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Early Barriers in the Matrix Photochemical Formation of *syn–anti* Randomized FC(O)SeF from the OCSe:F_2 Complex

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Abstract: The photochemically induced reaction of OCSe and F_2, isolated together in an Ar matrix at about 15 K, leads to formation of the hitherto-unknown fluorocarbonylselenyl fluoride FC(O)SeF. The reaction occurs via a van der Waals complex O=C=Se···F−F that favors very early formation of the *anti* conformer. The presence and subsequent decay of a band assigned to the F−F vibration correlated with perturbed OCSe bands seems to confirm this hypothesis. Subsequent irradiation of the matrix leads to randomized FC(O)SeF by a photochemically induced conformational equilibrium between *syn* and *anti* forms. Another photochemical reaction channel is the formation of CO and SeF_2 molecules, which are produced in the same matrix cage and then form a loose complex. The changes were monitored and the products characterized experimentally by their IR spectra, and the spectra analyzed in the light of the results of theoretical calculations.

Keywords: density functional calculations • fluorine • matrix isolation • photochemistry • selenium

Introduction

While halogenated sulfenylcarbonyl compounds XC(O)SY (X, Y = halogen) have been extensively studied,[1] the analogous selenocarbonyl compounds XC(O)SeY are still unknown. Matrix-isolation photochemistry is a very useful strategy for the isolation of novel species, either because they are unstable under normal conditions or because no chemical synthetic route has been found. In this context, the "phosgene family" was recently completed with the isolation of the last two unknown members O=CICl and O=CIBr by photochemical matrix reaction of CO with ICl or IBr.[2] New members of the XC(O)SY compounds such as BrC(O)SBr,[3] IC(O)SBr[1] and BrC(O)SCl[1] were also isolated from the reaction of OCS with the corresponding halogen or interhalogen compound. BrC(O)SCl was also obtained by photochemical rearrangement of matrix-isolated ClC(O)SBr.[4] Recently, several compounds of the type XC(S)SY (X, Y = halogen) have been isolated by photochemical reaction between CS_2 and XY.[5]

Here we present the isolation of the hitherto-unknown molecule FC(O)SeF by matrix photochemical reaction of OCSe and F_2, evidenced by FTIR spectroscopy. As far as we know, this is the first example of a member of the XC(O)SeY family of compounds, with X, Y = halogen. Moreover, studies on the −C(O)Se− group, restricted to some selenocarboxylic acids, are very scarce.[6,7]

Both the *syn* and *anti* conformations of fluorocarbonylselenyl fluoride were observed in matrix. According to quantum chemical calculations (see below) the *syn* form is thermodynamically more stable than the *anti* form. Photochemically produced FC(O)SeF has an early barrier of formation leading to the *anti* form at the beginning of irradiation. This is explained in terms of the intermediacy in the photochemical reaction of the van der Waals complex O=C=Se···F−F, which favors formation of the less stable *anti* conformer.

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The presence of the molecular complex and its role in the reaction mechanisms were monitored by IR spectroscopy. Not only absorptions associated with the OCSe moiety were observed, but also activation of the F–F vibrational mode was detected. An F–F stretching frequency of 899 cm^{-1} in the IR for liquid fluorine was reported by Jacob.[8] Prolonged irradiation of the matrix gives rise to a randomization process, in which the proportion of each conformer is approximately 50%. The novel species *syn*-FC(O)SeF, *anti*-FC(O)SeF and the O=C=Se···F–F complex were characterized by their IR spectra and by comparison with the results of quantum chemical calculations.

Results and Discussion

Experimental findings: Gaseous mixtures of OCSe and F_2 in Ar were co-deposited on the matrix support at 15 K. The strongest feature of the IR spectrum measured immediately after deposition was observed at 2009.0 cm^{-1}, corresponding to the ν(CO) mode of the OCSe molecule isolated in solid Ar.[9] In addition to the features corresponding to the fundamentals, overtones and combination bands of free OCSe, new absorptions appear in the spectra. The bands at 1940.5, 1912.5, 1237.8 and 964.8 cm^{-1} were assigned to the ν_1, $2\nu_2$, ν_4 and ν_2 modes of OCF_2,[10] chemically formed during deposition (see Supporting Information). The presence of an absorption centred at 851.7 cm^{-1} (Figure 1) in the spectra of the mixtures evidenced formation of the hitherto-unknown molecular complex between OCSe and F_2. In addition to this absorption, attributed to activation of the F–F stretching vibration in the complex, a feature at 2011.4 cm^{-1}, also shown in Figure 1, was assigned to the carbonyl stretching mode of OCSe in the van der Waals complex, in spite of the behavior observed with irradiation time, and also by comparison with the predictions of theoretical calculations (see below). Bands at 2138.5 and 2142.1 cm^{-1} are also observable as extremely weak features in the spectrum; the former is assigned to free CO (reported at 2138.2 cm^{-1} when isolated in an Ar matrix)[11] and the latter to a perturbed CO molecule (see Figure 2).

Subsequent irradiation of the matrix with broadband UV/Vis light leads to drastic changes in the IR spectra. While the absorptions corresponding to OCSe decrease to about 15% of their original values after 45 min of photolysis, that assigned to the OCSe···F_2 molecular complex completely disappeared after the matrix was irradiated for 3 min (see Supporting Information).

Several new absorptions develop on photolysis. To help in identifying the photoproducts, the intensities of the bands were plotted against irradiation time, and then grouped by similar behavior. In the spectral region characteristic of stretching of the CO molecule, a group of absorptions appear and grow with increasing irradiation time (Figure 2). A feature at 2140.1 cm^{-1}, which coincides with that observed on photolysis of OCSe isolated in an Ar matrix,[9] is assigned to a CO molecule perturbed by the presence of a Se atom in

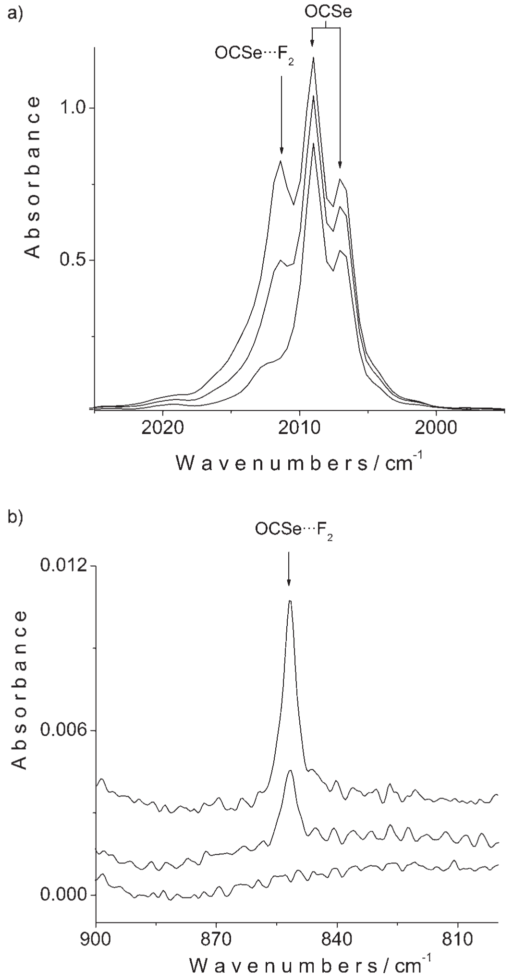


Figure 1. FTIR spectra of an Ar matrix containing OCSe, F_2 and Ar in the proportions 1:2:200 in the a) 2025 to 1990 cm^{-1} region and b) 900 to 800 cm^{-1} region immediately after deposition (top) and after 1 (middle) and 3 min (bottom) of photolysis.

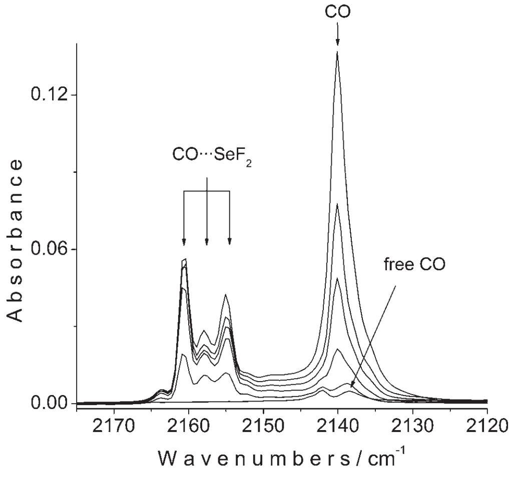


Figure 2. FTIR spectra of an Ar matrix containing OCSe, F_2 and Ar in the proportions 1:2:200 in the 2175 to 2120 cm^{-1} region immediately after deposition (bottom) and after 1, 3, 8, 15, and 45 min of photolysis.

Table 1. Wavenumbers and assignments of the IR absorptions appearing after broadband UV/Vis photolysis of an Ar matrix containing a mixture of OCSe and F_2.

Ar matrix	Assignment		Wavenumbers
$\tilde{\nu}$ [cm^{-1}]	Molecule	Vibrational mode	reported previously
2160.5/2157.9/2150.3	$OC\cdots SeF_2$	$\nu(CO)$	–
2140.1	$OC\cdots Se$	$\nu(CO)$	this work
1940.5/1936.1/1932.6	$O{=}CF_2$	$\nu(CO)$ (ν_1)	1941.4[a]
1912.5/1907/11904.5/1901.1/1898.0	$O{=}CF_2$	$2\nu_2$	1913.5[a]
1890.2/1882.2 1885.1	$O{=}CF_2\cdots F_2$?		–
1869.5	*trans*-$(FCO)_2$	$\nu_{as}(CO)$ (ν_9)	1860.2[b]
1855.6	$FCO^{\cdot}$	$\nu(CO)$	1855.0[c]
1845.7	*syn*-FC(O)SeF	$\nu(CO)$	this work
1808.0	*anti*-FC(O)SeF	$\nu(CO)$	this work
1267.0	$O{=}CF_2\cdots F_2$?		–
1237.8	$O{=}CF_2$	$\nu_{as}(CF_2)$ (ν_4)	1237.8[a]
1232.0/1229.4	$O{=}CF_2\cdots F_2$?		–
1117.5	*syn*-FC(O)SeF	$\nu(CF)$	this work
1098.0	*trans*-$(FCO)_2$	$\nu_{as}(CF)$ (ν_{10})	1101.3[b]
1089.0	*anti*-FC(O)SeF	$\nu(CF)$	this work
1079.5	*cis*-$(FCO)_2$	$\nu_{as}(CF)$ (ν_{10})	1080.3[b]
975.0	$O{=}CF_2\cdots F_2$?		–
964.8	$O{=}CF_2$	$\nu_s(CF_2)$ (ν_2)	965.5[a]
961.0	$O{=}CF_2\cdots F_2$?		–
774.7/769.3/767.1	$O{=}CF_2$	$\gamma(CO)$ (ν_6)	768.9
742.3/740.7	SeF_4	$\nu_s(SeF_2$ eq.) (ν_1)	742.5–738.2[d]
724.6/722.9	SeF_4	$\nu_{as}(SeF_2$ eq.) (ν_8)	721.8–727.8[d]
687.7/685.8	SeF_2	$\nu_s(SeF_2)$ (ν_1)	700–694[d]
678.9	*syn*-FC(O)SeF	$\nu(CSe)$	this work
674.0	*trans*-$(FCO)_2$	$\delta_{as}(OCF)$ (ν_{11})	673.5[b]
667.9	*anti*-FC(O)SeF	$\nu(CSe)$	this work
658.7/657.0	SeF_2	$\nu_{as}(SeF_2)$ (ν_3)	672–666[d]
599.2/597.2	SeF_4	$\nu_s(SeF_2$ ax.) (ν_2)	598.5–591.5[d]
566.3	$Se{=}SeF_2$	(ν_3)	572.7–568.4[d]
402.3	$Se{=}SeF_2$	(ν_1)	411.0–397.0[d]

[a] Reference [10]. [b] Reference [15]. [c] Reference [18]. [d] References [13] and [14].

the same matrix cage. Absorptions at 2160.5/2157.9/2150.3 exhibit different behavior with irradiation time, and are most plausibly assigned to a CO molecule interacting with another photoproduct.

The absorptions originally assigned to OCF_2 in the IR spectra taken immediately after deposition slightly grow on photolysis. The bands at 742.3/740.7, 724.6/722.9 and 599.2/597.2 cm^{-1} (see Supporting Information) are readily attributed to the SeF_4 molecule on the basis of comparison with the reported values for this species isolated in an argon matrix.[12] The features appearing at 687.7/685.8 and 658.7/657.0 cm^{-1} are tentatively assigned to SeF_2. The reported absorptions, slightly higher in energy, correspond to the compound obtained by reaction of fluorine with a heated 1:1 mixture of highly enriched ^{76}Se and ^{80}Se in an argon matrix.[13,14]

The IR features at 1869.5, 1098.0 and 674.0 cm^{-1} were attributed to the formation of *trans*-$(FCO)_2$, while the absorption at 1079.5 cm^{-1} was assigned to *cis*-$(FCO)_2$, accordingly to the reported vales for this species isolated in solid Ar.[15–17]

Signals at 566.3 and 402.3 cm^{-1} in the IR spectra of the irradiated matrices were tentatively assigned to $Se{=}SeF_2$, by comparison with the values reported previously for an isotopic mixture of the same compound highly enriched in ^{76}Se and ^{80}Se.[13,14]

Table 1 compiles the wavenumbers of all the absorptions that develop on photolysis, together with tentative assignments and values reported in the literature. Besides the features corresponding to the identified photoproducts, absorptions at 1845.7, 1808.0, 1117.5, 1089.0, 678.9 and 667.9 cm^{-1} appear and grow on photolysis (see Figures 3 and 4). Any attempt to assign these new bands to reported species failed. To help in the identification of the products, the intensities of the absorptions were plotted as a function of irradiation time and the bands were grouped into two sets, according to their kinetic behavior, as shown in Figure 5.

Our previous experimental results for the matrix reactions of halogens with OCS[1,3] or CS_2[5] allow us to suggest the formation of the hitherto unknown molecule FC(O)SeF, in the *syn* and *anti* forms. Several ab initio and DFT calculations were performed in order to compare the theoretical IR spectrum of each conformer with the experimental findings.

Theoretical study on FC(O)SeF: Two planar forms are expected for FC(O)SeF, as depicted in Figure 6: the *syn* con-

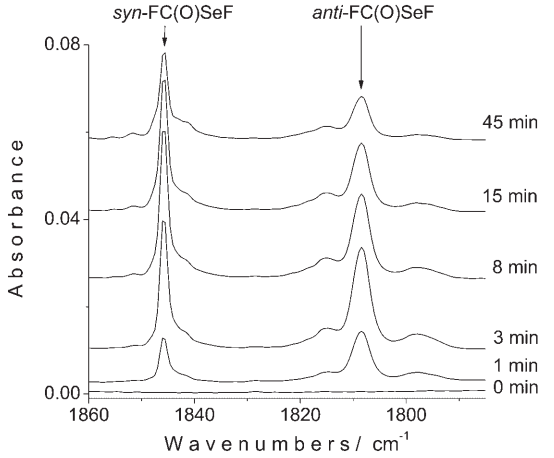


Figure 3. FTIR spectra of an Ar matrix containing OCSe, F_2 and Ar in the proportions 1:2:200 in the 1860 to 1780 cm^{-1} region immediately after deposition (bottom) and after 1, 3, 8, 15, and 45 min of photolysis.

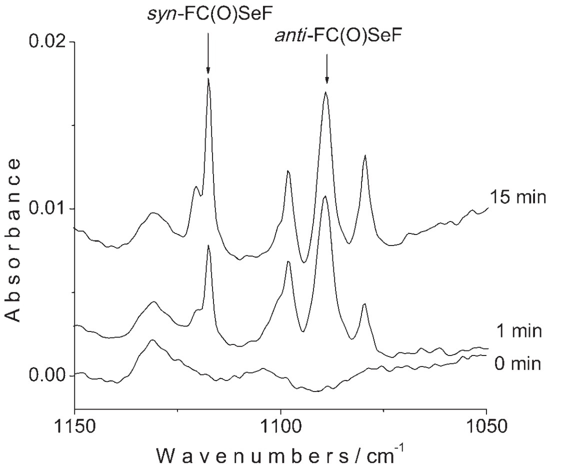


Figure 4. FTIR spectra of an Ar matrix containing OCSe, F_2 and Ar in the proportions 1:2:200 in the 1150 to 1050 cm^{-1} region immediately after deposition (bottom) and after 1 and 15 min of photolysis.

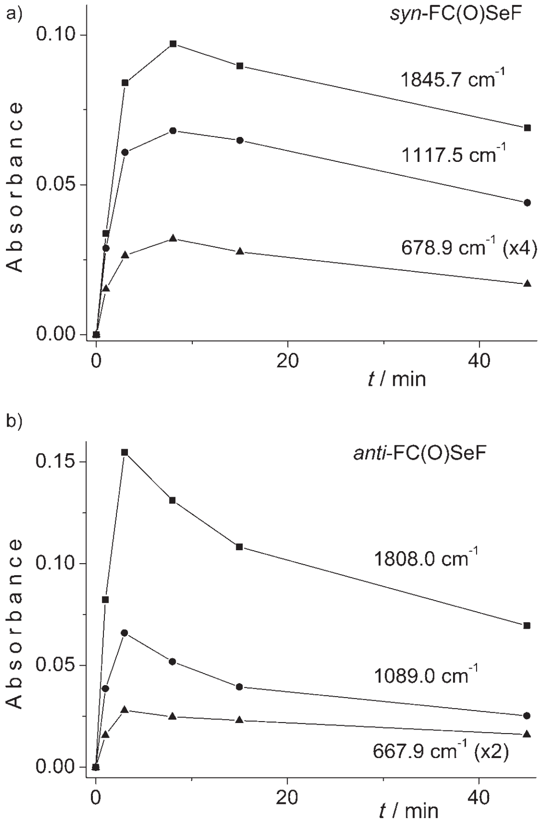


Figure 5. Plots as a function of irradiation time of the intensities of the bands assigned to a) *syn*-FC(O)SeF and b) *anti*-FC(O)SeF in the IR spectrum of an Ar matrix initially containing OCSe, F_2 and Ar in the proportions 1:2:200.

former, with the C=O double bond *syn* to the Se−F single bond, and the *anti* form with the C=O double bond *anti* to the Se−F single bond. The two structures were calculated with different theoretical models. In all cases they correspond to minima over the potential-energy surface for which no imaginary frequencies occur. All the calculations predict the *syn* form to be more stable than the *anti* form. The calculated dimensions for *syn*- and *anti*-FC(O)SeF and the theoretical energy differences of the two conformers are presented as Supporting Information.

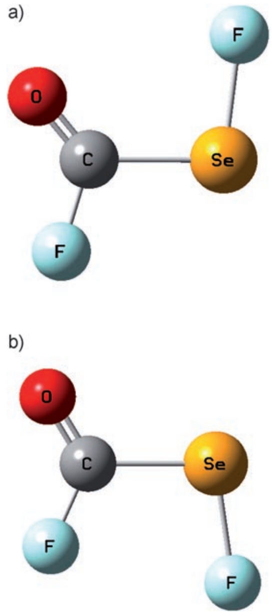


Figure 6. Molecular models (B3LYP/6-311+G*) of the *syn* and *anti* forms of FC(O)SeF.

To compare the theoretical predictions with the experimental findings, the IR spectra of both forms were calculated with different approximations. The theoretical anharmonic frequencies and IR intensities of *syn*- and *anti*-FC(O)SeF are presented in Table 2, together with the absorptions that appear in the IR spectra of the irradiated Ar matrix containing OCSe and F_2 that were tentatively assigned to these two species.

Theoretical study of molecular complexes between OCSe and F_2: The potential-energy surfaces for planar molecular complexes between OCSe and F_2 were investigated by means of the B3LYP/6-31+G* approximation. Two different interaction sites were assumed in the OCSe moiety: the oxygen and the selenium atom. For the interaction through the oxygen atom the potential-energy curve was calculated as the C=O···F intermolecular angle varied from 60 to 180° in steps of 10°. Two minima were found in this potential-energy curve, at 90 and 180°. When the same scan was performed for the O=C=Se···F−F complexes, only one minimum at 90° was found over the potential-energy curve. These three structures were then fully optimized and characterized as true energy minima for which no imaginary frequencies occur. The molecular models and calculated dimensions for these complexes are presented as Supporting Information.

The molecular complex binding through the Se atom is by far the more stable, with a predicted corrected binding energy of -8.16 kcal mol^{-1}. When binding through the O atom the stabilization of the complex with respect to the free monomers is slightly negative for the linear complex (-0.11 kcal mol^{-1}), while is predicted to be almost zero for the angular complex (see Supporting Information). The bonding properties of each of the complexes were interpreted by natural bond orbital (NBO) analysis in terms of "donor–acceptor" interactions.[19] Such an analysis predicts a charge transfer q from OCSe to the fluorine subunit of about 0.306 e for the O=C=Se···F−F molecular complex. The amount of charge transferred (q) is forecast to be much smaller for the Se=C=O···F−F molecular complexes: 0.002 and 0.001 e for the linear and angular structures, respective-

Table 2. Comparison between the experimental and calculated wavenumbers for the *syn* and *anti* forms of FC(O)SeF (intensities are given in parentheses).

	syn-FC(O)SeF			*anti*-FC(O)SeF		
Ar matrix	B3LYP/6-311+G*	MP2/6-311+G*	Ar matrix	B3LYP/6-311+G*	MP2/6-311+G*	Assignment
1845.7 (100)	1858.8 (94)	1856.8 (69)	1808.0 (100)	1825.1 (100)	1820.9 (90)	$\nu(C{=}O)$ (ν_1)
1117.5 (35)	963.0 (100)	991.4 (100)	1089.0 (42)	1055.0 (98)	1087.3 (100)	$\nu(C{-}F)$ (ν_2)
–	699.9 (6)	687.1 (7)	–	715.2 (8)	722.1 (10)	$\nu(Se{-}F)$ (ν_3)
678.9 (8)	626.4 (12)	612.6 (8)	667.9 (18)	617.9 (14)	606.4 (11)	$\nu(C{-}Se)$ (ν_4)
–	574.3 (1)	578.2 (2)	–	583.8 (2)	590.7 (2)	γ (ν_8)
–	379.8 (<1)	386.8(<1)	–	345.8 (1)	355.8 (2)	$\delta(FCO)$ (ν_5)
–	299.2 (<1)	312.4 (<1)	-	325.5 (<1)	340.2 (<1)	$\delta(FCSe)$ (ν_6)
–	150.0 (<1)	167.8 (1)	-	151.3 (<1)	172.2 (2)	$\delta(CSeF)$ (ν_7)
–	113.8 (<1)	104.0 (<1)	–	105.6 (<1)	89.9 (1)	τ (ν_9)

ly. The largest contribution to the stabilization energy of the $O{=}C{=}Se{\cdots}F{-}F$ complex arises from the interaction of the lone pair of the Se atom with the unfilled σ antibonding orbital of the fluorine molecule, as depicted in Figure 7. The calculated energy decrease due to this interaction reaches a value of 57.04 kcal mol^{-1}.

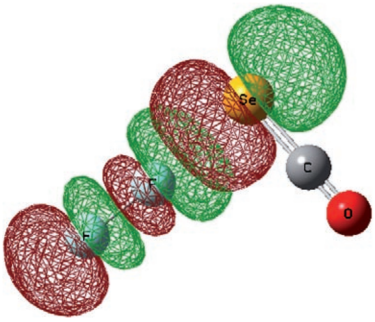
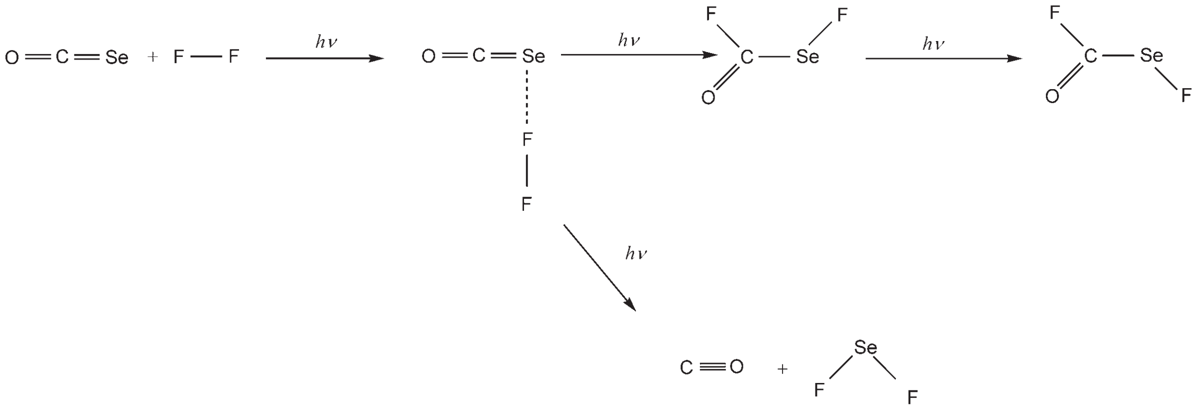


Figure 7. Schematic representation of the interaction between the lone pair of the Se atom of OCSe with the unfilled σ antibonding orbital of the F_2 molecule in the $O{=}C{=}Se{\cdots}F{-}F$ molecular complex.

The simulated IR spectrum of the most stable molecular complex between OCSe and F_2, calculated with the MP2/6-311+G* approximation, agrees reasonable well with the experimental findings (see Supporting Information). A small blue shift of the carbonyl stretching mode is predicted, together with a red shift of the $\nu(F{-}F)$ vibrational mode, activated in the IR as a consequence of the loss of symmetry of this fragment. The $\nu(C{=}Se)$ mode is red-shifted with respect to free $O{=}C{=}Se$, and the bending mode splits into two distinct in-plane and out-of-plane vibrations due to the lowering of symmetry of the OCSe moiety in the complex (from $D_{\infty h}$ to C_s). These three absorptions were not observed in the IR spectra, possibly because of their low intensities. The four remaining vibrations, which involve motions of the whole molecular complex, are characterized by wavenumbers well below the low-energy threshold (400 cm^{-1}) of the present IR study.

Reaction mechanisms of OCSe with F_2 isolated in solid Ar: Analysis of the different IR absorptions with increasing irradiation time gives us some clues for interpretation of the photochemical mechanisms in the matrix. The IR bands assigned to the $O{=}C{=}Se{\cdots}F_2$ complex decrease abruptly with increasing photolysis time, and disappear completely after 3 min of broad-band irradiation. Simultaneously, the absorptions corresponding to the *syn* and *anti* forms of FC(O)SeF first grow and then decrease on photolysis, but with different kinetics (Figure 5). Although *anti*-FC(O)SeF is predicted to be thermodynamically unfavorable relative to *syn*-FC(O)SeF, the photochemical reaction of OCSe with F_2 in an argon matrix initially leads to formation of the *anti* form, which evolves with increasing irradiation time into a 1:1 mixture of the two conformers. This behavior could be interpreted by the reaction mechanism presented in Scheme 1, in



Scheme 1. Outline of the photochemical reactions of OCSe and F_2 isolated together in a solid Ar matrix.

which the formation of fluorocarbonylselenyl fluoride is proposed to arise from photochemical evolution of the molecular complex O=C=Se···F–F. The geometry of the complex would favor the formation of the *anti* form over the *syn* form. By means of the randomization process reported previously for several members of the carbonyl sulfenyl family of compounds (e.g., refs. [4] and [20]), *anti*-FC(O)SeF is then transformed into *syn*-FC(O)SeF, and at longer irradiation times an approximately equimolar mixture of the two forms is obtained.

Another proposed photochemical reaction channel is formation of the CO and SeF_2 molecules. A similar evolution with irradiation time of a group of bands in the ν_{CO} spectral region at 2160.5/2157.9/2150.3 cm^{-1}, perturbed from the corresponding bands of free CO, and absorptions assigned to the SeF_2 molecule are observed. Although the reported IR modes for the SeF_2 molecule isolated in solid Ar correspond to an 1:1 isotopic mixture of ^{76}Se and ^{80}Se,[13,14] the features obtained here seemed to be shifted to lower energies. These findings suggest that the CO and SeF_2 molecules are produced in the same matrix cage, and, as they can not escape from it, a loose complex between them is likely formed. The other photoproducts identified during photolysis are formed by more complex mechanisms, which necessarily involved more than two molecules.

Conclusion

Fluorocarbonylselenyl fluoride FC(O)SeF was isolated for the first time by photochemical reaction of OCSe and F_2 in an argon matrix at about 15 K. The intermediacy of the van der Waals complex O=C=Se···F–F seems to play an important role in the formation of the photoproducts. Initially, *anti*-FC(O)SeF is formed, and it is then transformed, through a randomization process, into *syn*-FC(O)SeF. Both conformers were characterized, at least partially, by their IR spectra, aided by the comparison with the results of quantum chemical calculations.

Experimental Section

A sample of F_2 (Solvay, Germany) was transferred to a 1 L stainless steel container of the vacuum line and diluted 2:100 with Ar. A separate sample of OCSe (prepared according to ref. [21]) was mixed with argon in a 0.5 L glass container in a ratio of 1:100. Both containers were connected via needle valves and stainless steel capillaries to the spray-on nozzle of the matrix support. About 0.5–1 mmol of the gas mixtures were co-deposited over 10–20 min on the mirror plane of a rhodium-plated copper block held at 15 K. For the photolysis experiments radiation from a 150 W high-pressure mercury lamp (TQ150, Haereus, Hanau, Germany) was used over a period of 15 s to 45 min. The photolysis process was observed by IR spectroscopy. Details of the matrix apparatus are given elsewhere.[22] Matrix IR spectra were recorded on a IFS 66v/S spectrometer with a resolution of 1 cm^{-1}, in absorption/reflection mode as described in ref. [22]. The IR intensities were determined by integrating the areas of the absorptions with the OMNIC program.

Quantum-chemical calculations were performed with the Gaussian 98 program system[23] under the Linda parallel execution environment by using two coupled PCs. HF, MP2 and DFT (B3LYP) methods were used, in combination with different basis sets. Optimized geometries were sought by standard gradient techniques with simultaneous relaxation of all geometrical parameters. The calculated vibrational properties correspond in all cases to potential-energy minima for which no imaginary vibrational frequency was found. Anharmonic frequencies were calculated by using the Gaussian 03 program system.[24]

The binding energies of the molecular complexes were calculated by using the correction proposed by Nagy et al.[25] Basis-set superposition errors were calculated by applying the counterpoise procedure developed by Boys and Bernardi.[26]

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[1] Y. A. Tobón, L. I. Nieto, R. M. Romano, C. O. Della Védova, A. J. Downs, *J. Phys. Chem. A* **2006**, *110*, 2674–2681, and references therein.
[2] R. M. Romano, C. O. Della Védova, A. J. Downs, Y. A. Tobón, H. Willner, *Inorg. Chem.* **2005**, *44*, 3241–3248.
[3] R. M. Romano, C. O. Della Védova, A. J. Downs, *Chem. Commun.* **2001**, 2638–2639.
[4] R. M. Romano, C. O. Della Védova, A. J. Downs, T. M. Greene, *J. Am. Chem. Soc.* **2001**, *123*, 5794–5801.
[5] Y. A. Tobón, R. M. Romano, C. O. Della Védova, A. J. Downs, *Inorg. Chem.* **2007**, *46*, 4692–4703.
[6] H. Kageyama, T. Murai, T. Kanda, S. Kato, *J. Am. Chem. Soc.* **1994**, *116*, 2195–2196.
[7] S. Kato, Y. Kawahara, H. Kageyama, R. Yamada, O. Niyomura, T. Murai, T. Kanda, *J. Am. Chem. Soc.* **1996**, *118*, 1262–1267.
[8] E. Jacob, *Z. Anorg. Allg. Chem.* **1970**, *377*, 267–272.
[9] J. A. Gómez, R. M. Romano, unpublished results
[10] Y. Bouteiller, O. Abdelaoui, A. Schriver, L. Schriver-Mazzuoli, *J. Chem. Phys.* **1995**, *102*, 1731–1739.
[11] H. Dubost, *Chem. Phys.* **1976**, *12*, 139–151.
[12] C. J. Adams, A. J. Downs, *Spectrochim. Acta* **1972**, *28 A*, 1841–1854.
[13] A. Haas, H. Willner, *Z. Anorg. Allg. Chem.* **1979**, *454*, 17–23.
[14] H. Willner, *Z. Anorg. Allg. Chem.* **1981**, *481*, 117–125.
[15] S. Sander, H. Willner, L. Khriachtchev, M. Pettersson, M. Räsänen, E. Varetti, *J. Mol. Spectrosc.* **2000**, *203*, 145–150.
[16] J. R. Durig, S. C. Brown, S. E. Hannum, *J. Chem. Phys.* **1970**, *54*, 4428–4436.
[17] B. S. Ault, *Inorg. Chem.* **1985**, *24*, 1013–1015.
[18] D. E. Millican, M. E. Jacoxs, A. M. Bass, J. J. Comeford, D. E. Mann, *J. Chem. Phys.* **1965**, *42*, 3187–3195.
[19] A. E. Reed, L. A. Curtiss, F. Weinhold, *Chem. Rev.* **1988**, *88*, 899–926.
[20] C. O. Della Védova, H.-G. Mack, *Inorg. Chem.* **1993**, *32*, 948–950.
[21] K. Kondo, S. Yokoyama, N. Miyoshi, S. Murai, N. Sonoda, *Angew. Chem.* **1979**, *91*, 760–761; *Angew. Chem. Int. Ed.* **1979**, *18*, 691–691.
[22] H. Schnöckel, H. Willner in *Infrared and Raman Spectroscopy, Methods and Applications* (Ed.: B. Schrader), VCH, Weinheim, **1994**, p. 297.

[23] Gaussian 98, revision A.7, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, Jr., R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, A. G. Baboul, B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, J. L. Andres, M. Head-Gordon, E. S. Replogle and J. A. Pople, Gaussian Inc., Pittsburgh, PA, **1998**.

[24] Gaussian 03, revision C.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, Gaussian Inc., Wallingford, CT, **2004**.

[25] P. I. Nagy, D. A. Smith, G. Alagona, C. Ghio, *J. Phys. Chem.* **1994**, *98*, 486–493.

[26] S. F. Boys, F. Bernardi, *Mol. Phys.* **1970**, *19*, 553–566.

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