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RESEARCH FRONT

Aust. J. Chem. **2014**, *67*, 1195–1200
http://dx.doi.org/10.1071/CH14098

Full Paper

The Elusive Ethenediselone, Se=C=C=Se

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The neutral ethenediselone, Se=C=C=Se, has been characterised by neutralisation–reionisation mass spectrometry, which implies a minimum lifetime of the order of microseconds. Tetraselenafulvalene **1** and tetramethyltetraselenafulvalene **2** were used as precursor molecules. Flash vacuum thermolysis (FVT) of these compounds with isolation of the products in Ar matrices permitted the identification of ethyne, 2-butyne, CSe_2, and selenoketene, $H_2C{=}C{=}Se$, but at best traces of Se=C=C=Se survived the FVT/matrix isolation experiment. Multiconfigurational calculations indicate that Se=C=C=Se is a ground state triplet molecule with a very small singlet-triplet gap.

Manuscript received: 25 February 2014.
Manuscript accepted: 7 March 2014.

Introduction

Ethenedione, O=C=C=O, has been described as 'the holy grail of cumulene chemistry'.[1] However, neither the singlet nor the triplet state of this holy grail may ever be attained,[2] even though there has been no shortage of attempts.[3] Calculations indicate that the ground state is a triplet state.[4] Both the molecular cation radical of ethenedione, $O{=}C{=}C{=}O^{+\bullet}$, and the corresponding anion can be produced in the mass spectrometer where they are quite stable,[2] but a recovery signal was not observable in neutralisation–reionisation mass spectrometry (NRMS) experiments,[2] which means that the lifetime of the putative neutral C_2O_2 is less than the microsecond timescale of the NRMS experiment.

In contrast, thioxoethenone (O=C=C=S)[5] and ethenedithione (S=C=C=S)[6,7] have been produced and characterised by NRMS in the mass spectrometer as well as by matrix-isolation infrared (IR) and UV spectroscopies. S=C=C=S is thermodynamically quite stable, surviving flash vacuum thermolysis (FVT) at high temperatures;[7b] yet it is kinetically highly unstable, polymerising in the neat state at temperatures above 40 K. This may be due to its triplet ground state as predicted by theory.[4,8] Analysis of the IR spectrum of ^{13}C-labelled O=C=C=S indicated that this molecule has a triplet ground state.[5] The monoimine, SCCNH,[9] has been detected by NRMS, and the monoxime, OCCN–OH, has been observed in an Ar matrix,[10] but the neutral monoamine, OCCNH, does not survive the NRMS experiment.[11]

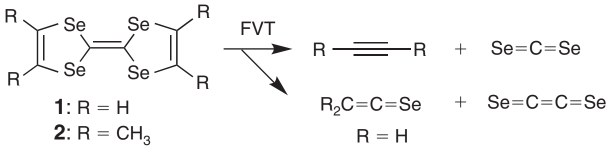
Extended sulfur-containing heterocumulenes of the type $S{=}C{=}(C)_n{=}C{=}S$ have been studied intensively.[12] It is a general observation that cumulenes of this type with an odd number of atoms are relatively stable (e.g. CO_2, C_3O_2, CS_2, C_3S_2, etc), whereas those with an even number are highly unstable. In the selenium series only CSe_2 is known. Compounds of the type $Se{=}C_n{=}Se$ are unknown, although calculations of their structures and properties have been reported.[13] However, several selenoketenes $R_2C{=}C{=}Se$ have been prepared.[14]

In this paper, we report an investigation into the existence of the diselenium analogue, ethenediselone, Se=C=C=Se (ionised or neutral), by means of NRMS, FVT, and matrix-isolation experiments. In addition, the electronic structures of C_2Se_2 were examined by quantum chemical calculations.

Results and Discussion

Mass Spectrometry

Tetraselenafulvalene **1** was the first precursor to be examined, as it can be expected to fragment to ethyne (HC≡CH), selenoketene ($H_2C{=}C{=}Se$), and ethenediselone (Se=C=C=Se) (Scheme 1). The 70 eV electron ionisation mass spectrum (EIMS) of **1** is illustrated in Fig. 1a. This spectrum features a base peak at *m*/*z* 394 corresponding to the molecular ion. Owing to the natural isotope distribution of selenium (^{74}Se : ^{76}Se : ^{77}Se : ^{78}Se : ^{80}Se : ^{82}Se = 0.9 : 9.4 : 7.6 : 23.8 : 49.6 : 8.7),



Scheme 1. Products of FVT of tetraselenafulvalenes.

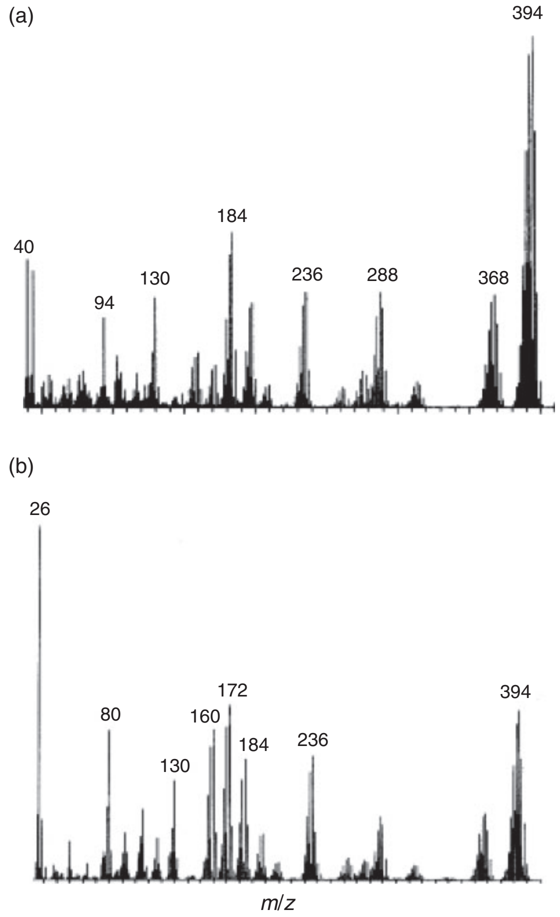


Fig. 1. (a) EIMS of tetraselenafulvalene **1** with an ion source temperature of 200°C. Assignments: 394 $\mathbf{1}^{+\bullet}$, 368 loss of C_2H_2, 288 loss of C_2H_2Se, 236 loss of Se_2, and 184 $C_2Se_2^{+\bullet}$. (b) The EIMS after FVT at 800–900°C. Assignments: 394 $M^{+\bullet}$, 368 loss of C_2H_2, 288 loss of C_2H_2Se, 236 loss of Se_2, 184 $C_2Se_2^{+\bullet}$, 106 $C_2H_2Se^{+\bullet}$, and 80 $Se^{+\bullet}$.

compositions are readily conferred to the various fragment ions: m/z 368 (loss of ethyne), m/z 288 (loss of C_2H_2Se), m/z 236 (loss of Se_2), m/z 130 $[C_4H_2Se]^{+\bullet}$, and m/z 94 $[CH_2Se]^{+\bullet}$. The abundant m/z 184 ion has the composition C_2Se_2 and therefore corresponds to the sought-after ethenediselone, $Se{=}C{=}C{=}Se^{+\bullet}$.

FVT of **1** at temperatures up to 800–900°C caused significant changes in the EIMS (Fig. 1b), which can be explained by thermal formation of selenium (m/z 80), diselenium (m/z 160), and carbon diselenide CSe_2 (m/z 172) ions. Note also that the ratio of m/z 184 (C_2Se_2) to unpyrolysed material (m/z 394) has increased significantly, thus suggesting the neutral C_2Se_2 molecules are formed in the thermolysis. The intensity of m/z 368 ($[M\text{–ethyne}]^{+\bullet}$) is also stronger relative to m/z 394, thereby indicating thermal loss of ethyne from **1**. Also note that an increased m/z 106 signal is present, corresponding to thermal formation of selenoketene, $H_2C{=}C{=}Se$.

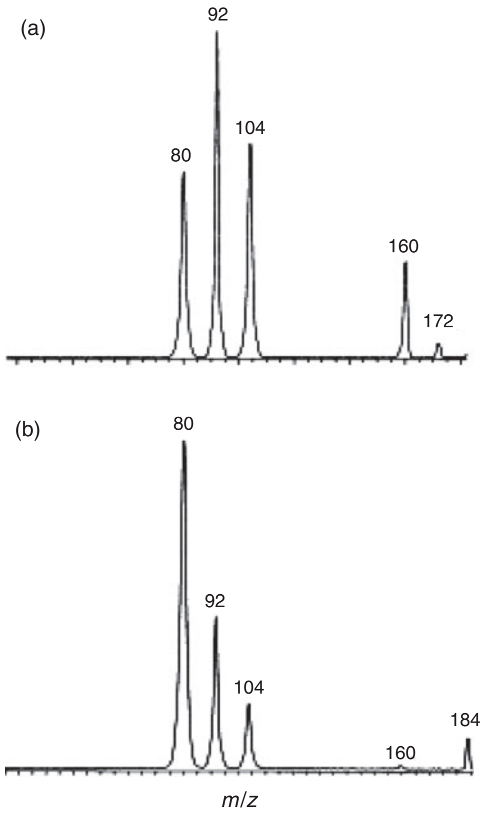


Fig. 2. (a) CAMS (oxygen as collision gas) of the m/z 184 ions generated by dissociative ionisation of tetramethyltetraselenafulvalene **2**. Assignments: 172 $CSe_2^{+\bullet}$, 160 $Se_2^{+\bullet}$, 104 $C_2Se^{+\bullet}$, 92 $CSe^{+\bullet}$, and 80 $Se^{+\bullet}$. (b) NRMS of the same ions (ammonia and oxygen as collision gases for neutralisation and reionisation, respectively). Assignments: 184 $C_2Se_2^{+\bullet}$, 160 $Se_2^{+\bullet}$, 104 $C_2Se^{+\bullet}$, 92 $CSe^{+\bullet}$, and 80 $Se^{+\bullet}$.

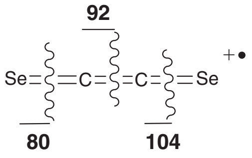


Chart 1. Fragmentation pattern of ethenediselone.

The tetramethyl derivative **2** is very stable thermally, undergoing only a small degree of pyrolysis at the highest temperatures attainable in our apparatus, even when the contact time is increased by placing a plug of quartz wool inside the pyrolysis tube. However, the behaviour was similar to that of **1**, affording the molecular ions of 2-butyne and CSe_2, whereas $H_2C{=}C{=}Se$ was, of course, absent. The migration of a methyl group is less likely than that of H, and there was no strong evidence for the presence of $Me_2C{=}C{=}Se$.

The collisional activation mass spectrum (CAMS) of the mass-selected m/z 184 ions originating from the molecular ion of **2** (dissociative ionisation) featured intense peaks at m/z 104, 92, and 80, in agreement with the expected connectivity (Fig. 2a and Chart 1).

Peaks at m/z 172 (loss of C) and 160 (loss of C_2) in Fig. 2a are less readily explained, but it is noted that loss of atoms from 'internal' positions of ionised cumulenes is not unprecedented. For example, the CAMS of $S{=}C{=}C{=}S$ featured peaks at m/z 76 (CS_2) and 64 (S_2) as well as 32 (S) and 44 (CS).[7b]

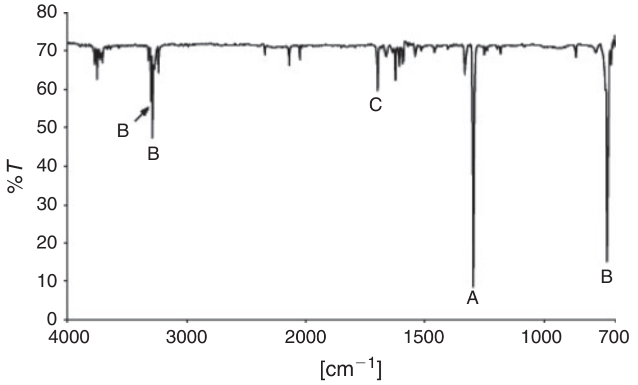


Fig. 3. IR spectrum (10 K, Ar matrix) of the products of pyrolysis of compound **1** (900°C, 10^{-5} hpa). A: CSe_2 1298 cm^{-1}; B: ethyne 3302, 3288, and 735 cm^{-1}; C: $CH_2{=}C{=}Se$ 1699 cm^{-1}.

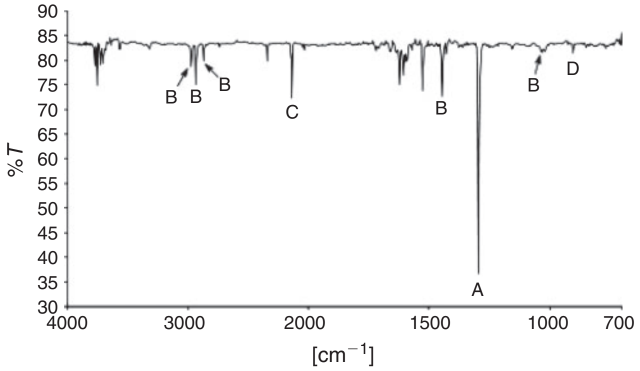


Fig. 4. IR spectrum (10 K, Ar matrix) of the products of pyrolysis of tetramethyltetrasenafulvalene **2** (1000°C, 10^{-5} hPa). A: CSe_2 1298 cm^{-1}; B: 2-butyne 2976, 2936, 2872, 1447, and 1036 cm^{-1} (see text for the possible presence of CSe). C: CO at 2138 cm^{-1}. D: A weak peak at 906 cm^{-1} may be ascribed to Se=C=C=Se (calculated 930 cm^{-1}).

Table 1. Calculated relative energies (kJ mol^{-1}) of the three lowest states of C_2Se_2 using various single-determinant methods using aug-cc-pVTZ basis set

Level^{A}	$^3\Sigma_g^-$	$^1\Delta_g^{B}$	$^1\Sigma_g^{+B}$
HF	0.0	27.4	98.5
B3LYP	0.0	13.2	56.7
MP2	0.0	14.0	25.1
MP3^{C}	0.0	15.6	34.9
MP4^{C}	0.0	10.1	31.0
CCSD	0.0	15.3	38.8
CCSD(T)^{C}	0.0	11.2	29.3

^{A}Based on fully optimised geometries unless otherwise noted.
^{B}Using an unrestricted Hartree–Fock (UHF) starting point.
^{C}Based on CCSD/aug-cc-pVTZ optimised geometries [r(C=C) = 1.269, 1.270, and 1.269 for $^3\Sigma_g^-$, $^1\Delta_g$, and $^1\Sigma_g^+$, respectively; r(C=Se) = 1.720, 1.718, and 1.719 Å, for $^3\Sigma_g^-$, $^1\Delta_g$, and $^1\Sigma_g^+$, respectively].

The neutralisation–reionisation mass spectrum of the *m*/*z* 184 ions is shown in Fig. 2b. The clear observation of a recovery signal at *m*/*z* 184 with qualitatively the same fragmentation pattern as in the CAMS provides strong evidence that neutral ethenediselone is stable in the gas phase on the microsecond timescale of the NRMS experiment. One should not expect an exact agreement between the CAMS and NRMS ion intensities; the strong *m*/*z* 80 peak in the NRMS is undoubtedly due to reionisation of selenium atoms formed in the neutralisation cell. Note however that the *m*/*z* 92 peak is not particularly strong in the NRMS, thereby indicating that Se=C=C=Se is reasonably stable towards fragmentation to CSe molecules. This is confirmed by calculations reported in the section *Calculations*.

Matrix-Isolation IR Spectroscopy

The IR spectrum of the products of FVT of the parent compound **1** isolated in an argon matrix (Fig. 3) is dominated by a strong absorption of CSe_2 at 1298 cm^{-1} as well as bands due to ethyne. The gas phase fundamental ν_3, the only strong absorption of CSe_2, occurs at 1303 cm^{-1}.[15] Selenoketene $H_2C{=}C{=}Se$ is positively identified by a medium-strength band at 1699 cm^{-1} and in excellent agreement with the previously determined value of 1699.7 cm^{-1}.[16] The other expected absorption at 736 cm^{-1} is obscured by the ethyne band at 735 cm^{-1}.

For Se=C=C=Se the only allowed absorption in the IR spectrum is predicted at 950 cm^{-1}, and it is relatively weak (53 kJ mol^{-1}) at the B3LYP/6–31G* level.[13] A value of 930–932 cm^{-1} is predicted for all three electronic states at the B3LYP/6–311++G(3df,2p) level (see Table S1, Supplementary Material). This predicted frequency value (~930 cm^{-1}) is readily confirmed by MP2, CCSD, and CASSCF calculations. Most interestingly, a weak peak at 906 cm^{-1} matches predictions for Se=C=C=Se in the analogous matrix-IR spectrum from the FVT of **2** (Fig. 4). In agreement with the mass spectrometry results, CSe_2 and 2-butyne are also identified in Fig. 4. Both 2-butyne[17] and CSe[18] are reported to have weak absorptions at 1036 cm^{-1}. A weak absorption at 1036 and 1022 cm^{-1} in Fig. 4 could be due to both of these compounds, but at any rate, the amount of CSe potentially formed is very small.

It is relevant to mention that the analogous FVT reactions of tetrathiafulvalene afforded acetylene, CS, CS_2, C_3S_2, and thioketene $H_2C{=}C{=}S$.[19] Sulfur has a lower tendency than oxygen to form double bonds to carbon, and selenium even less so, as suggested by the steeply increasing calculated heats of formation of ketene (−52.4 kJ mol^{-1}), thioketene (193.6 kJ mol^{-1}) and selenoketene (240.3 kJ mol^{-1}) at the G2(MP2) level of theory.[20]

Calculations

First we examine the ground-state electronic configuration of C_2Se_2. For the sulfur analogue (C_2S_2, ethenedithione), Ma and Wong,[8] through high-level multiconfiguration calculations, have clearly established that the triplet $^3\Sigma_g^-$ state is the ground state, in contrast to an early prediction of a singlet ground state.[7a] There are three possible electronic states of linear C_2Se_2, namely $^3\Sigma_g^-$, $^1\Delta_g$, and $^1\Sigma_g^+$, arising from two electrons occupying two degenerate π orbitals. Initially, we examined the relative energies of these three states of C_2Se_2 using various single determinant methods together with the triple-zeta aug-cc-pVTZ basis set (Table 1). For the singlet C_2Se_2, the open-shell $^1\Delta_g$ state is significantly more stable than the $^1\Sigma_g^+$ state at all levels of theory by more than 18 kJ mol^{-1} (Table 1). Hence, we examined only the $^1\Delta_g$ state in the following multiconfiguration calculations. All the single determinant methods, namely HF, B3LYP, MP2, MP3, MP4, CCSD, and CCSD(T), predicted a triplet $^3\Sigma_g^-$ ground state for C_2Se_2 (Table 1). Similar relative energies between the singlet $^1\Delta_g$ and triplet $^3\Sigma_g^-$ states were predicted by all the correlated methods. Our best estimate of the singlet-triplet gap for C_2Se_2 using the single determinant method

Table 2. Calculated S-T gap[A] (kJ mol^{-1}) of C_2Se_2 using various multiconfiguration methods together with aug-cc-pVDZ basis set

CAS[B]	Active orbitals	CASSCF[C]	CASPT2[C]	CASPT3[C]	MRCI[C]
(2,2)	$5\pi_u^2$	46.5	−1.6	−1.0	−0.4
(6,4)	$4\pi_g^4\ 5\pi_u^2$	20.9	14.5	4.4	5.8
(6,6)	$4\pi_g^4\ 5\pi_u^2\ 5\pi_g^0$	39.9	−1.8	−0.3	−0.3
(10,8)	$4\pi_u^4\ 4\pi_g^4\ 5\pi_u^2\ 5\pi_g^0$	14.9	0.3	0.5	0.5
(12,10)	$11\sigma_g^2\ 4\pi_u^4\ 4\pi_g^4\ 5\pi_u^2\ 5\pi_g^0\ 11\sigma_u^0$	12.9	0.5	0.8	0.4
(12,10)[D]	$11\sigma_g^2\ 4\pi_u^4\ 4\pi_g^4\ 5\pi_u^2\ 5\pi_g^0\ 11\sigma_u^0$	13.7	0.6	0.7	0.6
(14,12)	$10\sigma_u^2\ 11\sigma_g^2\ 4\pi_u^4\ 4\pi_g^4\ 5\pi_u^2\ 5\pi_g^0\ 11\sigma_u^0\ 12\sigma_g^0$	16.0	0.6	0.6	0.7
(20,16)[E]	$9\sigma_g^2\ 9\sigma_u^2\ 10\sigma_g^2\ 10\sigma_u^2\ 11\sigma_g^2\ 4\pi_u^4\ 4\pi_g^4\ 5\pi_u^2\ 5\pi_g^0\ 11\sigma_u^0\ 12\sigma_g^0\ 12\sigma_u^0$	15.0	1.7		

[A] Relative energy between the singlet $^1\Delta_g$ state and triplet $^3\Sigma_g^-$ state.

[B] Number of electrons and number of orbitals in the active space.

[C] Based on CASSCF optimised geometries.

[D] Larger aug-cc-pVTZ basis set.

[E] CAS(20,16) corresponds to the full-valence CAS of C_2Se_2.

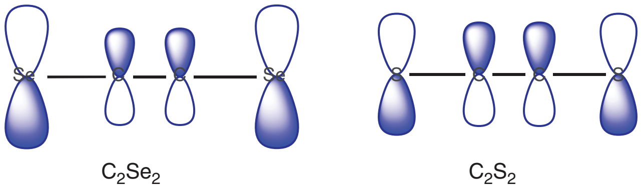
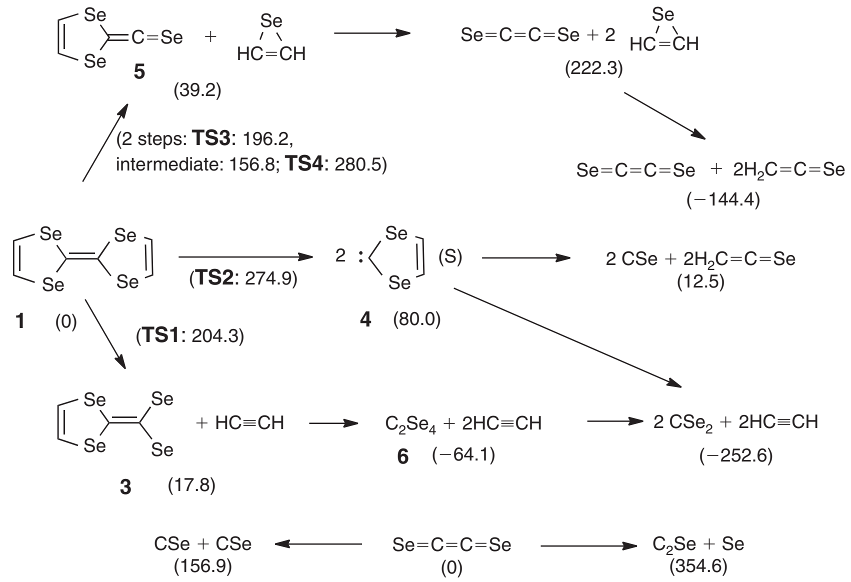


Fig. 5. Highest occupied molecular orbitals (HOMOs) of C_2Se_2 and C_2S_2.

(at CCSD(T)/aug-cc-pVTZ level) is 11.2 kJ mol^{-1}. The predicted C=C and C=Se bond lengths of the triplet ground state are 1.269 and 1.720 Å, respectively (at CCSD/aug-cc-pVTZ level). The central C=C double bond is shorter than that in C_2S_2 (1.278 Å) while the C=Se bonds are weaker than the corresponding C=S (1.572 Å). This is not surprising, as the C=Se π bond overlap is weaker than that in C=S.

Next, the singlet-triplet (S-T) gap of C_2Se_2 was investigated using multiconfiguration methods, which are expected to provide a proper description of the degeneracy problem involved. We have carried out a series of complete active space self-consistent field (CASSCF). CASSCF calculations with active space systematically expanded from the two-electron, two-orbital CAS (CASSCF(2,2)) to the 20-electron, 16-orbital CAS (CASSCF(20,16)), which represents the full-valence CASSCF, using the aug-cc-pVDZ basis set. The active orbitals involved in these CAS calculations are given in Table 2. The dominant configurations arise mainly from the excitation of the valence π electrons. Hence, one would expect an active space including all π orbitals (i.e. $4\pi_u$, $4\pi_g$, $5\pi_u$, and $5\pi_g$), for example CASSCF(10,8), to yield reliable result. In fact, further expansion of the active space to include the valence σ orbitals leads to small changes in the relative energies (Table 2). For our largest CASSCF calculation, CASSCF(20,16), the singlet $^1\Delta_g$ state lies 15.0 kJ mol^{-1} above the triplet $^3\Sigma_g^-$ ground state. However, inclusion of dynamic electron correlation at MP2 (CASPT2), MP3 (CASPT3), and CI (MRCI) levels significantly lower the S-T energy gap (Table 2). This clearly indicates that the CASSCF methods are not sufficient to describe properly the singlet-triplet gap. For the smaller active space which includes only the π orbitals, both CASPT3 and MRCI levels yield almost identical energy for the $^3\Sigma_g^-$ and $^1\Delta_g$ states. Further expansion of the π active space leads to a very small preference for the triplet state (by ~1 kJ mol^{-1}). At our best level of theory, CASPT2 (20,16), the triplet $^3\Sigma_g^-$ state is 1.7 kJ mol^{-1} more stable than the singlet $^1\Delta_g$ state. To examine the effect of basis set on the S-T gap, we have also performed CAS(12,10) calculations using the larger aug-cc-pVTZ basis set. The changes in relative energies on going from the aug-cc-pVDZ to aug-cc-pVTZ are very small, particularly at the correlated levels (Table 2). Hence, we have confidence in the predicted S-T gap of 1.7 kJ mol^{-1}. In summary, all the single- and multi-determinant methods predict a triplet ground for C_2Se_2, and there is no evidence for Hund's rule being violated. It is clear, however, that the singlet-triplet splitting is very small. For comparison, the calculated S-T gap for the sulfur analogue, C_2S_2, is 23.0 kJ mol^{-1}.[8] The large reduction in the S-T gap may be attributed to the fact the highest occupied molecular orbital (HOMO) of C_2Se_2 (namely $5\pi_u$) has a relatively larger contribution of the *p* orbitals of the terminal Se atoms (Fig. 5). In addition, the electron density of the HOMO is more spread out in C_2Se_2 because selenium has a larger atomic radius than sulfur. As a consequence, the electron-electron repulsion in the open-shell singlet $^1\Delta_g$ state is less severe in C_2Se_2. It is important to note that the HOMOs of both singlet and triplet states of C_2S_2 and C_2Se_2 are similar.

The free energies of reaction and activation at 900°C for the various possible fragmentation pathways of tetraselenafulvalene **1** were evaluated at the B3LYP/6–311++G(3df,2p) level (Scheme 2). The fragmentation of **1** to $CSe_2 + C_2H_2$ is the most favourable pathway both kinetically and thermodynamically. This dissociation process involves the loss of C_2H_2 to form a diselone-thioketene intermediate **3** in the first step, via transition state **TS1**. The observation of *m*/*z* 368 ions in EIMS (Fig. 1b) is consistent with the proposed mechanism. A cleavage of the central C=C bond in **1** to form two singlet 1,3-diselenolylidenes (**4**, 'diselenole carbenes'), stabilised by the neighbouring selenium lone pairs, requires a high activation barrier of 275 kJ mol^{-1} (via transition state **2**). A minor peak at 784 cm^{-1} in the IR spectrum (Fig. 3) may possibly be due to **4** (predicted frequency of 785 cm^{-1}). Dissociation of **1** to C_2Se_2 + selenirene is the least favourable pathway both kinetically and thermodynamically. This dissociation process involves initially the formation of a cyclic thioketene intermediate **5** (Scheme 2), which may correspond to the *m*/*z* 288 ions in EIMS (Fig. 1b). This step also requires a high activation barrier of 281 kJ mol^{-1}. The two possible fragmentations of C_2Se_2 require high energies (Scheme 2). Not surprisingly, therefore, there is little or no evidence for the formation of CSe and C_2Se in the experimental spectra. The corresponding standard free energies of reaction and activation at room temperature (298 K) and the optimised



Scheme 2. Fragmentation pathways of tetraselenafulvalene **1** and C_2Se_2. Calculated relative free energies (ΔG_{1173}, kJ mol^{-1}) at the B3LYP/6–311++G(3df,2p) level are given in parentheses.

geometries of transition states (**TS1**–**TS4**) and intermediates (**3**–**6**) are available in the Supplementary Material.

The IR spectra of the possible fragmentation products of **1** and **2** were also calculated at the B3LYP/6–311++G(3df,2p) level and showed good agreement with the experimental frequencies (Table S1 in the Supplementary Material).

Conclusion

The formation of selenoketene $CH_2{=}C{=}Se$ in the FVT of tetraselenafulvalene **1** is confirmed by mass spectrometry and IR spectroscopy. The existence of neutral ethenediselone, Se=C=C=Se, is established on the microsecond timescale of the NRMS experiment. This compound barely survives the millisecond timescale[21] of FVT/matrix isolation experiments, but a weak absorption at 906 cm^{-1} in the IR spectrum of the thermolyzate from **2** is in agreement with theoretical predictions for C_2Se_2. C_2Se_2 is predicted to be a ground state triplet molecule with a small singlet-triplet gap (1.7 kJ mol^{-1} at the CASPT2 (20,16) level).

Experimental

The apparatus for argon matrix isolation and IR spectroscopy employed a quartz thermolysis tube (150 mm length and 8 mm internal diameter) as described earlier.[22] BaF_2 optics were used for IR spectroscopy. The six-sector tandem mass spectrometer (Waters AutoSpec 6F) with E1 B1 c1 E2 c2 c3 E3 B2 c4 E4 geometry was fitted with a quartz thermolysis tube (50 mm length, 3 mm inner diameter) directly connected to the outer ion source as previously described.[23] The NRMS technique has been reported.[24] Compounds **1** and **2** were prepared according to literature procedures.[25]

Computational Methods

Ab initio and multiconfiguration self-consistent field calculations were carried out with *GAUSSIAN 09*[26] and *MOLPRO 2010*[27] programs. The structures and energies of the three electronic states of C_2Se_2 were investigated at the Hartree–Fock (HF), B3LYP, MP2, MP3, MP4, CCSD, and CCSD(T) levels. Multiconfiguration SCF calculations, including CASSCF,[28] second-order and third-order multireference perturbations CASPT2[29] and CASPT3,[29] and multireference configuration interaction (MRCI)[30] were carried out for the $^3\Sigma_g^-$ and $^1\Delta_g$, states of C_2Se_2. Restricted Hartree–Fock (RHF) was used for closed-shell species and the unrestricted Hartree–Fock (UHF) formalism was employed for the open-shell systems (namely $^3\Sigma_g^-$ and $^1\Delta_g$ states). Harmonic fundamental vibrations were calculated for C_2Se_2 and its fragmented products at the B3LYP/6–311++G(3df,2p) level. The directly calculated vibrational frequencies were scaled by a factor of 0.967.[31] For the fragmentation pathways of tetraselenafulvalenes, the energetics was examined at B3LYP/6–311++G(3df,2p) level.

Supplementary Material

Computational details are available from the Journal's website.

Acknowledgements

R.F. and P.G. acknowledge the FRS-FNRS for financial support for the acquisition of the AutoSpec 6F and for continuing support. The authors thank Professor Curt Wentrup, The University of Queensland, for valuable discussions and suggestions.

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