functional, by reoptimizing all the investigated geometries and computing activation and reaction energies (Table S1) Scalar relativistic effects were included in all calculations within the zeroth-order regular approximation\textsuperscript{13} (ZORA) as implemented in ADF. This level of theory is denoted as ZORA-xc/TZ2P(-ae). Starting from the OPBE optimized geometries (see main text), single point energies have been computed with eighteen different density functionals, i.e. ten GGAs (one dispersion-corrected GGA), two meta-GGAs, three hybrids and three meta-hybrids. In detail, BLYP,\textsuperscript{2} BP86,\textsuperscript{5,14} HTBS,\textsuperscript{15} PBE,\textsuperscript{16} mPW,\textsuperscript{17} PW91,\textsuperscript{18} revPBE,\textsuperscript{19} RPBE,\textsuperscript{20} mPBE\textsuperscript{21} were considered. In addition, the dispersion-corrected version of BP86 functional, BP86-D3(BJ), was also tested. TPSS\textsuperscript{22,23} and SCAN\textsuperscript{24} functionals were tested for the meta-GGAs category; PBE0,\textsuperscript{25} OPBE0\textsuperscript{4} and mPW1PW\textsuperscript{17} were tested for the hybrid category (the popular B3LYP was preliminarily tested in the main text); M06,\textsuperscript{11} M06-2X\textsuperscript{11} and TPSSH\textsuperscript{22} were tested for the meta-hybrid category. Frozen core (fc) approximation was not used, to allow for a rigorous comparison, since for hybrids and meta-hybrids fc is not available. All calculations are all-electron except when explicitly specified. Following this initial investigation, eighteen functionals were tested (M06-2X was included as the best performing preliminary functional, while the other four were excluded given their relatively poor performance) by running single-point energy calculations on ZORA-OPBE/TZ2P optimized geometries. All calculations were done without frozen core approximation to allow a rigorous comparison. In total, ten GGAs (one dispersion-corrected GGA), two meta-GGAs, three hybrids and three meta-hybrids were tested. The level of theory of these calculations is denoted as ZORA-xc/TZ2P-ae // ZORA-OPBE/TZ2P, and along the manuscript it will be referred to as xc // OPBE.
Extended Benchmark Discussion

The performances of DFT in reproducing CCSD(T) trends were tested as described in the additional computational details. The activation and reaction energies obtained with DFT employing the five preliminary functionals were then compared to the CCSD(T) computed reference values. The results are shown in the Table S2, while the deviation from CCSD(T) results is represented in Figure S1. While all five functionals recover the trends discussed for CCSD(T), with the exception of the heightening of the activation energy going from Te (+2) to Te (+4) which is recovered only by OPBE and M06-2X, it can be clearly seen that the cheaper functionals (i.e. GGAs or the dispersion corrected GGA) underestimate the activation energy for the reaction of sulfoxides, selenoxides and telluroxides, with BLYP-D3(BJ) providing the worst results, with errors larger than -15 kcal mol\(^{-1}\) in some cases. (Figure S1)
Figure S1. Deviation of the activation ($\Delta \Delta E^\ddagger$, A, C, E) and reaction ($\Delta \Delta E_r$, B, D, F) energies predicted at DFT (ZORA- \textit{xc}/TZ2P) level of theory from CCSD(T) reference values. A negative value means that DFT underestimates the energy, while a positive value means that DFT overestimates the energy. Data are grouped on chalcogen basis: sulfur (A/B, blue), selenium (C/D, orange), tellurium (E/F, black). Bar filling is used to denote the OS: the lowest OS (0) is in solid color, the intermediate OS (+2) is dashed (thin lines), while the highest (+4) is dashed (thick lines).

For the other GGAs and B3LYP, the error generally increases going from S to Se, and from the lowest to the highest OS, with all the reactions in the OS +4 systematically displaying the strongest deviations from the CCSD(T) activation energies. The situation is rather different for M06-2X activation energies, that agree almost perfectly with the highly-correlated single points. With this functional, no great error arises when going from the OS 0 to the OS +4, and the $\Delta E^\ddagger$ of reactions involving Se shows deviation only slightly larger than those involving S.

A somewhat different picture describes deviations in reaction energies. In this case, the performance of the functionals appears to be somewhat less systematic, with some changes with the chalcogen and with the OS. Particularly, OPBE functional seems to be the worst performer for reactions involving S, but is the best performer for reactions involving Se. On the other hand, while B3LYP appears to be the worst performer for Se and Te, it is the best performer for S, with OLYP and BLYP-D3(BJ) giving similar results. In this case, M06-2X neither excels nor completely fails, predicting reaction energies within ca. ±5 kcal mol$^{-1}$ with respect to CCSD(T), and always with the correct qualitative trend.

Considering these results, OLYP and OPBE functionals, benchmarked and popularly used to study S$_2$2 reactions$^{4,26,27}$ (such as chalcogenide oxidations$^{28,29}$) and E2 reactions,$^{30,31}$ do not perform equally well for the quantitative description of chalcogenoxide elimination activation energies, even if they can still be used with some caution to understand the trends in the energetics in analogous elimination reactions, since CCSD(T) trends in activation and reaction energies are properly recovered also with the cheapest GGA or dispersion corrected GGA functionals.

In this preliminary analysis, OPBE appears to be the best performing GGA (Figure S1). OPBE functional was already found to perform very well for geometry optimization of organochalcogenides.$^{32}$

Thus, starting from OPBE optimized geometries, 17 functionals were tested for single-point energy calculations as described. Activation and reaction energies computed at xc // OPBE level of theory clearly show that no cheap GGA functional can properly describe the title reactions. (Table S3) In contrast, the hybrid OPBE0, and the metrahybrid M06 and M06-2X provides good to excellent performances. (Figure S2)
Figure S2. Deviation of the activation (ΔΔE‡, A, C, E) and reaction (ΔΔEr, B, D, F) energies predicted at DFT (xc // OPBE) level of theory from CCSD(T) reference values. A negative value means that DFT underestimates the energy, while a positive value means that DFT overestimates the energy. Data are grouped on chalcogen basis: sulfur (A/B, blue), selenium (C/D, orange), tellurium (E/F, black). Bar filling is used to denote the OS: the lowest OS (0) is in solid color, the intermediate OS (+2) is dashed (thin lines), while the highest (+4) is dashed (thick lines).

Particularly, M06 // OPBE appears to be the best performing protocol for investigating reactions in the lowest oxidation state (OS 0) regardless of the chalcogen involved, while M06-2X // OPBE is the best approach to compute the activation energies in the highest OS (+4) for all chalcogens. OPBE0 // OPBE, on the other hand, gives a quite satisfying description of all Se reactions, with errors in reaction energies below 2.0 kcal mol\(^{-1}\) and errors in activation energies below 1.5 kcal mol\(^{-1}\) for all OSs.

Moreover, all three protocols predict activation and reaction energies that correlate very well against CCSD(T) ones, (Figure S3) with very similar R\(^2\) values in the range 0.97-0.99 for both activation and reaction energies and mean absolute errors of ca. 2.00 kcal mol\(^{-1}\) or lower for activation energies and between 2 – 4 kcal mol\(^{-1}\) for reaction energies. Thus, in our opinion, all these three approaches can be employed to investigate the title reaction since the trends are qualitatively and quantitatively reproduced with the hybrid (OPBE0) as well as with the two meta-hybrids (M06 and M06-2X) functionals, and each of the three functionals outperforms the other two in a specific subset of reactions, with M06 being in average the best among the three.
Figure S3. Correlation between xc // OPBE and CCSD(T) activation (A) and reaction energies (B). Blue dots: OPBE0 // OPBE; orange dots: M06-2X // OPBE; grey dots: M06 // OPBE. Statistical parameters (MAE: Mean Absolute Error, and R²) are reported near the linear fit.

For our ongoing investigation, we employ M06 // OPBE (main text) and M06-2X // OPBE as main methods.

Table S1. Activation and reaction electronic energies (kcal mol⁻¹) for the β-elimination reaction of chalcogenoxides (OS 0), chalcogeninic acids (OS +2) and chalcogenonic acids (OS +4). Level of theory: ZORA-OPBE/TZP-ae; TZ2P(-ae); QZ4P-ae.

| basis    | OS | S  | Se | Te  | S  | Se | Te  |
|----------|----|----|----|-----|----|----|-----|
|          |    |    |    |     |    |    |     |
| TZP-ae   | 0  | 28.97 | 17.65 | 13.42 | 19.33 | 2.74 | -5.37 |
|          | +2 | 35.91 | 23.28 | 18.15 | 31.89 | 13.91 | 4.48  |
|          | +4 | 53.00 | 27.66 | 20.71 | 28.96 | -11.78 | -27.20 |
| TZ2P-ae  | 0  | 29.42 | 18.85 | 16.14 | 19.70 | 4.14 | -0.74 |
|          | +2 | 36.46 | 24.69 | 21.24 | 32.47 | 15.61 | 9.38  |
|          | +4 | 53.60 | 28.99 | 21.98 | 29.29 | -10.79 | -25.01 |
| TZ2P-sc  | 0  | 29.49 | 18.73 | 15.84 | 19.60 | 3.75 | -0.94 |
|          | +2 | 36.50 | 24.59 | 20.96 | 32.41 | 15.16 | 9.17  |
|          | +4 | 53.71 | 29.05 | 21.86 | 29.08 | -10.74 | -24.64 |
| QZ4P-ae  | 0  | 30.77 | 19.17 | 16.66 | 21.28 | 4.16 | 0.00  |
|          | +2 | 37.66 | 24.91 | 21.77 | 33.73 | 15.31 | 10.00 |
|          | +4 | 54.58 | 29.14 | 22.32 | 30.01 | -11.01 | -24.74 |

Increasing the basis set from TZP to TZ2P leads to recovering 1-2 kcal mol⁻¹ in activation energy and has a somewhat more relevant impact on reaction energies, which are affected in the 1 – 4 kcal mol⁻¹ range. Furtherly increasing the basis set to QZ4P leads to energetics which differs from those obtained with TZ2P of only fractions of kcal mol⁻¹. Moreover, the (small) frozen core approximation
as applied to TZ2P basis set does not seem to affect the energetics, with deviations from the TZ2P-aer are only a few fractions of kcal mol\(^{-1}\). Thus, TZ2P basis set is deemed to be a reasonable compromise for the computation of chalcogenoxide elimination reactions, when small core approximation is available.

**Table S2.** Activation and reaction electronic energies (kcal mol\(^{-1}\)) for the \(\beta\)-elimination reaction of chalcogenoxides (minimal model) in OS 0, +2, +4. Level of theory: ZORA-xc/TZ2P(-ae)

| xc   | OS  | S  | Se | Te  | S  | Se | Te  |
|------|-----|----|----|-----|----|----|-----|
| OLYP | 0   | 28.39 | 18.38 | 16.27 | 12.91 | -2.63 | -6.82 |
|      | 2   | 34.97 | 24.13 | 21.38 | 25.89 | 8.95 | 3.30 |
|      | 4   | 50.85 | 26.71 | 20.53 | 20.31 | -18.91 | -31.83 |

| xc   | OS  | S  | Se | Te  | S  | Se | Te  |
|------|-----|----|----|-----|----|----|-----|
| BLYP-D3(BJ) | 0   | 23.22 | 13.75 | 12.16 | 13.77 | -0.78 | -3.87 |
|      | 2   | 30.09 | 19.70 | 17.32 | 27.63 | 11.40 | 6.49 |
|      | 4   | 44.95 | 20.70 | 15.07 | 20.17 | -18.32 | -29.82 |

| xc   | OS  | S  | Se | Te  | S  | Se | Te  |
|------|-----|----|----|-----|----|----|-----|
| OPBE | 0   | 29.49 | 18.73 | 15.84 | 19.60 | 3.75 | -0.94 |
|      | 2   | 36.50 | 24.59 | 20.96 | 32.41 | 15.16 | 9.17 |
|      | 4   | 53.71 | 29.05 | 21.86 | 29.08 | -10.74 | -24.64 |

| xc   | OS  | S  | Se | Te  | S  | Se | Te  |
|------|-----|----|----|-----|----|----|-----|
| B3LYP | 0   | 29.36 | 19.00 | 16.88 | 11.00 | -5.18 | -10.12 |
|      | 2   | 36.31 | 24.81 | 22.77 | 25.19 | 7.13 | 1.22 |
|      | 4   | 53.38 | 28.23 | 21.58 | 20.91 | -20.49 | -35.39 |

| xc   | OS  | S  | Se | Te  | S  | Se | Te  |
|------|-----|----|----|-----|----|----|-----|
| M06-2X | 0   | 31.99 | 22.36 | 20.71 | 13.92 | -2.16 | -8.87 |
|      | 2   | 38.77 | 27.78 | 27.06 | 29.04 | 10.69 | 4.29 |
|      | 4   | 59.24 | 37.36 | 31.34 | 27.37 | -11.48 | -28.48 |

**Table S3.** Activation and reaction electronic energies (kcal mol\(^{-1}\)) for the \(\beta\)-elimination reaction of chalcogenoxides (OS 0), chalcogeninic acids (OS +2) and chalcogenonic acids (OS +4). Level of theory: xc // OPBE.

| xc   | OS  | S  | Se | Te  | S  | Se | Te  |
|------|-----|----|----|-----|----|----|-----|
| BLYP | 0   | 24.01 | 15.05 | 13.79 | 9.21 | -5.51 | -9.23 |
|      | +2  | 30.05 | 20.6 | 18.72 | 22.52 | 6.39 | 0.87 |
|      | +4  | 45.43 | 21.71 | 16.45 | 14.54 | -24.50 | -36.51 |

| xc   | OS  | S  | Se | Te  | S  | Se | Te  |
|------|-----|----|----|-----|----|----|-----|
| Method  | Oxidation State | S   | Se  | Te  | S   | Se  | Te  |
|---------|----------------|-----|-----|-----|-----|-----|-----|
| BP86    | 0              | 24.10 | 14.35 | 12.37 | 15.85 | 0.77 | -3.50 |
|         | +2             | 30.87 | 20.14 | 17.39 | 29.29 | 12.69 | 6.72  |
|         | +4             | 47.17 | 22.69 | 16.45 | 23.10 | -16.68 | -29.74 |
| xc      | ΔE‡            |      |      |      |      |      |      |
| HTBS    | 0              | 24.52 | 14.30 | 11.96 | 18.25 | 2.95 | -1.61 |
|         | +2             | 31.50 | 20.11 | 16.97 | 31.42 | 14.71 | 8.57  |
|         | +4             | 47.97 | 23.29 | 16.78 | 26.39 | -13.67 | -27.07 |
| xc      | ΔE‡            |      |      |      |      |      |      |
| PBE     | 0              | 24.85 | 14.87 | 12.69 | 18.71 | 3.49 | -0.86 |
|         | +2             | 31.81 | 20.76 | 17.78 | 32.27 | 15.54 | 9.48  |
|         | +4             | 48.29 | 23.68 | 17.22 | 26.28 | -13.62 | -26.82 |
| xc      | ΔE‡            |      |      |      |      |      |      |
| mPW     | 0              | 24.91 | 15.17 | 13.36 | 16.04 | 0.99 | -3.12 |
|         | +2             | 31.60 | 20.94 | 18.28 | 29.39 | 12.85 | 7.04  |
|         | +4             | 47.84 | 23.36 | 17.23 | 23.21 | -16.59 | -29.41 |
| xc      | ΔE‡            |      |      |      |      |      |      |
| PW91    | 0              | 25.85 | 16.42 | 14.60 | 14.40 | -0.32 | -4.35 |
|         | +2             | 32.31 | 22.12 | 19.59 | 27.43 | 11.34 | 5.67  |
|         | +4             | 48.25 | 24.45 | 18.57 | 21.28 | -17.59 | -30.05 |
| xc      | ΔE‡            |      |      |      |      |      |      |
| revPBE  | 0              | 26.14 | 16.81 | 15.04 | 14.20 | -0.45 | -4.41 |
|         | +2             | 32.52 | 22.48 | 20.04 | 27.22 | 11.22 | 5.62  |
|         | +4             | 48.35 | 24.74 | 18.95 | 20.86 | -17.76 | -30.08 |
| xc      | ΔE‡            |      |      |      |      |      |      |
| RPBE    | 0              | 26.29 | 16.96 | 15.53 | 16.01 | 1.56 | -1.89 |
|         | +2             | 32.75 | 22.73 | 20.61 | 29.33 | 13.34 | 8.10  |
|         | +4             | 49.50 | 25.22 | 19.18 | 24.28 | -14.58 | -27.03 |
| xc      | ΔE‡            |      |      |      |      |      |      |
| mPBE    | 0              | 25.20 | 15.40 | 13.34 | 17.49 | 2.43 | -1.81 |
|         | +2             | 32.01 | 21.24 | 18.41 | 30.92 | 14.38 | 8.45  |
|         | +4             | 48.31 | 23.96 | 17.68 | 24.81 | -14.75 | -27.71 |
| xc      | ΔE‡            |      |      |      |      |      |      |
| TPSS    | 0              | 26.29 | 16.96 | 15.53 | 16.01 | 1.56 | -1.89 |
|         | +2             | 32.75 | 22.73 | 20.61 | 29.33 | 13.34 | 8.10  |
|         | +4             | 49.50 | 25.22 | 19.18 | 24.28 | -14.58 | -27.03 |
| xc      | ΔE‡            |      |      |      |      |      |      |
| SCAN    | 0              | 28.89 | 18.30 | 15.77 | 22.22 | 6.15 | 1.40  |
|         | +2             | 36.70 | 24.42 | 21.13 | 37.87 | 19.39 | 12.48 |
|         | +4             | 56.44 | 28.65 | 20.27 | 35.19 | -8.54 | -24.51 |
| xc      | ΔE‡            |      |      |      |      |      |      |
| xc   | OS  | S    | Se   | Te    | S    | Se   | Te    | ΔE‡ | ΔEᵣ      |
|------|-----|------|------|-------|------|------|-------|-----|----------|
| PBE0 | 0   | 31.00| 20.14| 17.39 | 19.15| 2.37 | -3.24 |     |          |
|      | +2  | 37.82| 25.82| 22.29 | 33.69| 14.85| 7.55  |     |          |
|      | +4  | 57.98| 32.42| 24.74 | 31.93| -10.44| -26.76|     |          |
| OPBE0| 0   | 34.39| 23.18| 20.08 | 19.92| 3.02 | -2.93 |     |          |
|      | +2  | 41.37| 28.84| 25.00 | 33.84| 15.04| 7.67  |     |          |
|      | +4  | 61.88| 36.47| 28.47 | 34.11| -8.14 | -25.06|     |          |
| mPW1PW| 0   | 31.08| 20.41| 17.87 | 16.98| 0.32 | -5.11 |     |          |
|      | +2  | 37.73| 25.98| 22.71 | 31.34| 12.66| 5.53  |     |          |
|      | +4  | 57.60| 32.16| 24.75 | 27.47| -11.35| -28.68|     |          |
| M06-2X| 0   | 30.57| 21.31| 19.81 | 13.66| -2.51| -8.95 |     |          |
|      | +2  | 36.60| 26.23| 23.76 | 28.88| 10.38| 2.51  |     |          |
|      | +4  | 58.52| 37.07| 30.59 | 27.47| -11.35| -28.68|     |          |
| M06  | 0   | 31.36| 23.66| 21.89 | 16.17| 1.71 | -2.03 |     |          |
|      | +2  | 37.91| 28.42| 25.92 | 31.10| 13.67| 7.88  |     |          |
|      | +4  | 58.93| 34.93| 27.65 | 28.86| -12.99| -28.45|     |          |
| TPSSh| 0   | 28.65| 18.80| 17.15 | 16.33| 1.14 | -2.90 |     |          |
|      | +2  | 35.11| 24.59| 22.18 | 30.07| 13.14| 7.33  |     |          |
|      | +4  | 53.29| 28.61| 22.04 | 26.60| -13.39| -27.15|     |          |
| BP86-D3(BJ)| 0 | 23.84| 14.12| 12.09 | 19.29| 4.49 | 0.74  |     |          |
|      | +2  | 30.54| 19.88| 17.11 | 33.09| 16.71| 11.21 |     |          |
|      | +4  | 47.50| 22.87| 16.46 | 27.55| -12.14| -24.94|     |          |
Table S4. Activation ($\Delta E^\ddagger$) and reaction ($\Delta E_r$) energies (kcal mol$^{-1}$) for the $\beta$-elimination reaction of chalcogenoxides (OS 0), chalcogeninic acids (OS +2) and chalcogenonic acids (OS +4).$^a$

| OS | Configuration | $\Delta E^\ddagger$ | $\Delta E_r$ |
|----|----------------|-----------------|-------------|
| 0  | RR             | 21.82 (22.34)   | 5.13 (6.65) |
|    | RS             | 28.21 (28.34)   | 10.43 (11.59) |
| Cys | RR             | 28.97 (30.27)   | 20.92 (22.76) |
|    | RS             | 31.54 (32.51)   | 22.03 (23.70) |
| + 4 | R              | 52.51 (52.73)   | 17.59 (18.87) |
| 0  | RR             | 17.53 (18.54)   | -6.05 (-2.86) |
|    | RS             | 19.95 (20.81)   | -4.33 (-1.35) |
| Sec | RR             | 19.96 (21.36)   | 4.17 (7.17)  |
|    | RS             | 24.96 (25.85)   | 6.85 (9.44)  |
| + 4 | R              | 32.52 (30.10)   | -21.72 (-23.04) |
| 0  | RR             | 17.45 (17.81)   | -10.61 (-4.66) |
|    | RS             | 18.21 (18.28)   | -9.83 (-4.20) |
| Tec | RR             | 19.00 (19.13)   | -1.04 (3.72) |
|    | RS             | 27.44 (26.83)   | 4.42 (8.51)  |

$^a$Electronic energies computed at M06-2X // OPBE (M06 // OPBE) level of theory.

Table S5. Electronic energies (kcal mol$^{-1}$) for the cysteine, selenocysteine and tellurocysteine chalcogenoxide elimination in OS 0, +2, +4. Level of theory: M06 // OPBE.

|         | R                  | TS                 | P                  | DHA                |
|---------|--------------------|--------------------|--------------------|--------------------|
| Cys 0   | RR                 | -2415.92           | -2393.58           | -515.03            | -1894.24           |
|         | RS                 | -2420.86           | -2392.52           |                    |                    |
| Sec 0   | RR                 | -2387.41           | -2368.87           | -496.03            |                    |
|         | RS                 | -2388.92           | -2368.11           |                    |                    |
| Tec 0   | RR                 | -2365.99           | -2348.18           | -476.41            |                    |
|         | RS                 | -2366.45           | -2348.17           |                    |                    |
| Cys 2   | RR                 | -2642.94           | -2612.67           | -725.94            |                    |
|         | RS                 | -2643.88           | -2611.37           |                    |                    |
| Sec 2   | RR                 | -2610.93           | -2589.57           | -709.52            |                    |
|         | RS                 | -2613.20           | -2587.35           |                    |                    |
| Tec 2   | RR                 | -2596.19           | -2577.06           | -698.23            |                    |
|         | RS                 | -2574.15           | -2574.15           |                    |                    |
| Cys 4   | R                  | -2866.97           | -2814.24           | -953.86            |                    |
| Sec 4   | R                  | -2790.65           | -2760.55           | -919.45            |                    |
| Tec 4   | R                  | -2768.99           | -2744.17           | -910.07            |                    |
Table S6: Activation and reaction Gibbs free energies (kcal mol$^{-1}$) for the minimal model reactions. Level of theory: M06 // OPBE.

| OS | ΔG‡ | ΔGr |
|----|-----|-----|
|    | S   | Se  | Te  | S   | Se  | Te  |
| 0  | 28.27 | 21.31 | 19.92 | 2.88 | -10.81 | -14.07 |
| +2 | 35.09 | 26.34 | 24.86 | 18.01 | 1.67  | -2.91  |
| +4 | 53.54 | 31.29 | 25.41 | 13.19 | -27.33 | -41.00 |

Table S7: Activation Gibbs free energies (kcal mol$^{-1}$) relative to the direct elimination mechanism of PhXEt (ΔG$_{elm}^\ddagger$), to the elimination mechanism of their hydrates (ΔG$_{hyd,elm}^\ddagger$), and reaction energies for the hydrates formation (ΔG$_{r,hyd}^\ddagger$). Level of theory: M06 // OPBE.

|          | ΔG$_{elm}^\ddagger$ | ΔG$_{r,hyd}^\ddagger$ | ΔG$_{hyd,elm}^\ddagger$ |
|----------|---------------------|------------------------|--------------------------|
| PhSEt    | 28.42               | 33.51                  | 29.57                    |
| PhSeEt   | 20.74               | 10.69                  | 30.15                    |
| PhTeEt   | 19.33               | -8.36                  | 35.65                    |

Table S8: Hirshfeld partial charges (a.u.) on the X = O oxygen atom of chalcogenoxides in different oxidation states.

|            | S      | Se     | Te      |
|------------|--------|--------|---------|
| 0          | -0.373 | -0.428 | -0.471  |
| 2          | -0.349 | -0.400 | -0.452  |
| 4          | -0.294 | -0.347 | -0.398  |
Table S9: Cartesian coordinates (Å), energies (a.u.) and imaginary frequencies (cm$^{-1}$) of the optimized structures (minimal model). Level of theory: ZORA-M06-2X/TZ2P-ae.

|          | HSOEt                      | HSO$_2$Et                   |
|----------|----------------------------|-----------------------------|
| E        | -2.603634                  | -3.052357                   |
| G        | -2.551961                  | -2.996529                   |
| N$_{imag}$ | 0                          | 0                           |
| S        | 0.900470000 -0.184160000 -0.654887000 | S -1.124629000 -0.504037000 0.186030000 |
| C        | 0.773510000 -0.011223000 -2.457782000 | O -1.520805000 -0.499162000 -1.415817000 |
| H        | -0.072061000 0.644721000 -2.657713000 | O -0.702374000 0.839479000 0.572283000 |
| H        | 1.695138000 0.470824000 -2.788091000 | H -0.711607000 -0.603706000 -1.930638000 |
| C        | 0.577903000 -1.385900000 -3.076558000 | C -2.852318000 -0.642875000 0.674535000 |
| H        | -0.312222000 -1.857525000 -2.663697000 | H -2.828532000 -0.495542000 1.753777000 |
| H        | 1.433965000 -2.030691000 -2.878903000 | H -3.344863000 0.213947000 0.214969000 |
| H        | 0.454829000 -1.301054000 -4.154679000 | C -3.467261000 -1.975666000 0.282263000 |
| O        | -0.425308000 -0.630228000 -0.156605000 | H -2.891588000 -2.808361000 0.686431000 |
| H        | 0.972478000 1.171434000 -0.482578000 | H -3.508102000 -2.077477000 -0.799594000 |
|          | HSO$_3$Et                   | HSeOEt                      |
| E        | -3.495405                   | -2.538755                   |
| G        | -3.434436                   | -2.986216                   |
| N$_{imag}$ | 0                          | 0                           |
| S        | -0.799121000 -0.749125000 2.006285000 | S 0.998020000 0.573340000 1.079203000 |
| O        | -1.043911000 -0.405773000 0.646639000 | O 0.125200000 0.742210000 0.351200000 |
| O        | -0.036344000 -2.154182000 2.003651000 | O -0.036344000 -0.858903000 2.949517000 |
| O        | -1.869874000 -0.858903000 2.949517000 | O -0.055632000 1.292175000 2.733276000 |
| C        | 0.450302000 0.330123000 2.654210000 | H 0.667288000 -0.030845000 3.657766000 |
| H        | -0.055632000 1.292175000 2.733276000 | C 1.677051000 0.392606000 1.758300000 |
| H        | 0.667288000 -0.030845000 3.657766000 | H 1.402211000 0.728661000 0.761347000 |
| H        | 2.149107000 -0.584449000 1.678979000 | H 2.149107000 -0.584449000 1.678979000 |
| H        | 2.397128000 1.091711000 2.178402000 | H 2.397128000 1.091711000 2.178402000 |
| H        | -0.440182000 -2.716502000 2.679175000 | H -0.440182000 -2.716502000 2.679175000 |
|          | HSeO$_2$Et                  | HSeOEt                      |
| E        | -2.538755                   | -2.986216                   |
| G        | -2.551961                   | -2.996529                   |
| N$_{imag}$ | 0                          | 0                           |
\[ G = -2.491158 \]
\[ N_{\text{imag}} = 0 \]

\[ G = -2.934661 \]
\[ N_{\text{imag}} = 0 \]

Se: 0.959934000, -0.195083000, -0.561664000
C: 0.808951000, -0.017521000, -2.511492000
H: -0.039212000, 0.642644000, -2.673934000
H: 1.722123000, 0.456747000, -2.868766000
C: 0.579147000, -1.397469000, -3.102481000
H: -0.287790000, -1.863391000, -2.635934000
H: 1.444217000, -2.042987000, -2.950857000
H: 0.354725000, -1.346410000, -4.203943000
O: -0.624689000, -0.770385000, -0.017842000

\[
E = -3.366323 \\
G = -3.311441 \\
N_{\text{imag}} = 0
\]

Se: -0.856465000, -0.749880000, 2.007708000
O: -1.138848000, -0.409628000, 0.477055000
O: 0.021145000, -2.268574000, 2.057598000
O: 0.015985000, -2.268574000, 2.057598000
C: 0.512947000, -0.028723000, 2.758182000
H: 0.718405000, 0.037078000, 0.617014000
C: 1.717233000, 0.422534000, 0.760133000
H: 1.429529000, 0.736019000, 2.146785000
H: 2.458976000, 1.119661000, -0.494095000

\[
E = -2.499384 \\
G = -2.454722 \\
N_{\text{imag}} = 0
\]

Te: 1.036274000, -0.184800000, -0.436996000
C: 0.854424000, -0.028723000, -2.567823000
H: 0.023566000, 0.653906000, -2.729271000
H: 1.766142000, 0.412890000, -2.965387000
C: 0.564849000, -1.410832000, -3.137056000
H: -0.302547000, -1.847973000, -2.645002000
H: 1.412206000, -2.083174000, -3.003823000
H: 0.354725000, -1.346410000, -4.203943000
O: -0.624689000, -0.770385000, -0.017842000

\[
E = -2.960916 \\
G = -2.911544 \\
N_{\text{imag}} = 0
\]

Te: -0.809819000, -0.648776000, 0.331982000
O: -1.084078000, -0.908492000, 0.415060000
O: -0.513330000, 1.116862000, 2.758182000
C: 0.718405000, 0.037078000, -0.781511000
C: 1.717233000, 0.422534000, 0.760133000
C: 1.429529000, 0.736019000, 0.760133000
H: 2.169003000, -0.565373000, 0.617014000
H: 2.458976000, 1.119661000, -0.565373000
H: -0.494095000, -2.875226000, 2.007708000
O: -0.624689000, -0.770385000, -0.017842000
H Te O₃Et

\[ E = -3.327297 \]
\[ G = -3.276403 \]
\[ N_{\text{imag}} = 0 \]

Te \(-0.961693000\) \(-0.755429000\) \(2.007580000\)
O \(-1.260701000\) \(-0.411323000\) \(0.292624000\)
O \(-2.293897000\) \(-0.956306000\) \(3.167356000\)
C \(0.569451000\) \(-0.054457000\) \(-2.925318000\)
H \(1.688846000\) \(0.376535000\) \(-2.903212000\)
C \(1.482908000\) \(0.752341000\) \(0.764363000\)
H \(2.187156000\) \(-0.551258000\) \(1.726887000\)
H \(2.536640000\) \(1.130328000\) \(2.130922000\)
H \(-0.467141000\) \(-3.076277000\) \(2.547073000\)

Transition states

HSOEt‡

\[ E = -2.552654 \]
\[ G = -2.506113 \]
\[ N_{\text{imag}} = -1196.554 \]

S \(0.615531000\) \(-0.607256000\) \(-0.681285000\)
C \(0.697727000\) \(-0.054457000\) \(-2.925318000\)
H \(-1.000850000\) \(0.675277000\) \(-2.909885000\)
H \(1.688846000\) \(0.376535000\) \(-2.903212000\)
C \(0.493121000\) \(-1.325894000\) \(-3.483676000\)
H \(0.417918000\) \(-2.017240000\) \(-2.311994000\)
H \(1.336845000\) \(-1.805800000\) \(-3.964033000\)
H \(-0.471932000\) \(-1.529778000\) \(-3.931415000\)
O \(0.417718000\) \(-2.094233000\) \(-1.065913000\)
H \(-0.655488000\) \(-0.157350000\) \(-0.552668000\)

HSO₂Et‡

\[ E = -2.990574 \]
\[ G = -2.939643 \]
\[ N_{\text{imag}} = -1151.962 \]

S \(-0.759711000\) \(-0.377310000\) \(0.043980000\)
O \(-0.289779000\) \(-0.324263000\) \(1.616145000\)
O \(-1.850612000\) \(-0.363551000\) \(1.661140000\)
S \(-2.969043000\) \(-0.691636000\) \(0.693802000\)
H \(-2.766271000\) \(-0.313052000\) \(1.687541000\)
H \(-3.422916000\) \(0.022787000\) \(0.020409000\)
H \(-2.059280000\) \(-0.359275000\) \(0.466016000\)
H \(-3.722955000\) \(-2.389116000\) \(-0.359275000\)
H \(-3.048669000\) \(-2.731315000\) \(1.312943000\)

HSO₃Et‡

\[ E = -3.401005 \]
\[ G = -3.348429 \]
\[ N_{\text{imag}} = -1452.626 \]
\[ \begin{align*}
S & \quad -1.121716000 \quad -0.167994000 \quad -0.044338000 \\
O & \quad -1.329719000 \quad 0.580395000 \quad -1.459338000 \\
O & \quad -0.818756000 \quad -1.591335000 \quad -0.430011000 \\
H & \quad -0.500974000 \quad 1.029954000 \quad -1.688517000 \\
C & \quad -3.231352000 \quad -0.794823000 \quad 0.807696000 \\
H & \quad -3.037978000 \quad -0.371990000 \quad 1.784886000 \\
H & \quad -3.771684000 \quad -0.145310000 \quad 0.138370000 \\
C & \quad -3.144191000 \quad 2.164930000 \quad -0.430011000 \\
H & \quad -2.967038000 \quad -2.102664000 \quad 1.428087000 \\
H & \quad -3.719920000 \quad -2.581868000 \quad 0.004859000 \\
H & \quad -2.967038000 \quad -2.813238000 \quad 1.428087000 \\
O & \quad 0.026775000 \quad 0.507704000 \quad 0.620085000
\end{align*} \]

\[ \text{HSeOEt}^2 \]

\[ \begin{align*}
E &= -2.503116 \\
G &= -2.459801 \\
N_{\text{imag}} &= -1241.307
\end{align*} \]

\[ \begin{align*}
\text{Se} & \quad 0.664109000 \quad -0.571446000 \quad -0.610955000 \\
C & \quad 0.710185000 \quad -0.050913000 \quad -2.928678000 \\
H & \quad 1.700356000 \quad 0.383202000 \quad -2.951155000 \\
H & \quad 0.491178000 \quad -1.338872000 \quad -3.474797000 \\
H & \quad 0.419965000 \quad -2.038763000 \quad -2.360444000 \\
H & \quad 1.327724000 \quad -1.796798000 \quad -3.989381000 \\
H & \quad -0.474186000 \quad -1.514190000 \quad -3.935125000 \\
O & \quad 0.426609000 \quad -2.184802000 \quad -1.069193000 \\
H & \quad -0.741719000 \quad -0.110682000 \quad -0.482546000
\end{align*} \]

\[ \text{HSeO}_2\text{Et}^2 \]

\[ \begin{align*}
E &= -2.941943 \\
G &= -2.894133 \\
N_{\text{imag}} &= -1259.306
\end{align*} \]

\[ \begin{align*}
\text{Se} & \quad -0.890089000 \quad -0.359284000 \quad 0.091687000 \\
O & \quad -0.243308000 \quad -0.328175000 \quad 1.763543000 \\
O & \quad -0.916023000 \quad -1.988474000 \quad -0.290897000 \\
H & \quad 0.714349000 \quad -0.434122000 \quad 1.729770000 \\
C & \quad 3.058325000 \quad -0.682793000 \quad 0.993777000 \\
H & \quad -2.767575000 \quad -0.298757000 \quad 1.964008000 \\
H & \quad 3.058325000 \quad 0.021468000 \quad 0.382825000 \\
C & \quad 3.221027000 \quad 2.066609000 \quad 0.797047000 \\
H & \quad -2.043265000 \quad -2.309460000 \quad 1.599470000 \\
H & \quad 3.961463000 \quad 2.386733000 \quad 0.074609000 \\
H & \quad -3.112266000 \quad 2.706858000 \quad 1.663957000
\end{align*} \]

\[ \text{HSeO}_3\text{Et}^2 \]

\[ \begin{align*}
E &= -3.306781 \\
G &= -3.258153 \\
N_{\text{imag}} &= -1362.078
\end{align*} \]

\[ \begin{align*}
\text{Se} & \quad -1.003311000 \quad -0.235649000 \quad -0.024539000 \\
O & \quad -1.397199000 \quad 0.613808000 \quad -1.526038000 \\
O & \quad -0.824244000 \quad -1.808182000 \quad -0.505883000 \\
H & \quad -0.587499000 \quad 1.052100000 \quad -1.827728000 \\
C & \quad -3.192342000 \quad -0.739062000 \quad 0.907109000 \\
H & \quad -2.974879000 \quad -0.396333000 \quad 1.909475000 \\
H & \quad -3.688365000 \quad -0.013566000 \quad 0.273325000 \\
C & \quad -3.204300000 \quad -2.110822000 \quad 0.589079000 \\
H & \quad -2.059542000 \quad -2.209089000 \quad 0.019738000 \\
H & \quad -3.871686000 \quad -2.410211000 \quad -0.211414000 \\
H & \quad -3.130499000 \quad 2.800528000 \quad 1.421781000 \\
O & \quad 0.372565000 \quad 0.438736000 \quad 0.471695000
\end{align*} \]
### HTeOEt‡

**E** = -2.466376  
**G** = -2.425441  
**N\text{imag}** = -1547.67

| Element | x  | y  | z    |
|---------|----|----|------|
| Te      | 0.717691000 | -0.546993000 | -0.502026000 |
| C       | 0.730457000  | -0.042527000  | -2.951886000  |
| H       | -0.060766000  | 0.694299000   | -2.965512000  |
| H       | 1.716914000   | 0.393305000   | -3.027228000  |
| C       | 0.494446000   | -1.346000000  | -3.478873000  |
| H       | 0.430229000   | -2.070205000  | -2.392538000  |
| H       | 1.391230000   | -1.794860000  | -4.019812000  |
| H       | -0.476931000  | -1.505007000  | -3.932176000  |
| O       | 0.441467000   | -2.281772000  | -1.096153000  |
| H       | -0.872431000  | -0.040440000  | -0.363196000  |

### HTeO2Et‡

**E** = -2.917792  
**G** = -2.872636  
**N\text{imag}** = -1394.095

| Element | x  | y  | z    |
|---------|----|----|------|
| Te      | 0.169944000  | 0.425500000  | -0.571995000 |
| C       | -0.526265000  | 2.034732000  | -2.325361000 |
| H       | -1.000502000  | 2.705954000  | -1.618683000 |
| H       | 0.428740000   | 2.390838000   | -2.686560000  |
| C       | -1.330276000  | 1.206658000   | -3.150879000  |
| H       | -1.193761000  | 0.019378000   | -2.525611000  |
| H       | -0.963982000  | 1.011174000   | -4.150810000  |
| H       | -2.401701000  | 1.345391000   | -3.075203000  |
| O       | -0.802496000  | -0.753233000  | -1.598220000  |
| O       | -1.226124000  | 1.207360000   | 0.543259000   |
| H       | -1.495078000  | 0.614649000   | 1.252263000   |

### HTeO3Et‡

**E** = -3.277349  
**G** = -3.232507  
**N\text{imag}** = -2056.57

| Element | x  | y  | z    |
|---------|----|----|------|
| Te      | -0.176370000  | 0.794425000  | -0.425664000  |
| C       | -0.614611000  | 2.178559000  | -2.513030000  |
| H       | -1.225913000  | 2.953491000  | -2.070419000  |
| H       | 0.429681000   | 2.444566000   | -2.630255000  |
| C       | -1.190285000  | 1.136442000   | -3.288725000  |
| H       | -1.168101000  | 0.155326000   | -2.516600000  |
| H       | -0.573497000  | 0.786183000   | -4.109662000  |
| H       | -2.240644000  | 1.262688000   | -3.525661000  |
| O       | -0.878326000  | -0.627460000  | -1.323886000  |
| O       | 1.719867000   | 0.542072000   | -0.640598000  |
| H       | 2.102670000   | 0.119757000   | 0.139982000   |
| O       | -0.405568000  | 0.668451000   | 1.340318000   |
### Products

#### Ethylene

| Element | X   | Y   | Z   |
|---------|-----|-----|-----|
| C       | 0.000000000 | 0.000000000 | -0.660928000 |
| C       | 0.000000000 | 0.000000000 | 0.660928000  |
| H       | 0.000000000 | 0.922016000 | -1.227432000 |
| H       | 0.000000000 | -0.922016000 | -1.227432000 |
| H       | 0.000000000 | -0.922016000 | 1.227432000  |

#### H\textsubscript{2}SO\textsubscript{2}

| Element | X   | Y   | Z   |
|---------|-----|-----|-----|
| S       | 2.111079000 | -2.340436000 | 0.000000000 |
| O       | 2.695473000 | -1.507982000 | -1.280660000 |
| O       | 2.695473000 | -1.507982000 | 1.280660000  |
| H       | 3.549930000 | -1.868426000 | 1.543830000  |
| H       | 3.549930000 | -1.868426000 | -1.543830000 |

#### H\textsubscript{2}SO\textsubscript{3}

| Element | X   | Y   | Z   |
|---------|-----|-----|-----|
| S       | -0.226382000 | 0.247576000 | -3.321460000 |
| O       | -0.025617000 | -0.112960000 | -4.880753000 |
| O       | 0.836256000  | 1.451440000  | -3.168841000 |
| O       | 0.346999000  | -0.867060000 | -2.591711000 |
| H       | 0.671838000  | -0.784517000 | -4.960688000 |
| H       | 1.699147000  | 1.079709000  | -2.921744000 |

#### H\textsubscript{2}SeO

| Element | X   | Y   | Z   |
|---------|-----|-----|-----|
| Se      | 0.556809000 | -0.513043000 | -2.002865000 |
| H       | 0.739044000 | -1.856659000 | -2.571693000 |
| O       | -0.027648000 | -1.058789000 | -0.384688000 |
| H       | 0.744018000 | -1.155073000 | 0.181889000  |

#### H\textsubscript{2}SeO\textsubscript{2}

| Element | X   | Y   | Z   |
|---------|-----|-----|-----|
| Se      | 2.042761000 | -2.402939000 | 0.000000000 |
| O       | 2.713800000 | -1.484126000 | -1.373406000 |
| O       | 2.713800000 | -1.484126000 | 1.373406000  |
| H       | 3.565762000 | -1.861030000 | 1.616124000  |
| H       | 3.565762000 | -1.861030000 | -1.616124000 |
\begin{table}
\centering
\begin{tabular}{lcccc}
 & \textbf{H$_2$SeO$_3$} & & \textbf{H$_2$TeO} & \\
 & E = -1.811006 & G = -1.808685 & N$_{\text{imag}}$ = 0 & E = -0.939915 \\
Se & -0.298748000 & 0.269677000 & -3.305146000 & \\
O & -0.031127000 & -0.138815000 & -4.998869000 & \\
O & 0.900360000 & 1.552116000 & -3.148517000 & \\
H & 0.384811000 & -0.957530000 & -2.528119000 & \\
H & 0.623250000 & -0.854077000 & -5.024308000 & \\
H & 1.723696000 & 1.142818000 & -2.840241000 & \\
\end{tabular}
\begin{tabular}{lcccc}
 & \textbf{H$_2$TeO$_2$} & & \textbf{H$_2$TeO$_3$} & \\
 & E = -1.380460 & G = -1.381103 & N$_{\text{imag}}$ = 0 & E = -1.799078 \\
Te & 1.945131000 & -2.467882000 & 0.000000000 & \\
O & 2.739107000 & -1.469612000 & -1.474585000 & \\
O & 2.739107000 & -1.469612000 & 1.474585000 & \\
H & 3.589270000 & -1.843073000 & 1.724039000 & \\
H & 3.589270000 & -1.843073000 & -1.724039000 & \\
\end{tabular}
\begin{tabular}{lcccc}
 & \textbf{H$_2$TeO} & & \textbf{H$_2$TeO$_3$} & \\
 & E = -1.380460 & G = -1.381103 & N$_{\text{imag}}$ = 0 & E = -1.799078 \\
Te & 0.550843000 & -0.427819000 & -2.064682000 & \\
H & 0.767167000 & -1.947558000 & -2.697693000 & \\
O & -0.035752000 & -1.045531000 & -0.292091000 & \\
H & 0.729965000 & -1.162656000 & 0.277110000 & \\
\end{tabular}
\caption{Cartesian coordinates (Å), energies (a.u.) and imaginary frequencies (cm$^{-1}$) of the optimized structures of the minimal model. Level of theory: ZORA-OPBE/TZ2P.}
\end{table}

\textbf{Reactants:}

\begin{tabular}{lcccc}
 & \textbf{HSOEt} & & \textbf{HSO$_2$Et} & \\
 & E = -1.838526 & G = -1.789445 & N$_{\text{imag}}$ = 0 & E = -2.105208 \\
S & 0.883283000 & -0.189967000 & -0.626942000 & \\
C & 0.743459000 & -0.038417000 & -2.440107000 & \\
H & -0.106255000 & 0.621821000 & -2.648643000 & \\
H & 1.667705000 & 0.470048000 & -2.749310000 & \\
C & 0.585860000 & -1.392523000 & -3.100297000 & \\
C & -0.319143000 & -1.897093000 & -2.748645000 & \\
H & 1.443506000 & -2.042920000 & -2.895737000 & \\
H & 0.504384000 & -1.275234000 & -4.186363000 & \\
O & -0.435774000 & -0.556839000 & -0.048887000 & \\
H & 1.031678000 & 1.187320000 & -0.526563000 & \\
\end{tabular}

\begin{tabular}{lcccc}
 & \textbf{HSO$_2$Et} & & \textbf{HSO$_2$Et} & \\
 & E = -2.105208 & G = -2.052069 & N$_{\text{imag}}$ = 0 & \\
S & -1.113042000 & -0.493863000 & 0.157285000 & \\
C & -1.498222000 & -0.408033000 & -1.465806000 & \\
O & -0.677254000 & 0.827407000 & 0.628222000 & \\
O & -0.670544000 & -0.587350000 & -1.933309000 & \\
C & -2.852085000 & -0.657182000 & 0.645343000 & \\
C & -2.813462000 & -0.489154000 & 1.728090000 & \\
H & -3.364758000 & 0.196831000 & 0.187539000 & \\
C & -3.481633000 & -1.990445000 & 0.299552000 & \\
O & -2.915060000 & -2.827090000 & 0.722591000 & \\
H & -3.550321000 & -2.133455000 & -0.782125000 & \\
H & -4.495739000 & -2.039107000 & 0.711183000 & \\
\end{tabular}
HSO$_3$Et

$E = -2.374253$
$G = -2.316030$
$N_{imag} = 0$

S  -0.821418000  -0.764702000  1.999013000
O  -1.088881000  -0.422703000  0.633092000
O  -0.087569000  -2.206174000  1.975130000
O  -1.874186000  -0.838235000  2.980762000
C   0.460738000  0.304577000  2.629056000
H  -0.055222000  1.267623000  2.726320000
H   0.678213000  -0.057617000  3.639416000
H   0.464705000  -1.299435000  4.219562000

HSeO$_3$Et

$E = -2.254115$
$G = -2.202215$
$N_{imag} = 0$

Se  0.932794000  -0.208876000  -0.523842000
C   0.769100000  -0.048366000  -2.495690000
H  -0.091292000  0.608038000  -2.658274000
H   1.682425000  0.465123000  -2.822156000
C   0.593193000  -1.406396000  -3.136011000
H  -0.294021000  -1.914461000  -2.744987000
H   1.462089000  -2.052927000  -2.968589000
H   0.464705000  -1.299435000  -4.219562000
O  -0.573399000  -0.565494000  0.028662000
H   1.053099000  1.308993000  -0.431046000

HSO$_2$Et

$E = -2.048818$
$G = -2.00009$
$N_{imag} = 0$

Se  -0.996671000  -0.552955000  0.174900000
O   -1.460770000  -0.413407000  -1.595937000
O  -0.571591000  0.931848000  0.683332000
H  -0.620353000  -0.420369000  -2.075381000
H   -2.894009000  -0.693349000  0.675387000
C   -2.871939000  -0.488760000  1.751759000
H   -3.357517000  0.158662000  0.168149000
C   -3.531141000  -2.023209000  0.339882000
H   -3.017276000  -2.859871000  0.826742000
H   -3.539999000  -2.205260000  -0.738431000
H  -4.570856000  -2.035920000  0.688162000

HSeO$_2$Et
| Element | X      | Y      | Z      |
|---------|--------|--------|--------|
| C       | 1.744636000 | 0.458670000 | 1.760623000 |
| H       | 1.473517000 | 0.785631000 | 0.753530000 |
| H       | 2.252722000 | -0.506752000 | 1.692900000 |
| H       | 2.453379000 | 1.185197000 | 2.175034000 |
| H       | -0.582494000 | -2.880532000 | 2.646793000 |

**HTeOEt**

\[ E = -1.752452 \]

\[ G = -1.710653 \]

\[ N_{\text{imag}} = 0 \]

| Element | X      | Y      | Z      |
|---------|--------|--------|--------|
| Te      | 0.992851000 | -0.219434000 | -0.386571000 |
| C       | 0.789522000 | -0.072048000 | -2.543493000 |
| H       | -0.075568000 | 0.583896000 | -2.684278000 |
| H       | 1.688810000 | 0.446406000 | -2.897786000 |
| C       | 0.596729000 | -1.427456000 | -3.189793000 |
| H       | -0.285951000 | -1.938081000 | -2.790908000 |
| H       | 1.463999000 | -2.081752000 | -3.044182000 |
| H       | 0.450610000 | -1.315610000 | -4.271243000 |
| O       | -0.698845000 | -0.582210000 | 0.155826000 |
| H       | 1.076547000 | 1.492488000 | -0.319066000 |

**HTeO2Et**

\[ E = -2.027944 \]

\[ G = -1.982966 \]

\[ N_{\text{imag}} = 0 \]

| Element | X      | Y      | Z      |
|---------|--------|--------|--------|
| Te      | -0.847200000 | -0.588340000 | 0.201166000 |
| O       | -1.375061000 | -0.439238000 | -1.707963000 |
| O       | -0.469531000 | 1.099638000 | 0.700132000 |
| H       | -0.569600000 | -0.289138000 | -2.220881000 |
| C       | -2.930875000 | -0.735968000 | 0.713930000 |
| H       | -2.948510000 | -0.514412000 | 1.787540000 |
| H       | -3.368283000 | 0.117407000 | 0.184389000 |
| C       | -3.591558000 | -2.055703000 | 0.373662000 |
| H       | -3.125216000 | -2.899534000 | 0.895021000 |
| H       | -3.559322000 | -2.260000000 | -0.700883000 |
| H       | -4.646964000 | -2.036472000 | 0.672453000 |

**HTeO3Et**

\[ E = -2.221698215494857 \]

\[ G = -2.173802 \]

\[ N_{\text{imag}} = 0 \]

| Element | X      | Y      | Z      |
|---------|--------|--------|--------|
| Te      | -0.968970000 | -0.799592000 | 1.981356000 |
| O       | -1.271584000 | -0.488636000 | 0.248993000 |
| O       | -0.036830000 | -2.507810000 | 2.108654000 |
| O       | -2.305729000 | -0.900382000 | 3.167688000 |
| C       | 0.611196000 | 0.467243000 | 2.694013000 |
| H       | 0.107372000 | 1.433017000 | 2.814123000 |
| H       | 0.831707000 | 0.056659000 | 3.684776000 |
| C       | 1.799290000 | 0.517871000 | 1.760963000 |
| H       | 1.516962000 | 0.862078000 | 0.762242000 |
| H       | 2.288003000 | -0.455870000 | 1.667871000 |
| H       | 2.534950000 | 1.223796000 | 2.165222000 |
| H       | -0.608343000 | -3.072877000 | 2.651665000 |
## Transition states

### HSOEt$^2$

|   | E = -1.791535 | G = -1.747369 |
|---|---------------|---------------|
| N$_{imag}$ | -690.977      |               |

| S   | 0.621299000  | -0.629890000 | -0.633772000 |
| C   | 0.697864000  | -0.037448000 | -2.982045000 |
| H   | -0.115589000 | 0.683163000  | -2.934632000 |
| H   | 1.693588000  | 0.395852000  | -2.923345000 |
| C   | 0.501666000  | -1.310347000 | -3.510141000 |
| H   | 0.412713000  | -1.973643000 | -2.275596000 |
| H   | 1.353234000  | -1.838700000 | -3.938566000 |
| H   | -0.471973000 | -1.561513000 | -3.931145000 |
| O   | 0.404010000  | -2.107664000 | -1.100453000 |
| H   | -0.656612000 | -0.160011000 | -0.499706000 |

### HSO$_2$Et$^+$

|   | E = -2.047034 | G = -1.998381 |
| N$_{imag}$ | -436.564      |               |

| S   | -0.685762000  | -0.365880000 | 0.062512000 |
| O   | -0.171914000  | -0.289466000 | 1.633551000 |
| O   | -0.728487000  | -1.873709000 | -0.329342000 |
| H   | 0.795532000   | -0.305557000 | 1.609068000 |
| C   | -3.074621000  | -0.709458000 | 0.718390000 |
| H   | 2.865399000   | -0.332296000 | 1.716939000 |
| H   | -3.457448000  | 0.024035000  | 0.012187000 |
| C   | -3.175942000  | -2.060522000 | 0.467108000 |
| H   | -1.770452000  | -2.174606000 | -0.035639000 |
| H   | -3.694325000  | -2.411069000 | -0.424739000 |
| H   | -3.086082000  | -2.773272000 | 1.286265000 |

### HSO$_2$Et$^+$

|   | E = -2.288666 | G = -2.239037 |
| N$_{imag}$ | -1121.322      |               |

| S   | -0.668885000  |               |
| O   | -0.156582000  |               |
| O   | 0.575923000   | 0.062509000   |
| H   | 0.156137600   | -2.165909000  |
| C   | 0.830611000   | 1.080532000   |
| H   | 0.154823000   |               |
| C   | 0.593992000   |               |
| H   | 0.006129000   |               |
| H   | 0.143045200   |               |
| O   | 0.498116000   | 0.592114000   |

### HSeOEt$^2$

|   | E = -1.752708 | G = -1.711613 |
| N$_{imag}$ | -794.737      |               |

| Se  | 0.665809000  | -0.590524000 | -0.587056000 |
| C   | 0.711446000  | -0.038338000 | -2.964664000 |
| H   | -0.901383000 | 0.695890000  | -2.941865000 |
| H   | 1.709678000  | 0.395504000  | -2.961671000 |
| C   | 0.495406000  | -1.325681000 | -3.489546000 |
| H   | 0.420016000  | -2.005794000 | -2.329840000 |

### HSeO$_2$Et$^+$

|   | E = -2.009636 | G = -1.964222 |
| N$_{imag}$ | -719.861      |               |

| Se  | -0.853727000 | -0.351775000 | 0.120258000 |
| O   | -0.145910000 | -0.304093000 | 1.787404000 |
| O   | 0.094766100  | -0.200379000 | -0.264233000 |
| H   | 0.809382000  | -0.391837000 | 1.663256000 |
| C   | -3.127971000 | -0.701591000 | 1.025251000 |
| H   | 2.322650000  | -2.773272000 | 0.024035000 |

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S22
HTeOEt‡

\[ E = -2.207825 \]
\[ G = -2.161719 \]
\[ N_{\text{imag}} = -935.661 \]

Se  
-1.026349000  
-0.236525000  
-0.056360000

O  
-1.350339000  
0.617639000  
-1.613309000

O  
-0.842781000  
-1.837655000  
-0.517384000

H  
-0.516352000  
1.083569000  
-1.789338000

C  
-3.215694000  
-0.736815000  
0.918215000

H  
-2.958775000  
-0.384995000  
1.916848000

H  
-3.743679000  
-0.011793000  
0.299510000

C  
-3.206050000  
-2.108298000  
0.597056000

H  
-2.070090000  
-2.188894000  
0.013468000

H  
-3.884405000  
-2.429688000  
-0.195052000

H  
-3.091051000  
-2.806382000  
1.427664000

O  
0.344185000  
0.423736000  
0.495329000

HTeO2Et‡

\[ E = -1.994550 \]
\[ G = -1.951254 \]
\[ N_{\text{imag}} = -848.914 \]

Te  
0.712690000  
-0.562841000  
-0.486540000

C  
0.735608000  
-0.032269000  
-2.976323000

H  
-0.059552000  
0.711295000  
-2.976761000

H  
1.733094000  
0.401403000  
-3.027263000

C  
0.500201000  
-1.332938000  
-3.490459000

H  
0.429214000  
-2.040878000  
-2.366431000

H  
1.330313000  
-1.820174000  
-4.003811000

H  
-0.480285000  
-1.520996000  
-3.930364000

O  
0.430652000  
-2.292341000  
-1.131183000

H  
-0.891735000  
-0.050460000  
-0.340264000

HTeO3Et‡
\[ E = -2.186857 \]
\[ G = -2.142527 \]
\[ N_{\text{imag}} = -707.937 \]

\[
\begin{align*}
\text{Te} & \quad -0.133355000 & 0.790972000 & -0.457365000 \\
\text{C} & \quad -0.613903000 & 2.190528000 & -2.535783000 \\
\text{H} & \quad -1.223461000 & 2.957062000 & -2.058019000 \\
\text{H} & \quad 0.425848000 & 2.477870000 & -2.695535000 \\
\text{C} & \quad -1.207786000 & 1.135542000 & -3.284937000 \\
\text{H} & \quad -1.159798000 & 0.163094000 & -2.517298000 \\
\text{H} & \quad -0.620369000 & 0.145683000 & -4.135019000 \\
\text{H} & \quad -2.275798000 & 1.244678000 & -3.484641000 \\
\text{O} & \quad -0.875011000 & 0.713323000 & 1.315487000 \\
\text{H} & \quad 0.425848000 & 2.957062000 & -2.058019000 \\
\text{O} & \quad 2.076579000 & 0.145683000 & -4.135019000 \\
\text{O} & \quad -0.875011000 & 0.713323000 & 1.315487000 \\
\text{O} & \quad 2.076579000 & 0.145683000 & -4.135019000 \\
\text{O} & \quad -0.405435000 & 0.713323000 & 1.315487000 \\
\end{align*}
\]

**Products**

| E (\text{E}) | G (\text{G}) | \text{N}_{\text{imag}} |
|---|---|---|
| Ethylene | -1.174318 | 0 |
| H\text{$_2$SO} | -0.632976 | 0 |
| H\text{$_2$SO$_2$} | -0.879244 | 0 |
| H\text{$_2$SO$_3$} | -1.153595 | 0 |
| H\text{$_2$SeO} | -0.602264 | 0 |
| H\text{$_2$SeO$_2$} | -0.850341 | 0 |
Table S11: Cartesian coordinates (Å), energies (a.u.) and imaginary frequencies (cm$^{-1}$) of the optimized structures of the minimal model. Level of theory: ZORA-OLYP/TZ2P

| Structure     | Reactants | HSOEt       | HSO$_2$Et    |
|---------------|-----------|-------------|--------------|
| $\text{E} =$ | $-1.769872$ | $-1.721144$ | $-2.027787$  |
| $\text{G} =$ | $-1.769872$ | $-1.721144$ | $-1.975195$  |
| $\text{N}_{\text{imag}} =$ | $0$       | $0$         | $0$          |
| $\text{S}$   | $0.886206000$ | $-0.184592000$ | $-1.097728000$ |
| $\text{O}$   | $0.746073000$ | $-0.035847000$ | $-1.489404000$ |
| $\text{H}$   | $-0.105186000$ | $0.620950000$ | $-0.6614919000$ |
| $\text{H}$   | $1.668929000$ | $0.470565000$ | $0.658457000$ |

| Structure     | H$_2$SeO$_3$ | $\text{E} =$ | $-1.096063$ |
|---------------|--------------|--------------|-------------|
| $\text{G} =$ | $-1.808685$  | $-1.086645$  | $-1.0787809$ |
| $\text{N}_{\text{imag}} =$ | $0$       | $0$         | $0$          |
| $\text{Se}$  | $-0.285588000$ | $0.263833000$ | $-0.306690000$ |
| $\text{O}$   | $-0.045796000$ | $-0.151524000$ | $-5.039445000$ |
| $\text{O}$   | $0.914325000$ | $1.591638000$ | $-3.132045000$ |
| $\text{O}$   | $0.384997000$ | $-0.972380000$ | $-2.514340000$ |
| $\text{H}$   | $0.611188000$ | $-0.867544000$ | $-5.030324000$ |
| $\text{H}$   | $1.723116000$ | $1.150480000$ | $-2.822976000$ |

| Structure     | H$_2$TeO   | $\text{E} =$ | $-0.579634$ |
|---------------|------------|--------------|-------------|
| $\text{G} =$ | $-0.586078$  | $-0.586078$  | $-0.586078$  |
| $\text{N}_{\text{imag}} =$ | $0$       | $0$         | $0$          |
| $\text{Te}$  | $0.561225000$ | $-0.425479000$ | $-2.051028000$ |
| $\text{H}$   | $0.767415000$ | $-1.953095000$ | $-5.030324000$ |
| $\text{O}$   | $0.914325000$ | $1.591638000$ | $-3.132045000$ |
| $\text{O}$   | $0.384997000$ | $-0.972380000$ | $-5.030324000$ |
| $\text{H}$   | $1.723116000$ | $1.150480000$ | $-2.822976000$ |

| Structure     | H$_2$TeO$_2$ | $\text{E} =$ | $-1.086645$ |
|---------------|--------------|--------------|-------------|
| $\text{G} =$ | $-0.840300$  | $-0.840300$  | $-0.840300$  |
| $\text{N}_{\text{imag}} =$ | $0$       | $0$         | $0$          |
| $\text{Te}$  | $1.975002000$ | $-2.472030000$ | $0.000000000$ |
| $\text{O}$   | $2.732156000$ | $-1.451505000$ | $-1.502903000$ |
| $\text{O}$   | $0.914325000$ | $1.591638000$ | $-3.132045000$ |
| $\text{O}$   | $0.384997000$ | $-0.972380000$ | $-5.030324000$ |
| $\text{H}$   | $0.611188000$ | $-0.867544000$ | $-5.030324000$ |
| $\text{H}$   | $1.723116000$ | $1.150480000$ | $-2.822976000$ |

| Structure     | H$_2$TeO$_3$ | $\text{E} =$ | $-1.087809$ |
|---------------|--------------|--------------|-------------|
| $\text{G} =$ | $-1.087809$  | $-1.087809$  | $-1.087809$  |
| $\text{N}_{\text{imag}} =$ | $0$       | $0$         | $0$          |
| $\text{Te}$  | $1.975002000$ | $-2.472030000$ | $0.000000000$ |
| $\text{O}$   | $2.732156000$ | $-1.451505000$ | $-1.502903000$ |
| $\text{O}$   | $0.914325000$ | $1.591638000$ | $-3.132045000$ |
| $\text{O}$   | $0.384997000$ | $-0.972380000$ | $-5.030324000$ |
| $\text{H}$   | $0.611188000$ | $-0.867544000$ | $-5.030324000$ |
| $\text{H}$   | $1.723116000$ | $1.150480000$ | $-2.822976000$ |

G = -0.606432
$\text{N}_{\text{imag}} =$ $0$
HSO₃Et

E = -2.281745  
G = -2.224105  
N_{imag} = 0

S  -0.832695000  -0.766307000  1.999798000
O  -1.099441000  -0.429897000  0.626102000
O  -0.084838000  -2.219553000  1.983688000
O  -1.891605000  -0.839925000  2.983712000
C  0.463675000  0.315494000  2.633278000
H  -0.049120000  1.278580000  2.727805000
H  0.682990000  -0.049897000  3.640635000
C  1.705770000  0.416636000  1.758190000
H  1.455161000  0.763954000  0.753866000
H  2.220570000  -0.543426000  1.677449000
H  2.397917000  1.136127000  2.206731000
H  -0.470362000  -2.727198000  2.716291000

HSeOEt

E = -1.714984  
G = -1.670566  
N_{imag} = 0

Se  0.937414000  -0.201800000  -0.504183000
C  0.770910000  -0.046524000  -2.504594000
H  -0.089177000  0.608042000  -2.664582000
H  1.684459000  0.463667000  -2.830268000
C  0.592648000  -1.412079000  -3.144946000
H  -0.294826000  -1.918133000  -2.754649000
H  1.460743000  -2.058173000  -2.976641000
H  0.465534000  -1.305315000  -4.228038000
O  -0.579896000  -0.565159000  0.049635000
H  1.050893000  1.321672000  -0.413228000

HSeO₂Et

E = -1.973795  
G = -1.925701  
N_{imag} = 0

Se  -0.977707000  -0.553044000  0.181514000
O  -1.448479000  -0.425732000  -1.612435000
O  -0.551928000  0.944647000  0.685827000
H  -0.609668000  -0.392802000  -2.098193000
C  -2.902570000  -0.693036000  0.682401000
H  -2.883823000  -0.488579000  1.757148000
H  -3.361315000  0.155221000  0.168448000
C  -3.540902000  -2.030098000  0.344000000
H  -3.028420000  -2.865280000  0.833222000
H  -3.546606000  -2.212204000  -0.733339000
H  -4.580703000  -2.040855000  0.689972000

HSeO₃Et

E = -2.165769
\[
\begin{array}{cccc}
\text{Se} & -0.891470000 & -0.779526000 & 1.999787000 \\
\text{O} & -1.198080000 & -0.459108000 & 0.447307000 \\
\text{O} & -0.016841000 & -2.368150000 & 2.069245000 \\
\text{O} & -2.088947000 & -0.875199000 & 3.085470000 \\
\text{C} & 0.545508000 & 0.411225000 & 2.670436000 \\
\text{H} & 0.020250000 & 1.366628000 & 2.757234000 \\
\text{H} & 0.748583000 & 0.014635000 & 3.667722000 \\
\text{C} & 1.486276000 & 0.769166000 & 0.753727000 \\
\text{H} & 2.256395000 & -0.502321000 & 1.691002000 \\
\text{H} & 2.468718000 & 1.187065000 & 2.174420000 \\
\text{H} & -0.588207000 & -2.921837000 & 2.629074000 \\
\end{array}
\]

\[G = -2.114660 \quad N_{\text{imag}} = 0\]

\[
\begin{array}{cccc}
\text{Se} & -0.891470000 & -0.779526000 & 1.999787000 \\
\text{O} & -1.198080000 & -0.459108000 & 0.447307000 \\
\text{O} & -0.016841000 & -2.368150000 & 2.069245000 \\
\text{O} & -2.088947000 & -0.875199000 & 3.085470000 \\
\text{C} & 0.545508000 & 0.411225000 & 2.670436000 \\
\text{H} & 0.020250000 & 1.366628000 & 2.757234000 \\
\text{H} & 0.748583000 & 0.014635000 & 3.667722000 \\
\text{C} & 1.486276000 & 0.769166000 & 0.753727000 \\
\text{H} & 2.256395000 & -0.502321000 & 1.691002000 \\
\text{H} & 2.468718000 & 1.187065000 & 2.174420000 \\
\text{H} & -0.588207000 & -2.921837000 & 2.629074000 \\
\end{array}
\]

\[\text{HTeOEt} \quad E = -1.687642 \quad G = -1.646228 \quad N_{\text{imag}} = 0\]

\[
\begin{array}{cccc}
\text{Te} & 0.996033000 & -0.212919000 & -0.364435000 \\
\text{C} & 0.789761000 & -0.071766000 & -2.550728000 \\
\text{H} & -0.075313000 & 0.581657000 & -2.689917000 \\
\text{H} & 1.688862000 & 0.446623000 & -2.903718000 \\
\text{C} & 0.597021000 & -1.433761000 & -3.200528000 \\
\text{H} & -0.284642000 & -1.945052000 & -2.802991000 \\
\text{H} & 1.464999000 & -0.075313000 & -2.550728000 \\
\text{H} & 0.451515000 & -1.319990000 & -4.281172000 \\
\text{O} & -0.709185000 & -0.576255000 & 0.180166000 \\
\text{H} & 1.079652000 & 1.505590000 & -0.302549000 \\
\end{array}
\]

\[\text{HTeO}_{2}\text{Et} \quad E = -1.956182 \quad G = -1.909584 \quad N_{\text{imag}} = 0\]

\[
\begin{array}{cccc}
\text{Te} & -0.825587000 & -0.583021000 & 0.213043000 \\
\text{O} & -1.358650000 & -0.471942000 & -1.718323000 \\
\text{O} & -0.456715000 & 1.126948000 & 0.688842000 \\
\text{H} & -0.566821000 & -0.268976000 & -2.238425000 \\
\text{C} & -2.937287000 & -0.735824000 & 0.725792000 \\
\text{H} & -2.988368000 & -0.523831000 & 1.799612000 \\
\text{H} & -3.371018000 & 0.117966000 & 0.197651000 \\
\text{C} & -3.600503000 & -2.059892000 & 0.372806000 \\
\text{H} & -3.136231000 & -2.906223000 & 0.890377000 \\
\text{H} & -3.565096000 & -2.256184000 & -0.702130000 \\
\text{H} & -4.655844000 & -2.040780000 & 0.669321000 \\
\end{array}
\]

\[\text{HTeO}_{3}\text{Et} \quad E = -2.139122 \quad G = -2.092000 \quad N_{\text{imag}} = 0\]

\[
\begin{array}{cccc}
\text{Te} & -0.989889000 & -0.802000000 & 1.984126000 \\
\text{O} & -1.298418000 & -0.501381000 & 0.236998000 \\
\text{O} & -0.030339000 & -2.517068000 & 2.125674000 \\
\text{O} & -2.338655000 & -0.898470000 & 3.177185000 \\
\text{C} & 0.619305000 & 0.482983000 & 2.698746000 \\
\text{H} & 0.117441000 & 1.448139000 & 2.812632000 \\
\text{H} & 0.837427000 & 0.069990000 & 3.686832000 \\
\text{C} & 1.812061000 & 0.524310000 & 1.760122000 \\
\text{H} & 1.532997000 & 0.872239000 & 0.762917000 \\
\text{H} & 2.292983000 & -0.452248000 & 1.667497000 \\
\end{array}
\]
|        | HSOEt\textsuperscript{\textdagger} | HSO\textsubscript{2}Et\textsuperscript{\textdagger} |
|--------|----------------------------------|----------------------------------|
| E      | -1.724630                       | -1.972063                       |
| G      | -1.681268                       | -1.924821                       |
| \(N_{imag}\) | -947.285                       | -897.183                       |

|        | HSO\textsubscript{3}Et\textsuperscript{\textdagger} |
|--------|----------------------------------|
| E      | -2.200711                       |
| G      | -2.152137                       |
| \(N_{imag}\) | -1230.495                       |

|        | HSeOEt\textsuperscript{\textdagger} | HSeO\textsubscript{2}Et\textsuperscript{\textdagger} |
|--------|----------------------------------|----------------------------------|
| E      | -1.685686                       | -1.935338                       |
| G      | -1.645254                       | -1.890901                       |
| \(N_{imag}\) | -899.872                       | -1000.123                       |

|        | S 0.616276000 -0.642266000 -0.599550000 | S -0.672849000 -0.370955000 0.048323000 |
|--------|----------------------------------|----------------------------------|
|        | C 0.703089000 -0.027084000 -2.998359000 | O -0.156910000 -0.274184000 1.638310000 |
|        | H -0.109774000 0.691141000 -2.953717000 | O -0.710051000 -1.878744000 -0.335115000 |
|        | H 1.698155000 0.402024000 -2.937355000 | H 0.812860000 -0.300103000 1.623647000 |
|        | C 0.502712000 -1.321507000 -3.496222000 | C -3.079643000 -0.702662000 0.715538000 |
|        | H 0.408131000 -1.975624000 -2.314383000 | H -2.879495000 -0.325159000 1.713597000 |
|        | H 1.352948000 -1.835385000 -3.943806000 | H -3.474345000 0.023926000 0.011597000 |
|        | H -0.463870000 -1.555412000 -3.941981000 | C -3.146659000 -2.066263000 0.455242000 |
|        | O 0.392102000 -2.119615000 -1.076256000 | H -1.813659000 -2.199479000 -0.026371000 |
|        | H -0.659450000 -0.156437000 -0.467679000 | H -3.699646000 -2.412398000 -0.416738000 |
|        |                                  | H -3.094500000 -2.765746000 1.288301000 |

|        | HSeO\textsubscript{2}Et\textsuperscript{\textdagger} |
|--------|----------------------------------|
| E      | -1.685686                       |
| G      | -1.645254                       |
| \(N_{imag}\) | -899.872                       |

|        | Se 0.662368000 -0.599419000 -0.541261000 | Se -0.651562000 -0.328128000 -0.010148000 |
|--------|----------------------------------|----------------------------------|
|        | C 0.715274000 -0.027252000 -2.991715000 | O -0.093899000 -0.276039000 1.737575000 |
HSeO3Et‡

E = -2.123199
G = -2.077982
Nimag = -762.759

H -0.089847000 0.700791000 -2.964128000 O -0.713986000 -1.981119000 -0.410006000
H 1.712634000 0.402397000 -2.980134000 H 0.869877000 -0.378719000 1.712933000
C 0.497886000 -1.334060000 -3.485545000 C -3.054533000 -0.700539000 0.708515000
H 0.417664000 -2.003952000 -2.363444000 H -2.856588000 -0.336473000 1.712635000
H 1.338240000 -1.823788000 -3.978202000 H -3.499774000 0.026686000 0.035255000
H -0.471575000 -1.536627000 -3.941700000 C -3.131611000 -2.075016000 0.436886000
O 0.411461000 -2.207534000 -1.077912000 H -1.874921000 -2.258101000 -0.059397000
H -0.753786000 -0.110720000 -0.405266000 H -3.746911000 -2.398047000 -0.402219000

HTeOEt‡

E = -1.661712
G = -1.623607
Nimag = -933.114

Se -0.968524000 -0.215988000 -0.057843000 O -1.329598000 0.658874000 -1.625784000
O -0.802895000 -1.826913000 -0.528164000 H -0.496787000 1.114968000 -1.839754000
C -3.269870000 -0.756176000 0.952127000 H -3.004422000 -0.417276000 1.950146000
H -3.779321000 -0.024610000 0.330200000 C -3.215662000 -2.123560000 0.594451000
H -2.111397000 -2.198239000 0.031146000 H -3.896475000 -2.437906000 -0.198531000
H -3.112572000 -2.832030000 1.417897000 O 0.426111000 0.442693000 0.470726000

HTeO2Et‡

E = -1.922111
G = -1.879597
Nimag = -1060.447

Te 0.712818000 -0.569694000 -0.436853000 Te 0.160292000 0.409007000 -0.511593000
C 0.736970000 -0.022430000 -3.007302000 C -0.552347000 2.094834000 -2.395368000
H -0.061720000 0.713610000 -2.997665000 H -1.032495000 2.777920000 -1.698845000
H 1.733692000 0.407726000 -3.048101000 H 0.437813000 2.406236000 -2.717268000
C 0.501986000 -1.339540000 -3.492237000 C -1.325166000 1.218699000 -3.192860000
H 0.429275000 -2.035191000 -2.394704000 H -1.186281000 0.061742000 -2.511569000
H 1.330905000 -1.821797000 -4.011726000 H -0.930346000 0.952740000 -4.173193000
H -0.474195000 -1.524626000 -3.942266000 H -2.408299000 1.332197000 -3.151733000
O 0.425836000 -2.301882000 -1.109474000 O -0.829237000 -0.739713000 -1.610653000
H -0.895248000 -0.046340000 -0.288979000 H -1.241918000 1.174700000 0.684026000

HTeO3Et‡

E = -2.106398
G = -2.062707
$N_{\text{imag}} = -545.639$

|   |   |   |   |
|---|---|---|---|
|Te | -0.130280000 | 0.771878000 | -0.398351000 |
|C  | -0.626244000 | 2.225258000 | -2.588496000 |
|H  | -1.235839000 | 2.982559000 | -2.102303000 |
|H  | 0.417340000  | 0.786362000 | -4.159234000 |
|C  | -1.217148000 | 1.141562000 | -3.307162000 |
|H  | -1.172767000 | 0.194558000 | -2.554102000 |
|H  | -0.632926000 | 0.786362000 | -4.159234000 |
|H  | -2.283760000 | 1.252235000 | -3.513411000 |
|O  | -0.876286000 | 0.661010000 | -1.302207000 |
|O  | 1.817287000  | 0.451919000 | -0.575807000 |
|H  | 2.119971000  | 0.107359000 | 0.281365000  |
|O  | -0.400480000 | 0.671066000 | 1.387554000  |

Products

### Ethylene

|   |   |   |   |
|---|---|---|---|
|E  | -1.139577 |   |   |
|G  | -1.110555 |   |   |
|N_{\text{imag}} | 0 |   |   |

### H$_2$SO

|   |   |   |   |
|---|---|---|---|
|E  | -0.609715 |   |   |
|G  | -0.611198 |   |   |
|N_{\text{imag}} | 0 |   |   |

### H$_2$SO$_2$

|   |   |   |   |
|---|---|---|---|
|E  | -0.846951 |   |   |
|G  | -0.844209 |   |   |
|N_{\text{imag}} | 0 |   |   |

### H$_2$SO$_3$

|   |   |   |   |
|---|---|---|---|
|E  | -1.109808 |   |   |
|G  | -1.106208 |   |   |
|N_{\text{imag}} | 0 |   |   |

### H$_2$SeO

|   |   |   |   |
|---|---|---|---|
|E  | -0.579597 |   |   |
|G  | -0.584105 |   |   |
|N_{\text{imag}} | 0 |   |   |

### H$_2$SeO$_2$

|   |   |   |   |
|---|---|---|---|
|E  | -0.819948 |   |   |
|G  | -0.819863 |   |   |
|N_{\text{imag}} | 0 |   |   |

---

S30
Table S12: Cartesian coordinates (Å), energies (a.u.) and imaginary frequencies (cm\(^{-1}\)) of the optimized structures of the minimal model. Level of theory: ZORA-B3LYP/TZ2P ae.

### Reactants

#### HSOEt

| Element | X | Y | Z  |
|---------|---|---|----|
| S       | 0.892074000 | -0.182223000 | -0.627575000 |
| C       | 0.758794000 | -0.024622000 | -2.453091000 |
| H       | -0.087716000 | 0.630844000 | -2.656913000 |
| H       | 1.680141000 | 0.469071000 | -2.773006000 |
| C       | 0.582114000 | -1.393371000 | -3.094828000 |
| H       | -0.313372000 | -1.883398000 | -2.714137000 |

| Energy   | -2.109460 |
| Imaginary Frequency | 0 |

#### HSO\(_2\)Et

| Element | X | Y | Z  |
|---------|---|---|----|
| S       | 1.105560000 | -0.496789000 | 0.176800000 |
| C       | 1.501894000 | -0.454506000 | -1.451749000 |
| O       | 0.983883000 | 1.690125000 | -5.157640000 |
| H       | 1.680141000 | 0.469071000 | -2.773006000 |
| C       | 0.582114000 | -1.393371000 | -3.094828000 |
| H       | -0.313372000 | -1.883398000 | -2.714137000 |

| Energy   | -2.441496 |
| Imaginary Frequency | 0 |
HSO₃Et

$E = -2.766837$
$G = -2.707426$

$N_{\text{imag}} = 0$

S       -0.820088000  -0.758031000  2.003072000
O       -1.076394000  -0.421018000  0.635949000
O       -0.062267000  -2.189431000  1.997531000
C       -1.885484000  -0.849362000  2.966304000
C       -0.048322000  -0.036384000  3.647479000
C       -1.693625000  0.406914000  1.758227000
C       -0.677261000  3.647479000  0.758390000
H       -2.186999000  -0.560296000  1.677979000
H       -2.399131000  1.115197000  2.192655000
H       -0.457506000  -2.733927000  2.694965000

HSeOEt

$E = -2.049620$
$G = -2.003623$

$N_{\text{imag}} = 0$

Se      0.951197000  -0.193537000  -0.523928000
C      0.793073000  -0.032723000  -2.511719000
H     -0.057365000  0.626155000  -2.672398000
H     1.707206000  0.455917000  -2.851855000
C     0.585312000  -1.405911000  -3.126353000
H    -0.290380000  -1.892111000  -2.696017000
H     1.450744000  -2.052365000  -2.971609000
H     0.425305000  -1.316160000  -4.202079000
O    -0.569369000  -0.620676000  -0.022191000
H   1.002637000  1.317610000  -0.393345000

HSeO₂Et

$E = -2.381599$
$G = -2.331570$

$N_{\text{imag}} = 0$

Se      -0.983255000  -0.544303000  0.209710000
O    -1.464685000  -0.514938000  -1.568507000
O    -0.594223000  0.985337000  0.627161000
H     0.652059000  -0.438763000  -2.087392000
C    -2.892373000  -0.686988000  0.711561000
H   -2.883512000  -0.518120000  1.788197000
H   -3.342271000  0.173869000  0.220276000
H   -3.525666000  -2.011899000  0.320757000
O    -3.019327000  -2.857827000  0.788745000
H   -3.507747000  -2.153957000  -0.758540000
H   -4.567003000  -2.034533000  0.646597000

HSeO₃Et

$E = -2.640756$
$G = -2.588013$

$N_{\text{imag}} = 0$
Se  -0.880514000  -0.765551000  2.004314000  E = -2.016045
O   -1.175655000  -0.443725000  0.454718000
O    0.005369000  -2.325078000  0.028502000
O   -2.086735000  -0.889640000  3.073323000  G = -1.973216
C    0.535940000  0.420575000  2.681618000  \( N_{\text{imag}} = 0 \)
H    0.535940000  0.420575000  2.681618000  HTeOEt
H    0.739320000  0.028502000  3.675639000
C    1.740331000  0.449143000  1.759690000  HTeOEt
H    2.215823000  -0.527812000  1.695400000
H   -0.551296000  -2.917649000  2.607599000

O    0.024791000  1.378703000  2.761475000
H    0.739320000  0.028502000  3.675639000  HTeO_2Et
C    1.740331000  0.449143000  1.759690000  HTeO_2Et
H    2.215823000  -0.527812000  1.695400000
H   -0.551296000  -2.917649000  2.607599000

E = -2.359351
G = -2.312190
\( N_{\text{imag}} = 0 \)

Te    1.025109000  -0.190380000  -0.390813000
C    0.828692000  -0.049984000  -2.564938000
H   -0.012416000  0.624287000  -2.712931000
H    1.373626000  0.421121000  -2.937516000
C    0.577754000  -1.423195000  -3.171047000
H   -0.299625000  -1.891777000  -2.725132000
H    1.430042000  -2.090757000  -3.032729000
C    0.399472000  -1.335702000  -4.244389000
O   -0.664816000  -0.923099000  -0.089194000
H    0.975864000  1.514895000  -0.281193000

\( N_{\text{imag}} = 0 \)

E = -2.606878
G = -2.558528

Te    -0.986134000  -0.779768000  2.002378000
O   -1.295007000  -0.478255000  0.258491000
O    0.011787000  -2.451124000  2.141292000
O   -2.339053000  -0.921851000  3.180849000
C    0.604487000  0.502723000  2.708469000
H    0.124754000  1.476326000  2.794487000
H    0.818585000  0.114046000  3.702042000
C    1.796637000  0.493607000  1.764836000
H    1.516757000  0.816518000  0.763622000
H    2.247575000  -0.494926000  1.698261000
H    2.551081000  1.184145000  2.146144000
H   -0.553446000  -3.125942000  2.546676000

\( N_{\text{imag}} = 0 \)

\( N_{\text{imag}} = 0 \)
Transition states

|                  | HSOEt‡ |                  | HSO₂Et‡ |
|------------------|--------|------------------|---------|
| E                | -2.062665 | E                | -2.383637 |
| G                | -2.017813 | G                | -2.334720 |
| N_{imag}         | -1162.901 | N_{imag}         | -1202.516 |

|                  |                  |                  |
|------------------|------------------|------------------|
| S                 | 0.615312000      | S                | -0.695082000 |
| C                 | 0.701871000      | O                | -0.205627000 |
| H                 | 1.691968000      | H                | 0.761334000  |
| C                 | 0.501176000      | C                | -3.040632000 |
| H                 | 0.408752000      | H                | -3.460272000 |
| H                 | 1.348102000      | H                | -3.460272000 |
| H                 | -0.459427000     | C                | -3.123134000 |
| O                 | 0.393894000      | O                | -1.827185000 |
| H                 | -0.654901000     | H                | -3.716004000 |
|                  |                  | H                | -3.083111000 |

|                  |                  |                  |
|------------------|------------------|------------------|
|                  | HSO₃Et‡          |                  | HSeO₂Et‡     |
|                  |                  |                  |
| E                | -2.681772        | E                | -2.342060    |
| G                | -2.631291        | G                | -2.295986    |
| N_{imag}         | -1365.669        | N_{imag}         | -1220.814    |

|                  |                  |                  |
|------------------|------------------|------------------|
| S                 | -1.070438000     | S                | -0.140587000 |
| O                 | -1.253578000     | O                | 0.593595000  |
| O                 | -0.810172000     | O                | -1.590517000 |
| H                 | -0.440521000     | H                | 1.097802000  |
| C                 | -3.317843000     | C                | -0.821509000 |
| H                 | -3.097985000     | H                | 0.396077000  |
| H                 | -3.846733000     | H                | -0.172051000 |
| C                 | -3.152229000     | C                | -2.178529000 |
| H                 | -1.947983000     | H                | -2.086513000 |
| H                 | -3.723127000     | H                | -2.609352000 |
| H                 | -2.959867000     | H                | 1.429768000  |
| O                 | 0.059177000      | O                | 0.523074000  |

S34
\[ E = -2.595768 \]
\[ G = -2.548874 \]
\[ N_{\text{imag}} = -855.202 \]

\[ \text{Se} \quad 0.958626000 \quad -0.210749000 \quad -0.043677000 \]
\[ \text{O} \quad -1.346500000 \quad 0.652368000 \quad -1.589866000 \]
\[ \text{O} \quad -0.791561000 \quad -1.808969000 \quad -0.517115000 \]
\[ \text{H} \quad -0.523218000 \quad 1.086991000 \quad -1.866022000 \]
\[ \text{C} \quad -3.267755000 \quad -0.758197000 \quad 0.945132000 \]
\[ \text{H} \quad -3.018118000 \quad -0.415237000 \quad 1.940139000 \]
\[ \text{H} \quad -3.756776000 \quad -0.030865000 \quad 0.310497000 \]
\[ \text{C} \quad -3.212926000 \quad -2.123683000 \quad 0.596121000 \]
\[ \text{H} \quad -2.109981000 \quad -2.204870000 \quad 0.044035000 \]
\[ \text{H} \quad -3.887640000 \quad -2.435294000 \quad -0.197490000 \]
\[ \text{H} \quad -3.128875000 \quad -2.822928000 \quad 1.423845000 \]
\[ \text{O} \quad 0.440676000 \quad 0.455335000 \quad 0.451002000 \]

\[ \text{HSeO}_3\text{Et}^\ddagger \]

\[ \text{HTeO}_3\text{Et}^\ddagger \]

\[ E = -1.989151 \]
\[ G = -1.949652 \]
\[ N_{\text{imag}} = -1097.587 \]

\[ \text{Se} \quad 0.715640000 \quad -0.562291000 \quad -0.432798000 \]
\[ \text{C} \quad 0.734585000 \quad -0.027511000 \quad -3.007383000 \]
\[ \text{H} \quad -0.062797000 \quad 0.702502000 \quad -2.995815000 \]
\[ \text{H} \quad 1.725331000 \quad 0.403043000 \quad -3.051146000 \]
\[ \text{C} \quad 0.501367000 \quad -1.344028000 \quad -3.489180000 \]
\[ \text{H} \quad 0.428471000 \quad -2.042198000 \quad -2.407659000 \]
\[ \text{H} \quad 1.327844000 \quad -1.813453000 \quad -4.056101000 \]
\[ \text{H} \quad -0.469073000 \quad -1.520678000 \quad -3.949491000 \]
\[ \text{O} \quad 0.424826000 \quad -2.293664000 \quad -1.095009000 \]
\[ \text{H} \quad -0.885995000 \quad -0.041922000 \quad -0.289868000 \]

\[ \text{Te} \quad 0.171018000 \quad 0.388960000 \quad -0.518112000 \]
\[ \text{C} \quad -0.543797000 \quad 2.080451000 \quad -2.381263000 \]
\[ \text{H} \quad -1.016669000 \quad 2.747002000 \quad -1.671139000 \]
\[ \text{H} \quad 0.435216000 \quad 2.400269000 \quad -2.711562000 \]
\[ \text{C} \quad -1.324355000 \quad 1.213791000 \quad -3.180332000 \]
\[ \text{H} \quad -1.199132000 \quad 0.059939000 \quad -2.530523000 \]
\[ \text{H} \quad -0.940749000 \quad 0.977304000 \quad -4.168097000 \]
\[ \text{H} \quad -2.401336000 \quad 1.345933000 \quad -3.134580000 \]
\[ \text{O} \quad -0.831556000 \quad -0.751309000 \quad -1.598797000 \]
\[ \text{O} \quad -1.222635000 \quad 1.185105000 \quad 0.645783000 \]
\[ \text{H} \quad -1.467705000 \quad 0.560956000 \quad 1.340749000 \]
HTeO₃Et‡
E = -2.572483
G = -2.527343
Nimag = -628.462

Te -0.139912000 0.769383000 -0.382258000
C -0.633816000 2.224919000 -2.587440000
H -1.244212000 2.976230000 -2.104874000
H 0.408833000 2.488227000 -2.711751000
C -1.215135000 1.144835000 -3.311127000
H -1.170457000 0.197885000 -2.566624000
H -0.624794000 0.801330000 -4.158461000
H -2.275183000 1.258866000 -3.526039000
O -0.855440000 -0.661142000 -1.301360000
O 1.794988000 0.488686000 -0.567045000
H 2.131025000 0.094128000 0.252536000
O -0.396996000 0.631154000 1.400243000

Products

Ethylene
E = -1.325471
G = -1.295669
Nimag = 0

H₂SO
E = -0.766465
G = -0.767606
Nimag = 0

H₂SeO
E = -0.732397
G = -0.736529
Nimag = 0

H₂SeO₂
E = -1.044768
G = -1.044244
Nimag = 0
Se 0.560621000 -0.510247000 -2.008774000 Se 2.045825000 -2.406492000 0.000000000
H 0.740937000 -1.860968000 -2.584426000 O 2.711784000 -1.479148000 -1.402296000
O -0.035426000 -1.059934000 -0.371384000 O 2.711784000 -1.479148000 1.402296000
H 0.746092000 -1.152415000 0.187227000 H 3.566246000 -1.864232000 1.635673000
H 3.566246000 -1.864232000 -1.635673000

**SeH**

E = -1.347944
G = -1.347017
N\text{imag} = 0

Se -0.297092000 0.262863000 -3.299571000
O -0.041484000 -0.153480000 -5.030869000
O 0.914364000 1.581813000 -3.132078000
O 0.374582000 -0.976457000 -2.505672000
H 0.613360000 -0.871217000 -5.055205000
H 1.738512000 1.170666000 -2.821804000

**H\text{SeO}**

E = -1.031938
G = -1.347017
N\text{imag} = 0

Se -0.297092000 0.262863000 -3.299571000
O -0.041484000 -0.153480000 -5.030869000
O 0.914364000 1.581813000 -3.132078000
O 0.374582000 -0.976457000 -2.505672000
H 0.613360000 -0.871217000 -5.055205000
H 1.738512000 1.170666000 -2.821804000

**H\text{SeO}_3**

E = -1.031938
G = -1.337807
N\text{imag} = 0

Se -0.297092000 0.262863000 -3.299571000
O -0.041484000 -0.153480000 -5.030869000
O 0.914364000 1.581813000 -3.132078000
O 0.374582000 -0.976457000 -2.505672000
H 0.613360000 -0.871217000 -5.055205000
H 1.738512000 1.170666000 -2.821804000

**H\text{SeO}_2**

Te 1.953687000 -2.473526000 0.000000000
O 2.737345000 -1.460319000 -1.503462000
O 2.737345000 -1.460319000 1.503462000
H 3.586754000 -1.849544000 1.744009000
H 3.586754000 -1.849544000 -1.744009000

**H\text{TeO}**

E = -0.706699
G = -0.713044
N\text{imag} = 0

Te 0.557230000 -0.422498000 -2.068003000
H 0.767736000 -1.953885000 -2.710449000
O -0.046353000 -1.050897000 -0.278178000
H 0.733611000 -1.156285000 0.279274000

**H\text{TeO}_3**

E = -1.338868
G = -1.338868
N\text{imag} = 0

Te -0.391864000 0.286298000 -3.274119000
O -0.051326000 -0.197707000 -5.135135000
O 0.976771000 1.668108000 -3.094347000
O 0.373528000 -1.084305000 -2.405253000
H 0.597294000 -0.918950000 -5.166666000
H 1.797837000 1.260742000 -2.775676000

Table S13: Cartesian coordinates (Å), energies (a.u.) and imaginary frequencies (cm⁻¹) of the optimized structures of the minimal model. Level of theory: ZORA-BLYP-D3(BJ)/TZ2P.

**Reactants**

**HSOEt**

E = -1.755476
G = -1.707843
N\text{imag} = 0

S 0.899361000 -0.183046000 -0.610734000
C 0.766651000 -0.017647000 -2.465562000
H -0.082098000 0.645042000 -2.664084000
H 1.696662000 0.473543000 -2.782270000
C 0.580074000 -1.396389000 -3.099389000
H -0.320522000 -1.880008000 -2.707019000

**HSO2Et**

E = -2.011166
G = -1.959875
N\text{imag} = 0

S -1.088188000 -0.498441000 0.185813000
O -1.511945000 -0.449704000 -1.481575000
O -0.649949000 0.853210000 0.625107000
H -0.680746000 -0.582722000 -1.977654000
C -2.867134000 -0.647274000 0.674067000
H -2.842586000 -0.485759000 1.757587000
| Element | X       | Y       | Z    |
|---------|---------|---------|------|
| H       | 1.438890000 | -2.047560000 | -2.897505000 |
| H       | 0.471812000 | -1.302463000 | -4.185803000 |
| O       | -0.443277000 | -0.613002000 | -0.074085000 |
| H       | 0.991171000 | 1.207700000 | -0.485043000 |
| H       | -3.361588000 | 0.207168000 | 0.199162000 |
| C       | -3.485121000 | -1.994215000 | 0.296779000 |
| H       | -3.521169000 | -2.118362000 | -0.789162000 |
| H       | -4.507988000 | -2.056771000 | 0.685436000 |

**HSO$_3$Et**

E = -2.255623  
G = -2.199416  
$N_{\text{imag}} = 0$

| Element | X       | Y       | Z    |
|---------|---------|---------|------|
| S       | -0.834180000 | -0.755369000 | 1.998102000 |
| O       | -1.081423000 | -0.415631000 | 0.610168000 |
| O       | -0.047353000 | -2.215389000 | 1.991846000 |
| C       | -0.679321000 | 1.305274000 | 2.741991000 |
| C       | 1.432272000 | 0.338211000 | 2.653227000 |
| H       | -0.449543000 | -2.746253000 | 2.709181000 |

**HSeO$_3$Et**

E = -1.703921  
G = -1.660639  
$N_{\text{imag}} = 0$

| Element | X       | Y       | Z    |
|---------|---------|---------|------|
| Se      | 0.966061000 | -0.185644000 | -0.504712000 |
| C       | 0.810383000 | -0.021098000 | -2.533737000 |
| H       | -0.032565000 | 0.655759000 | -2.693028000 |
| H       | 1.741943000 | 0.450770000 | -2.866847000 |
| C       | 0.576659000 | -1.405878000 | -3.127020000 |
| H       | -0.308230000 | -1.870867000 | -2.690130000 |
| H       | 1.436712000 | -2.066411000 | -2.962965000 |
| H       | 0.410978000 | -1.332537000 | -4.208887000 |
| O       | -0.555719000 | -0.689442000 | -0.099474000 |
| H       | 0.952480000 | 1.351546000 | -0.385811000 |

| Element | X       | Y       | Z    |
|---------|---------|---------|------|
| Se      | -0.963044000 | -0.545241000 | 0.217966000 |
| C       | -1.478752000 | -0.507111000 | -1.600931000 |
| O       | -0.552378000 | 0.997665000 | 0.657515000 |
| H       | -0.649284000 | -0.447313000 | -2.114458000 |
| C       | -2.910740000 | -0.681631000 | 0.721241000 |
| H       | -2.902089000 | -0.507853000 | 1.802071000 |
| H       | 3.352716000 | 0.180995000 | 0.215091000 |
| H       | -3.530888000 | -2.018233000 | 0.322865000 |
| O       | -3.014729000 | -2.862089000 | 0.797601000 |
| H       | 3.498787000 | -2.157802000 | -0.761711000 |
| H       | -4.579469000 | -2.053148000 | 0.641285000 |

**HSeO$_2$Et**

E = -1.961296  
G = -1.914401  
$N_{\text{imag}} = 0$

| Element | X       | Y       | Z    |
|---------|---------|---------|------|
| Se      | 0.966061000 | -0.185644000 | -0.504712000 |
| O       | -1.478752000 | -0.507111000 | -1.600931000 |
| O       | -0.552378000 | 0.997665000 | 0.657515000 |
| H       | -0.649284000 | -0.447313000 | -2.114458000 |
| C       | -2.910740000 | -0.681631000 | 0.721241000 |
| H       | -2.902089000 | -0.507853000 | 1.802071000 |
| H       | 3.352716000 | 0.180995000 | 0.215091000 |
| H       | -3.530888000 | -2.018233000 | 0.322865000 |
| O       | -3.014729000 | -2.862089000 | 0.797601000 |
| H       | 3.498787000 | -2.157802000 | -0.761711000 |
| H       | -4.579469000 | -2.053148000 | 0.641285000 |

**HSeO$_3$Et**

E = -2.145492  
G = -2.096144  
$N_{\text{imag}} = 0$
| Element | X         | Y         | Z         |
|---------|-----------|-----------|-----------|
| Se      | -0.899499000 | -0.763889000 | 2.004450000 |
| O       | -1.180391000 | -0.437765000 | 0.426793000 |
| O       | 0.038497000  | -2.352022000 | 2.096720000 |
| O       | -2.132738000 | -0.892707000 | 3.080073000 |
| C       | 0.550126000  | 0.444416000  | 2.698063000 |
| H       | 0.032064000  | 1.404620000  | 2.773867000 |
| H       | 0.748651000  | 0.037948000  | 3.692509000 |
| O       | 0.748651000  | 1.745492000  | 1.756963000 |
| C       | 1.454099000  | 0.770256000  | 0.751854000 |
| H       | 0.032064000  | 1.404620000  | 2.773867000 |
| H       | 0.748651000  | 0.037948000  | 3.692509000 |
| H       | 0.146200000  | 0.770256000  | 0.751854000 |
| H       | 1.745492000  | 1.756963000  | 1.756963000 |
| H       | 2.489133000  | 1.231175000  | 2.141864000 |
| H       | -0.558703000 | -2.954888000 | 2.588083000 |

**HTeOEt**

E = -1.681111
G = -2.454722
N_{imag} = 0

Te  1.049118000  -0.172126000  -0.374687000
C  0.863411000  -0.033312000  -2.590862000
H  0.043467000  0.672991000  -2.743921000
H  1.798694000  0.399453000  -2.961157000
C  0.559841000  -1.417502000  -3.161555000
H  -0.325017000  -1.849057000  -2.680200000
H  1.399740000  -2.108670000  -3.019234000
H  0.361312000  -1.351627000  -4.238415000
O  -0.629838000  -0.804559000  0.075949000
H  0.877885000  1.550607000  -0.277813000

**HTeOEt**

E = -2.960916
G = -1.640792
N_{imag} = 0

Te  1.049118000  -0.172126000  -0.374687000
C  0.863411000  -0.033312000  -2.590862000
H  0.043467000  0.672991000  -2.743921000
H  1.798694000  0.399453000  -2.961157000
C  0.559841000  -1.417502000  -3.161555000
H  -0.325017000  -1.849057000  -2.680200000
H  1.399740000  -2.108670000  -3.019234000
H  0.361312000  -1.351627000  -4.238415000
O  -0.629838000  -0.804559000  0.075949000
H  0.877885000  1.550607000  -0.277813000

**HTeOEt**

E = -2.125367
G = -2.080207
N_{imag} = 0

Te  -1.008873000  -0.775302000  2.004401000
O  -1.294275000  -0.471351000  0.229847000
O  0.053606000  -2.457924000  2.174325000
O  -2.397374000  -0.929189000  3.179829000
C  0.619646000  0.527332000  2.728635000
H  0.136834000  1.504871000  2.812165000
H  0.828510000  0.120885000  3.721438000
C  1.797339000  0.491015000  1.760970000
H  1.501629000  0.810497000  0.757272000
H  2.232885000  -0.510253000  1.696677000
H  2.572469000  1.178106000  2.124483000
H  -0.544374000  -3.153189000  2.517442000
Transition states

**HSOEt‡**

|       |        |        |        |        |        |        |        |        |        |        |        |
|-------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|
|       | S      | C      | H      | H      | C      | H      | S      | G      | N                  |
|       | -1.718466 | -1.676352 | 0.617815000 | -0.705000000 | -0.113504000 | 0.504335000 | 0.409530000 | 1.355276000 | 0.370330000 | -0.663312000 | 0.015852000 |
|       | -0.617815000 | -0.705000000 | -0.647549000 | -0.015959000 | 0.694665000 | -1.324575000 | -1.985020000 | -1.832581000 | -2.135749000 | -0.148989000 | -0.448596000 |
|       | -0.557046000 | -3.022412000 | -2.961290000 | -3.496809000 | -0.951218000 | -2.339082000 | -3.953554000 | -3.948380000 | -1.051012000 | -0.448596000 | -0.812714000 |
|       | E = -1.963209 | G = -1.917658 | Nimag = -1235.674 |       |       |       |       |       |       |       |       |
|       | -1.682011 | -1.642591 | -0.016492000 | -3.020089000 |       |       |       |       |       |       |       |
|       | -1.682011 | -1.642591 | -0.016492000 | -3.020089000 |       |       |       |       |       |       |       |
|       | -1.682011 | -1.642591 | -0.016492000 | -3.020089000 |       |       |       |       |       |       |       |
|       | -1.682011 | -1.642591 | -0.016492000 | -3.020089000 |       |       |       |       |       |       |       |
|       | -1.682011 | -1.642591 | -0.016492000 | -3.020089000 |       |       |       |       |       |       |       |
|       | -1.682011 | -1.642591 | -0.016492000 | -3.020089000 |       |       |       |       |       |       |       |
|       | -1.682011 | -1.642591 | -0.016492000 | -3.020089000 |       |       |       |       |       |       |       |
|       | -1.682011 | -1.642591 | -0.016492000 | -3.020089000 |       |       |       |       |       |       |       |
|       | -1.682011 | -1.642591 | -0.016492000 | -3.020089000 |       |       |       |       |       |       |       |
|       | -1.682011 | -1.642591 | -0.016492000 | -3.020089000 |       |       |       |       |       |       |       |
|       | -1.682011 | -1.642591 | -0.016492000 | -3.020089000 |       |       |       |       |       |       |       |
|       | -1.682011 | -1.642591 | -0.016492000 | -3.020089000 |       |       |       |       |       |       |       |
|       | -1.682011 | -1.642591 | -0.016492000 | -3.020089000 |       |       |       |       |       |       |       |
|       | -1.682011 | -1.642591 | -0.016492000 | -3.020089000 |       |       |       |       |       |       |       |
|       | -1.682011 | -1.642591 | -0.016492000 | -3.020089000 |       |       |       |       |       |       |       |
|       | -1.682011 | -1.642591 | -0.016492000 | -3.020089000 |       |       |       |       |       |       |       |
|       | -1.682011 | -1.642591 | -0.016492000 | -3.020089000 |       |       |       |       |       |       |       |
|       | -1.682011 | -1.642591 | -0.016492000 | -3.020089000 |       |       |       |       |       |       |       |
|       | -1.682011 | -1.642591 | -0.016492000 | -3.020089000 |       |       |       |       |       |       |       |
|       | -1.682011 | -1.642591 | -0.016492000 | -3.020089000 |       |       |       |       |       |       |       |
HTeOEt‡

\[
\begin{align*}
E &= -2.112501 \\
G &= -2.068635 \\
N_{\text{imag}} &= 577.266
\end{align*}
\]

HTeO\textsubscript{2}Et‡

\[
\begin{align*}
E &= -1.661737 \\
G &= -1.624512 \\
N_{\text{imag}} &= 815.819
\end{align*}
\]

HTeO\textsubscript{2}Et‡

\[
\begin{align*}
E &= -1.920476 \\
G &= -1.879261 \\
N_{\text{imag}} &= -1059.052
\end{align*}
\]

HTeO\textsubscript{3}Et‡

\[
\begin{align*}
E &= -2.101359 \\
G &= -2.058659
\end{align*}
\]
\[
\text{Imag} = -375.447
\]

| Element | X | Y | Z |
|---------|---|---|---|
| Te | -0.181115000 | 0.756717000 | -0.336826000 |
| C   | -0.616730000 | 2.233347000 | -2.598377000 |
| H   | -1.222118000 | 3.006225000 | -2.132497000 |
| H   | 0.442620000 | 2.460066000 | -2.695278000 |
| C   | -1.213832000 | 1.141786000 | -3.317313000 |
| H   | -1.210427000 | 0.202878000 | -2.587080000 |
| H   | 0.613063000 | 0.782245000 | -4.158799000 |
| H   | 2.270106000 | 1.285673000 | -3.561538000 |
| O   | -0.913941000 | -0.703154000 | -1.255487000 |
| O   | 1.795475000 | 0.527137000 | -0.606126000 |
| H   | 0.723840000 | -1.804661000 | -2.520433000 |
| O   | 1.213832000 | 0.000000000 | -0.666527000 |
| S   | 0.559060000 | 0.000000000 | -0.666527000 |
| C   | 0.000000000 | 0.000000000 | 0.666527000 |
| H   | 0.723840000 | -1.804661000 | -2.520433000 |
| H   | 0.000000000 | 0.925831000 | -1.238838000 |
| C   | 0.000000000 | 0.925831000 | 1.238838000 |
| H   | 0.000000000 | 0.925831000 | 1.238838000 |

**Products**

**Ethylene**

\[
E = -1.133714
\]
\[
G = -1.105060
\]
\[
\text{Imag} = 0
\]

**H₂SO²**

\[
E = -1.0833417
\]
\[
G = -0.831593
\]
\[
\text{Imag} = 0
\]

**H₂SO³**

\[
E = -0.833417
\]
\[
G = -0.831593
\]
\[
\text{Imag} = 0
\]

**H₂SeO**

\[
E = -0.571450
\]
\[
G = -0.576561
\]
\[
\text{Imag} = 0
\]

**H₂SeO²**

\[
E = -0.809411
\]
\[
G = -0.810176
\]
\[
\text{Imag} = 0
\]

Se 0.564824000 -0.503414000 -2.019380000
H 0.744456000 -1.868648000 -2.600755000
Se 2.040298000 -2.414313000 0.000000000
O 2.707444000 -1.471978000 -1.436560000

**H₂SO**

\[
E = -0.599814
\]
\[
G = -0.601947
\]
\[
\text{Imag} = 0
\]
Table 14: Cartesian coordinates (Å), energies (a.u.) and imaginary frequencies (cm$^{-1}$) of the optimized structures of the amino acid model. Level of theory: ZORA-OPBE/TZ2P.

Cysteine (Cys)

### OS 0

**Diastereoisomer RR**

- $E = -3.114592$
- $G = -3.039314$
- $N_{\text{imag}} = 0$

| Atom | X  | Y  | Z  |
|------|----|----|----|
| C    | 1.361043000 | -3.364659000 | 7.422847000 |
| C    | 2.672631000 | -3.535233000 | 6.662354000 |
| N    | 1.449242000 | -2.899622000 | 8.803205000 |
| H    | 2.283307000 | -3.256833000 | 9.258633000 |
| H    | 1.481511000 | -1.888393000 | 8.857489000 |
| H    | 0.779673000 | -2.616275000 | 6.863802000 |
| C    | 0.455888000 | -4.621294000 | 7.361200000 |
| O    | 0.372289000 | -5.330911000 | 6.389202000 |

**Diastereoisomer RS**

- $E = -3.120126$
- $G = -3.043733$
- $N_{\text{imag}} = 0$

| Atom | X  | Y  | Z  |
|------|----|----|----|
| C    | 1.357074000 | -3.345061000 | 7.418504000 |
| C    | 2.672048000 | -3.509194000 | 6.661331000 |
| N    | 1.441363000 | -2.952876000 | 8.820300000 |
| H    | 2.306359000 | -3.297014000 | 9.231826000 |
| H    | 1.412932000 | -1.947029000 | 8.939010000 |
| H    | 0.786364000 | -2.572215000 | 6.881039000 |
| C    | 0.454460000 | -4.600307000 | 7.298716000 |
| O    | 0.353074000 | -5.250549000 | 6.284982000 |
O  -0.252299000  -4.793523000  8.477416000  O  -0.217955000  -4.838181000  8.419349000
H   0.085963000  -4.063042000  9.060775000  H   0.151369000  -4.132112000  9.027624000
H   2.492137000  -3.838534000  5.628059000  H   2.479793000  -3.880778000  5.647127000
H   3.236827000  -2.595746000  6.662688000  H   3.204000000  -2.553705000  6.587626000
S   3.843303000  -4.725926000  7.426404000  S   3.893320000  -4.671838000  7.347033000
H   3.160331000  -5.795679000  6.880186000  H   2.996842000  -5.719821000  7.247909000
O   5.151415000  -4.598844000  6.734184000  O   4.107115000  -4.389949000  8.798749000

Diastereoisomer RR
E = -3.382538
G = -3.302564
N_{imag} = 0

Diastereoisomer RS
E = -3.381145
G = -3.299501
N_{imag} = 0

Diastereoisomer R
E = -3.648052
G = -3.563229
N_{imag} = 0
Selenocysteine (Sec)

Diastereoisomer RR

| Element | x   | y     | z     |
|---------|-----|-------|-------|
| C       | 1.312131000 | -3.388869000 | 7.371770000 |
| C       | 1.708072000 | -2.907955000 | 8.691531000 |
| N       | 2.175123000 | -3.273435000 | 8.947424000 |
| H       | 1.754271000 | -1.896806000 | 8.723874000 |
| H       | 0.734994000 | -2.595356000 | 6.873092000 |
| C       | 0.275609000 | -4.532397000 | 7.537100000 |
| C       | -0.164794000 | -4.625977000 | 8.787045000 |
| H       | 0.396006000 | -3.932997000 | 9.247507000 |
| H       | 2.085760000 | -4.154731000 | 5.477742000 |
| H       | 3.091000000 | -2.915914000 | 6.223705000 |
| Se      | 3.790137000 | -5.207923000 | 7.139985000 |
| H       | 4.551343000 | -4.980246000 | 5.980873000 |
| O       | 4.330866000 | -4.527665000 | 8.451562000 |
| E       | -3.064330   |
| G       | -2.992225   |
| N\text{imag} | 0           |

Diastereoisomer RS

| Element | x   | y     | z     |
|---------|-----|-------|-------|
| C       | 1.341395000 | -3.328169000 | 7.402313000 |
| C       | 1.465896000 | -2.993720000 | 8.815731000 |
| N       | 2.356738000 | -3.338103000 | 9.181465000 |
| H       | 1.421502000 | -1.994236000 | 8.972492000 |
| H       | 0.760896000 | -2.534389000 | 6.905799000 |
| C       | 0.281730000 | -4.574957000 | 7.260867000 |
| O       | -0.200119000 | -4.855503000 | 8.395889000 |
| O       | 0.202464000 | -4.172031000 | 9.014853000 |
| H       | 2.427881000 | -3.852182000 | 5.604480000 |
| H       | 3.167970000 | -2.521479000 | 6.532161000 |
| Se      | 3.982529000 | -4.708680000 | 7.365543000 |
| H       | 2.977795000 | -5.843663000 | 7.364797000 |
| O       | 4.146302000 | -4.283094000 | 8.955465000 |
| E       | -3.065621   |
| G       | -2.993086   |
| N\text{imag} | 0           |

OS +2

Diastereoisomer RR

| Element | x   | y     | z     |
|---------|-----|-------|-------|
| C       | 1.247933000 | -3.451915000 | 7.271115000 |
| C       | 2.301433000 | -4.029650000 | 6.336863000 |
| E       | -3.328293   |
| G       | -3.252265   |
| N\text{imag} | 0           |

Diastereoisomer RS

| Element | x   | y     | z     |
|---------|-----|-------|-------|
| C       | 1.161215000 | -3.414109000 | 7.367359000 |
| C       | 2.458140000 | -3.863771000 | 6.707755000 |
| E       | -3.330708   |
| G       | -3.254717   |
| N\text{imag} | 0           |
**OS +4**

*Diastereoisomer R*

\[ E = -3.529472 \]
\[ G = -3.448890 \]
\[ N_{imag} = 0 \]

| C     | 1.205741000 | -3.402581000 | 7.383195000 |
|-------|-------------|--------------|-------------|
| C     | 2.517257000 | -3.739342000 | 6.862708000 |
| N     | 1.263309000 | -2.908011000 | 8.747864000 |
| H     | 2.083999000 | -3.260527000 | 9.236911000 |
| H     | 1.285102000 | -1.896314000 | 8.751873000 |
| H     | 0.761403000 | -2.617876000 | 6.751873000 |
| C     | 0.160040000 | -4.554425000 | 7.272147000 |
| O     | 0.007629000 | -5.193672000 | 6.262810000 |
| O     | -0.549837000 | -4.688527000 | 8.382522000 |
| H     | -0.141006000 | -4.005360000 | 8.982793000 |
| H     | 2.337350000 | -4.244066000 | 5.729452000 |
| H     | 3.155226000 | -2.861875000 | 6.541336000 |
| Se    | 3.703388000 | -4.959009000 | 7.655226000 |
| O     | 5.197304000 | -4.582726000 | 6.753014000 |
| H     | 5.495487000 | -5.450422000 | 6.430426000 |
| O     | 3.393108000 | -6.512483000 | 7.404089000 |
| O     | 3.890264000 | -4.392060000 | 9.150542000 |

**Tellurocysteine (Tec)**

*Diastereoisomer RR*

\[ E = -3.035861 \]
\[ G = -2.966670 \]
\[ N_{imag} = 0 \]

| C     | 1.274768000 | -3.396115000 | 7.367023000 |
|-------|-------------|--------------|-------------|
| C     | 2.335371000 | -3.771570000 | 6.340704000 |

*Diastereoisomer RS*

\[ E = -3.036569 \]
\[ G = -2.966790 \]
\[ N_{imag} = 0 \]

| C     | 1.326104000 | -3.308957000 | 7.393763000 |
|-------|-------------|--------------|-------------|
| C     | 2.599513000 | -3.432308000 | 6.568042000 |
Diastereoisomer RR

\[ E = -3.309378 \]

\[ G = -3.236009 \]

\[ N_{imag} = 0 \]

Diastereoisomer RS

\[ E = -3.312769 \]

\[ G = -3.238733 \]

\[ N_{imag} = 0 \]

Diastereoisomer R

\[ E = -3.499352 \]

\[ G = -3.424786 \]

\[ N_{imag} = 0 \]
|     | X         | Y         | Z         |
|-----|-----------|-----------|-----------|
| H   | 0.67470500 | -2.60699200 | 6.76163900 |
| C   | 0.08704100 | -4.49917900 | 7.42845400 |
| O   | -0.06267900 | -5.32551100 | 6.56304200 |
| O   | -0.68220300 | -4.38946600 | 8.50753200 |
| H   | -0.24202100 | -3.66589100 | 9.02326300 |

**Transition states**

**Cysteine (Cys)**

|     | X         | Y         | Z         |
|-----|-----------|-----------|-----------|
| H   | 0.08704100 | -4.49917900 | 7.42845400 |
| O   | -0.06267900 | -5.32551100 | 6.56304200 |
| O   | -0.68220300 | -4.38946600 | 8.50753200 |
| H   | -0.24202100 | -3.66589100 | 9.02326300 |

**Diastereoisomer RR**

|     | X         | Y         | Z         |
|-----|-----------|-----------|-----------|
| E   | -3.083027 |           |           |
| G   | -3.011276 |           |           |
| N_{imag} | -422.916 |           |           |

**Diastereoisomer RS**

|     | X         | Y         | Z         |
|-----|-----------|-----------|-----------|
| E   | -3.081687 |           |           |
| G   | -3.010054 |           |           |
| N_{imag} | -434.133 |           |           |

**Diastereoisomer RR**

|     | X         | Y         | Z         |
|-----|-----------|-----------|-----------|
| E   | -3.338185 |           |           |
| G   | -3.261795 |           |           |
| N_{imag} | -237.662 |           |           |

**Diastereoisomer RS**

|     | X         | Y         | Z         |
|-----|-----------|-----------|-----------|
| E   | -3.336744 |           |           |
| G   | -3.260480 |           |           |
| N_{imag} | -246.121 |           |           |
|          |          |          |          |          |          |          |          |          |          |          |
|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|
| H        | 1.437899000 | -4.193635000 | 8.431225000 |          | H        | 1.523704000 | -4.140444000 | 8.424139000 |
| C        | 1.043254000 | -2.007263000 | 7.797258000 |          | C        | 1.085738000 | -1.983583000 | 7.782577000 |
| O        | 1.959696000 | -1.422959000 | 8.329010000 |          | O        | 2.025373000 | -1.385016000 | 8.252604000 |
| O        | -0.213582000 | -1.527004000 | 7.773165000 |          | O        | -0.174679000 | -1.512569000 | 7.823030000 |
| H        | -0.697858000 | -2.195639000 | 7.235191000 |          | H        | -0.682746000 | -2.194713000 | 7.324073000 |
| H        | 2.501395000 | -4.408621000 | 5.788416000 |          | H        | 2.412124000 | -4.403991000 | 5.704905000 |
| H        | 3.241402000 | -3.014362000 | 6.756534000 |          | H        | 3.326298000 | -3.029559000 | 6.629680000 |
| S        | 3.171310000 | -5.320782000 | 8.207043000 |          | S        | 3.264882000 | -5.253934000 | 8.136187000 |
| O        | 2.730747000 | -6.592752000 | 7.253874000 |          | O        | 4.473365000 | -4.240772000 | 8.584713000 |
| H        | 2.889195000 | -7.395885000 | 7.771284000 |          | H        | 4.910206000 | -4.639788000 | 9.351707000 |
| O        | 1.910002000 | -4.930752000 | 9.049292000 |          | O        | 2.010132000 | -4.901732000 | 9.007044000 |

**OS + 4**

Diastereoisomer R‡

\[ E = -3.577164 \]

\[ G = -3.500280 \]

\[ N_{\text{imag}} = -923.920 \]

|          |          |          |          |          |          |          |          |          |          |          |
|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|
| C        | 1.143373000 | -3.340871000 | 7.121417000 |          | C        | 2.387529000 | -3.725583000 | 6.596527000 |
| C        | 2.387529000 | -3.725583000 | 6.596527000 |          | N        | -0.106867000 | -3.799374000 | 6.577427000 |
| H        | -0.060161000 | -3.985916000 | 5.581908000 |          | H        | -0.470783000 | -4.626839000 | 7.039097000 |
| H        | 1.382950000 | -4.182854000 | 8.321262000 |          | C        | 1.078068000 | -2.001788000 | 7.811365000 |
| O        | 2.031912000 | -1.440536000 | 8.297886000 |          | O        | -0.167810000 | -1.502994000 | 7.842700000 |
| O        | -0.688477000 | -2.168380000 | 7.334475000 |          | H        | 2.448095000 | -4.380344000 | 5.728187000 |
| H        | 3.232423000 | -3.055505000 | 6.748469000 |          | H        | 3.057263000 | -5.281909000 | 8.104983000 |
| S        | 2.757134000 | -6.754586000 | 7.475372000 |          | H        | 3.399758000 | -7.353034000 | 7.892331000 |
| O        | 1.826816000 | -5.022464000 | 8.982049000 |          | O        | 4.299476000 | -5.376264000 | 8.847713000 |

**Selenocysteine (S)**

Diastereoisomer RR‡

\[ E = -3.044680 \]

\[ G = -2.976393 \]

\[ N_{\text{imag}} = -685.642 \]

Diastereoisomer RS‡

\[ E = -3.043997 \]

\[ G = -2.975799 \]

\[ N_{\text{imag}} = -685.542 \]
|     |    |    |    |
|-----|----|----|----|
| H   |  1.316627000 | -4.159483000 | 8.372035000 |
| C   |  1.133356000 | -2.026337000 | 7.799713000 |
| O   |  2.099548000 | -1.445833000 | 8.244070000 |
| O   | -0.104467000 | -1.505340000 | 7.813790000 |
| H   | -0.635272000 | -2.199295000 | 7.353399000 |
| H   |  2.420219000 | -4.446788000 | 5.761525000 |
| H   |  3.229284000 | -3.066034000 | 6.655070000 |
| Se  |  3.217216000 | -5.279005000 | 8.193951000 |
| O   |  1.785046000 | -5.003566000 | 9.078996000 |
| H   |  4.109692000 | -4.230826000 | 8.789563000 |

OS +2

Diastereoisomer RR‡

\[
\begin{align*}
E &= -3.302279 \\
G &= -3.229911 \\
N_{imag} &= -446.269
\end{align*}
\]

Diastereoisomer RS‡

\[
\begin{align*}
E &= -3.299445 \\
G &= -3.226799 \\
N_{imag} &= -485.027
\end{align*}
\]

OS +4

Diastereoisomer R‡

\[
\begin{align*}
E &= -3.494309 \\
G &= -3.421170 \\
N_{imag} &= -992.359
\end{align*}
\]
Tellurocysteine (Tec)

Diastereoisomer RR‡

E = -3.019898
G = -2.954042
N_{imag} = -795.527

| C   | -0.200464000 | -1.481043000 | 7.748656000 |
| C   | -0.697999000 | -2.202583000 | 7.291044000 |
| N   | 2.461145000 | -4.317190000 | 5.726619000 |
| H   | 3.219991000 | -2.965317000 | 6.734401000 |
| Se  | 3.108164000 | -5.277014000 | 8.147319000 |
| O   | 2.735223000 | -6.842516000 | 7.340007000 |
| H   | 3.399478000 | -7.470439000 | 7.770030000 |
| O   | 1.763954000 | -5.004447000 | 9.113379000 |
| O   | 4.462503000 | -5.542531000 | 8.982785000 |

Diastereoisomer RS‡

E = -3.020093
G = -2.954040
N_{imag} = -785.411

| C   | 1.165536000 | -3.420388000 | 7.222460000 |
| C   | 2.418081000 | -3.803902000 | 6.614653000 |
| N   | -0.091615000 | -3.831993000 | 6.639949000 |
| H   | -0.043328000 | -3.953168000 | 5.634199000 |
| H   | -0.459273000 | -4.682964000 | 7.049950000 |
| H   | 1.270568000 | -4.150596000 | 8.362320000 |
| C   | 1.138396000 | -2.027736000 | 7.796425000 |
| O   | 2.111212300 | -1.448082000 | 8.224776000 |
| O   | -0.095755000 | -1.479858000 | 7.815047000 |
| H   | -0.633829000 | -2.191577000 | 7.362613000 |
| H   | 2.379038000 | -4.403210000 | 5.702913000 |
| H   | 3.204990000 | -3.051035000 | 6.612935000 |
| Te  | 3.281872000 | -5.384524000 | 8.194155000 |
| O   | 1.698232000 | -5.030347000 | 9.117856000 |
| H   | 4.277859000 | -4.213759000 | 8.887651000 |

Diastereoisomer RR‡

E = -3.289338
G = -3.218804
N_{imag} = -659.574

| C   | 1.164129000 | -3.366615000 | 7.200951000 |
| C   | 2.448848000 | -3.724640000 | 6.674750000 |
| N   | -0.057264000 | -3.876157000 | 6.628265000 |
| H   | 0.026467000 | -4.067071000 | 5.635484000 |
| H   | -0.390888000 | -4.719143000 | 7.082747000 |
| H   | 1.290975000 | -4.095827000 | 8.434507000 |
| C   | 1.054858000 | -1.982960000 | 7.763464000 |
| O   | 1.989984000 | -1.352990000 | 8.211283000 |
| O   | -0.204112000 | -1.509726000 | 7.750669000 |

Diastereoisomer RS‡

E = -3.285616
G = -3.215442
N_{imag} = -693.493

| C   | 1.163226000 | -3.384058000 | 7.179939000 |
| C   | 2.386892000 | -3.773958000 | 6.545290000 |
| N   | -0.109469000 | -3.839244000 | 6.672641000 |
| H   | -0.102760000 | -3.997019000 | 5.670547000 |
| H   | -0.444882000 | -4.681013000 | 7.127438000 |
| H   | 1.370095000 | -4.125419000 | 8.386990000 |
| C   | 1.121429000 | -1.999678000 | 7.770789000 |
| O   | 2.088414000 | -1.385469000 | 8.160110000 |
| O   | -0.131175000 | -1.511716000 | 7.842742000 |
|     | X         | Y         | Z         |
|-----|-----------|-----------|-----------|
| H   | -0.699694| 7.291703  | 0.664215  |
| H   | 2.486426 | 6.677285  | 0.320360  |
| H   | 3.206538 | 2.486426  | 3.232239  |
| Te  | 3.322239 | 0.699694  | 3.322239  |
| O   | 2.803281 | 3.322239  | 3.206538  |
| H   | 2.889760 | 3.206538  | 3.322239  |
| O   | 1.727567 | 3.206538  | 0.893600  |

OS + 4
Diastereoisomer R⁺

E = -3.474151
G = -3.402874
Nimag = -667.160

|     | X         | Y         | Z         |
|-----|-----------|-----------|-----------|
| C   | 1.135624 | -3.350053 | 7.225570  |
| C   | 2.393595 | -3.642969 | 6.585120  |
| N   | -0.093832 |-3.858866 | 6.670838  |
| H   | -0.037319 |-4.063711 | 5.679926  |
| H   | -0.427867 | -4.683733 | 7.158169 |
| H   | 1.270046 | -3.954741 | 8.314062 |
| C   | 1.026176 | -1.897441 | 7.712594 |
| O   | 1.967122 | -1.257293 | 8.108890 |
| H   | -0.229254 | -1.450660 | 7.673164 |
| H   | -0.722542 | -2.203842 | 7.263170 |
| H   | 2.422128 | -4.294801 | 5.711462 |
| H   | 3.171866 | -2.881669 | 6.629123 |
| Te  | 3.229249 | -5.261074 | 8.216152 |
| O   | 2.778821 | -6.903050 | 7.252253 |
| H   | 3.294003 | -7.610320 | 7.671382 |
| O   | 1.720830 | -4.955045 | 9.229544 |
| O   | 4.652079 | -5.730016 | 9.200523 |

Products

Dehydroalanine (DHA)

E = -2.469125
G = -2.415400
Nimag = 0
Table S15: Cartesian coordinates (Å), energies (a.u.) and imaginary frequencies (cm\(^{-1}\)) of the optimized structures for the phenyl alky1 model. Level of theory: ZORA-OPBE/TZ2P.

|   | S               | Se              | TS-S             |
|---|-----------------|-----------------|------------------|
|   | E= -4.36879005  | E= -4.31404411  |                  |
| S |                 |                 |                  |
| E= -4.31404411 |                  |                  |
| Nimag=0         |                  |                  |
| S | 0.702976000    | -0.021646000    | -0.429614000     |
| C | 0.215099000    | -0.092471000    | -2.192161000     |
| H | -0.676853000   | 0.538623000     | -2.291863000     |
| H | 1.035281000    | 0.369686000     | -2.753595000     |
| C | -0.041767000   | -1.521809000    | -2.623307000     |
| H | -0.837405000   | -1.975438000    | -2.025132000     |
| H | 0.856544000    | -2.141751000    | -2.528542000     |
| H | -0.354649000   | -1.542336000    | -3.673239000     |
| O | -0.486184000   | -0.409853000    | 0.375305000      |
| C | 0.881344000    | 1.772559000     | -0.354549000     |
| C | -0.133651000   | 2.525807000     | 0.224133000      |
| C | 2.059304000    | 2.375632000     | -0.790486000     |
| C | 0.019469000    | 3.904259000     | 0.333840000      |
| C | 2.201256000    | 3.754333000     | -0.681240000     |
| C | 1.181069000    | 4.519947000     | -0.122144000     |
| H | -1.024247000   | 2.020293000     | 0.090123000      |
| H | 2.868198000    | 1.775105000     | -1.205138000     |
| H | -0.773241000   | 4.500000000     | 0.783832000      |
| H | 3.118157000    | 4.231276000     | -1.023600000     |
| H | 1.298986000    | 5.598150000     | -0.030058000     |
| Te | 1.027580000 | -0.121299000 | -0.515212000 |
| C | 0.060500000 | -0.135609000 | -2.460770000 |
| H | -0.794210000 | 0.535477000 | -2.392590000 |
| H | 0.766882000 | 0.324793000 | -3.161329000 |
| C | -0.356124000 | -1.531875000 | -2.872166000 |
| H | -1.022759000 | -1.983107000 | -2.129958000 |
| H | 0.503927000 | 2.198023000 | -3.007251000 |
| H | -0.897215000 | -1.501377000 | -3.826258000 |
| O | -0.365030000 | -0.504620000 | -0.583854000 |
| C | 1.079404000 | 2.021213000 | -0.422422000 |
| C | 0.077594000 | 2.650693000 | 0.307806000 |
| C | 2.094684000 | 2.759310000 | -1.025701000 |
| C | 0.081825000 | 4.038647000 | 0.416951000 |
| C | 2.091696000 | 4.147143000 | -0.913078000 |
| C | 1.085118000 | 4.785499000 | -0.193922000 |
| H | -0.692178000 | 2.047196000 | 0.786896000 |
| H | 2.893820000 | 2.268138000 | -1.581124000 |
| H | -0.701415000 | 4.538289000 | 0.985469000 |
| H | 2.881757000 | 4.730155000 | -1.384010000 |
| H | 1.087599000 | 5.870500000 | -0.103870000 |
| TS-Se | E= -4.28306160 |                  |                  |
| TS-Te | E= -4.25786474 |                  |                  |

S553
E= -4.78448763  
Nimag=-918.7

Se 0.479246000 -0.549543000 -0.640645000  
C 0.928599000 0.000025000 -2.902710000  
H 0.136610000 0.746302000 -2.935762000  
H 1.902076000 0.418833000 -2.648305000  
C 0.833162000 -1.173874000 -3.672452000  
H 0.487967000 -2.051278000 -2.652210000  
H 1.760190000 -1.603841000 -4.052994000  
H -0.029068000 -1.275929000 -3.433199000  
C -1.447246000 -0.356086000 -0.606662000  
C -2.272952000 -1.459422000 -0.387541000  
C -1.999878000 0.915135000 -0.750489000  
C -3.652220000 -1.283772000 -0.338069000  
C -3.380345000 1.076572000 -0.697767000  
C -4.211498000 -0.019885000 -0.493309000  
H -1.844102000 -2.448661000 -0.270439000  
H -1.352999000 1.776715000 -0.888205000  
O -4.291982000 -2.148829000 -0.170163000  
H -3.805382000 2.071897000 -0.818752000  
H -5.291276000 0.111159000 -0.449861000  
O 0.169949000 -2.553103000 -1.591953000  
O 0.968165000 -3.012574000 -1.301725000  
H 0.819129000 1.188710000 0.864382000

TS Se-hyd

Te 0.645700000 -0.506900000 -0.371400000  
C 0.910600000 0.412500000 -2.793900000  
H 0.145000000 1.167500000 -2.623400000  
H 1.922700000 0.769000000 -2.608500000  
C 0.677100000 -0.653900000 -3.676000000  
H 0.405700000 -1.687500000 -2.378800000  
H 1.532000000 -1.068200000 -4.213300000  
H -0.267400000 -0.666400000 -4.220000000  
O 0.170300000 -2.338900000 -1.771400000  
C -1.462800000 -0.231400000 -0.288600000  
C -2.347800000 -1.298100000 -0.447300000  
C -1.953800000 1.051700000 -0.046900000  
C -3.719200000 -1.072300000 -0.373700000  
C -3.327000000 1.264600000 0.027400000  
C -4.214000000 0.205900000 -0.136700000  
H -1.975400000 -2.300400000 -0.633200000  
H -1.264400000 1.880100000 0.094600000  
H -4.404100000 -1.909900000 -0.498000000  
H -3.702100000 2.270000000 0.214100000  
H -5.287700000 0.375500000 -0.076400000  
H 0.936800000 -2.917000000 -1.669700000  
H 1.004900000 1.261000000 0.572600000  
H 1.016700000 1.080900000 1.520800000

TS Te-hyd

E= -4.77396504  
Nimag=-868.02
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