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Article

Trifluoroselenoacetic acid, $CF_3C(O)SeH$: Preparation and Properties

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The hitherto unknown trifluoroselenoacetic acid was prepared through the reaction of trifluoroacetic acid with Woollins' reagent. The compound was fully characterized by mass spectrometry, ^{1}H, ^{19}F, ^{77}Se, and ^{13}C NMR, UV−visible, IR and Raman spectroscopy, and the boiling point at 46 °C was estimated from the vapor pressure curve. An IR matrix isolation study revealed the presence of two different syn−anti and anti−syn conformers. The IR spectra of the two stereoisomers have been assigned, aided by DFT, and ab initio calculations. The UV photolysis of Ar matrix isolated $CF_3C(O)SeH$ yielded CO, OCSe, CF_3SeH, and CHF_3. Apart from CF_3SeH, these products were also obtained by vacuum flash-pyrolysis (310 °C) of gaseous $CF_3C(O)SeH$. Instead of CF_3SeH, CF_2Se, and HF were detected among the pyrolysis products. The different decomposition pathways of $CF_3C(O)SeH$ are discussed.

Introduction

Since the first preparation of trifluoroacetic acid in 1922 from the oxidation of trifluoromethylcyclohexane with nitric acid,[1] this compound was the subject of several studies that revealed their interesting properties. It is a strong acid (pK_a = 0.23), a convenient solvent, and an useful reagent in organic and inorganic synthesis.[2−4] On the other hand, trifluorothioacetic acid was unknown until 1960, when it was prepared from trifluoroacetic anhydride and hydrogen disulfide at 200 °C.[5] This acid was used for obtaining novel compounds, such as $CF_3C(O)SX$ (X = halogen) molecules.[6,7] However, the seleno-derivative has remained unknown.

As an extension of our recent work on the parent selenocarboxylic acid, $CH_3C(O)SeH$,[8] we report in this paper the preparation of the trifluoroselenoacetic acid, $CF_3C(O)SeH$. The compound was fully characterized using mass spectrometry, ^{1}H, ^{19}F, ^{77}Se, and ^{13}C NMR, UV−visible, IR and Raman spectroscopy, and its vapor pressure curve. Conformational properties, the thermal behavior, and the photochemistry of $CF_3C(O)SeH$ were studied by means of Ar matrix-isolation FTIR spectroscopy and DFT/ab initio MP2 calculations.

Experimental Section

Chemicals. Trifluoroacetic acid (Aldrich) was dried in presence of 5% of trifluoroacetic anhydride and P_2O_5 by reflux in an N_2 atmosphere. Fractional distillation under N_2 atmosphere was performed and further purification was achieved by repeated trap-to-trap condensation in vacuum. Woollins' reagent, $Ph_2P_2Se_4$, was prepared according to the reported procedure.[9]

Vapor Pressure. The vapor pressure of the liquid sample was measured in the range from 220−268 K in a small vacuum line equipped with a calibrated capacitance manometer (MKS Baratron, AHS-100) and a sample reservoir.

Mass Spectrometry. $CF_3C(O)SeH$ (0.2 μL of a 0.6 mM solution) in chloroform, prepared in a vacuum line, were injected into a Shimadzu QP-5050 GC-Mass spectrometer equipped with a chemical-isobutanol ionization source and a FS-OV-1-CB-0.25 column.

NMR Spectroscopy. For the ^{1}H, ^{19}F, ^{13}C, and ^{77}Se NMR measurements, neat samples were held in flame-sealed, thin-walled 4 mm tubes, which were placed inside 5 mm NMR tubes. CD_3OD was used as external lock and reference. The spectra were recorded with a Bruker Avance 250 spectrometer operating at 250.13, 235.36, 62.90, and 47.72 MHz for ^{1}H, ^{19}F, ^{13}C, and

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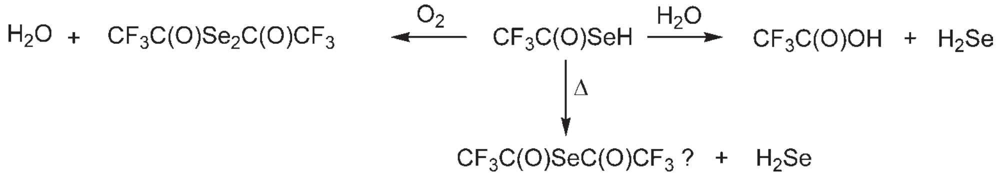
Scheme 1. Chemical Properties of $CF_3C(O)SeH$



^{77}Se spectra, respectively. The samples were maintained at −30 °C during the measurements.

UV−visible Spectroscopy. UV−vis spectrum of gaseous $CF_3C(O)SeH$ at 0.7 mbar was recorded using a glass cell (optical path length 10 cm) equipped with quartz windows and placed in the sample compartment of a Lambda 900 spectrometer (Perkin-Elmer, Norwalk, CT). The measurements were carried out in the spectral range 200−600 nm.

Vibrational Spectroscopy. The IR spectrum of the vapor was recorded at a resolution of 2 cm^{-1} in the range 4000−400 cm^{-1} with a Bruker Vector 25 spectrometer. The Raman spectrum was measured on a liquid sample sealed in 4 mm glass tube using a Bruker-Equinox 55 FRA 106/S FT-Raman spectrometer and a 1064 nm Nd:YAG laser (150 mW).

Matrix Measurements. A few milligrams of pure $CF_3C(O)SeH$ were transferred to a small U-trap connected to the inlet nozzle of the matrix apparatus. A stream of Ar (2 mmol h^{-1}) was directed over the sample held at −125 °C, and the resulting gas mixture was condensed onto the mirror plane of a rhodium plated copper support held at 15 K. For the pyrolysis experiments, the heated nozzle (i.d. 4 mm, length 20 mm quartz tube with an end orifice of 1 mm) was adjusted to 310 °C. Photolysis experiments were performed with a high-pressure mercury lamp (TQ 150, Heraeus) using a water-cooled quartz lens optic. Details of the matrix apparatus are given elsewhere.[10] IR spectra of the Ar matrices were recorded in the reflectance mode by means of a transfer optic using the Bruker IFS 66v spectrometer. An MCT-600 detector, together with a KBr/Ge beam splitter, was used in the region 5000−650 cm^{-1}. 100 scans were added for the spectra with an apodized resolutions of 0.5 and 0.15 cm^{-1}.

Theoretical Calculations. All quantum chemical calculations were performed with the Gaussian 03 program package.[11] Second-order Moller−Plesset (MP2) and density-functional (DFT) B3LYP methods were employed using the 6-311++G** basis set. Geometries were optimized by standard gradient techniques with simultaneous relaxation of all geometric parameters.

Results and Discussion

$CF_3C(O)SeH$ was prepared by treating $CF_3C(O)OH$ with an excess of Woollins' reagent, $Ph_2P_2Se_4$,[9,12] at 70 °C. After 68 h, the reaction mixture was separated by repeated trap-to-trap fractional condensation in vacuum. A pure sample of the compound was retained in the −110 °C trap, while $CF_3C(O)OH$ and a small amount of H_2Se were found in traps held at −70 and −196 °C, respectively. Starting from about 13 mmol of $CF_3C(O)OH$, approximately 0.6 mmol of pure $CF_3C(O)SeH$ were obtained. For the spectroscopical studies, the results of several preparations were collected together. The colorless liquid revealed a melting point of −145(2) °C. The vapor pressure in the temperature range 220−268 K, follows the equation $\ln p\,[\mathrm{atm}] = 11.88 - 3785/T\,[\mathrm{K}]$, giving an extrapolated boiling point of 319 K (Figures S1 and S2 in the Supporting Information).

Stored in a sealed glass vessel at ambient temperatures the compound decomposed slightly within a few hours, as is evidenced by the formation of a yellow solid, presumably $CF_3C(O)SeC(O)CF_3$, and liberation of H_2Se. In contact with air, trifluoroselenoacetic acid is rapidly oxidized to the corresponding diselenide, $CF_3C(O)Se_2C(O)CF_3$. Hydrolysis results in the formation of trifluoroacetic acid and hydrogen selenide. $CF_3C(O)OH$ and H_2Se were identified by their IR spectrum, while $CF_3C(O)Se_2C(O)CF_3$ was proposed by means of its IR and Raman spectra.[13] Scheme 1 summarizes these reactions.

Mass Spectrometry. The most intense peaks in the chemical-ionization mass spectrum of $CF_3C(O)SeH$ are arising from the $[CF_3]^+$ and $[OCCF]^+$ fragments, at m/z 69 and 59, respectively (see Figure S3 in the Supporting Information). The peaks observed at m/z 130 ($[CF_2{}^{80}Se]^+$), 108 ($[OC^{80}Se]^+$), 97 ($[OCCF_3]^+$), 80 ($[^{80}Se]^+$), 78 ($[CF_2CO]^+$), and 50 ($[CF_2]^+$) are consistent with the constitution of the molecule (Figure S4, Supporting Information).

NMR Spectroscopy. The ^1H NMR spectrum of neat $CF_3C(O)SeH$ shows a singlet at 3.1 ppm but no ^{77}Se satellites because of intermolecular proton-exchange decoupling (see Figure S5, Supporting Information). The chemical shift is in the range 2.59−4.74 ppm previously reported for related selenocarboxylic acids RC(O)SeH.[14] In the ^{19}F NMR spectrum, a singlet at −78.6 ppm is observed for the CF_3 group (Figure S6, Supporting Information), and a singlet also appeared in the ^{77}Se NMR spectrum (Figure S7, Supporting Information) at 412.8 ppm, which is close to the chemical shift obtained for $4\text{-}CH_3OC_6H_4C(O)SeH$ (427.5 ppm).[15]

The ^{13}C NMR spectrum revealed two quartets (Figure S8, Supporting Information). The one attributed to the CF_3 group is centered at 115.5 ppm ($^1J_{(C-F)} = 291.2$ Hz),

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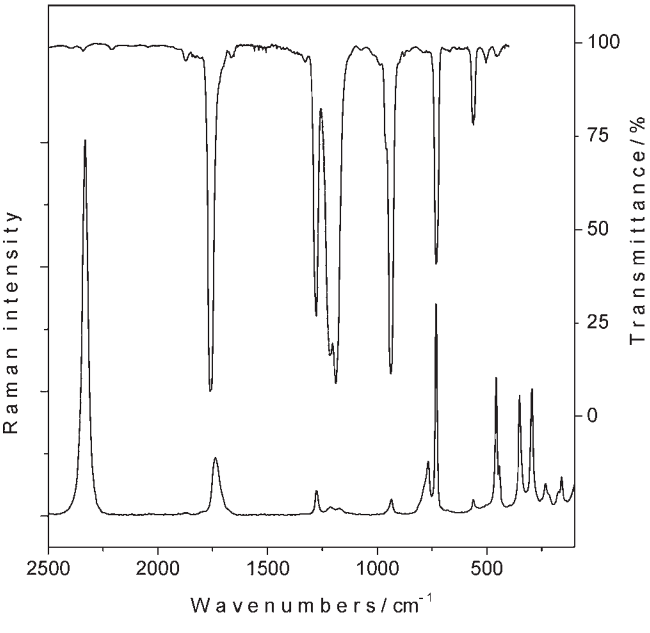

Figure 1. Gas-phase FTIR spectrum at 3 mbar, 2 cm^{-1} resolution, and an optical path length of 20 cm^{-1} (top) and Raman spectrum of the liquid at room temperature with excitation at 1064 nm and 150 mW (bottom) of $CF_3C(O)SeH$.

while the signal assigned to the C═O is centered at 184.7 ($^2J_{(C-C-F)}$ = 43.4 Hz). These results are consistent with the corresponding values reported for trifluoroacetic acid (CF_3 115.0 ppm, $^1J_{(C-F)}$ = 282 Hz; C═O: 163.0 ppm, $^2J_{(C-C-F)}$ = 44 Hz).[16,17]

UV−visible Spectroscopy. The vapor-phase UV−visible spectrum of $CF_3C(O)SeH$ recorded in the range from 200 to 600 nm exhibits an absorption centered at 251 nm, which is attributed to the $\mathrm{lp}(\pi)_{Se} \rightarrow \pi^*_{C=O}$ transition (Figure S9, Supporting Information). The 20 nm batochromic shift with respect to the corresponding absorption of selenoacetic acid,[8] is attributed to the inductive effect of the CF_3 group.

Vibrational Spectroscopy. The vapor-phase IR and the Raman spectra of liquid $CF_3C(O)SeH$ are presented in Figure 1. Table 1 compiles observed band positions and presents a tentative assignment.

The IR absorption at 1759 cm^{-1} is readily assigned to the ν(C═O) vibrational mode. This wavenumber is very close to the 1758 cm^{-1} value reported for $CF_3C(O)SH$.[18] The band at 1277 cm^{-1} is associated with the ν(C−C) mode, which is close to the corresponding mode of trifluoroacetic acid reported at 1286 cm^{-1}.[19] The features appearing in the 1200 cm^{-1} spectral region are arising from the CF_3 stretching vibrations. The Raman spectrum of liquid $CF_3C(O)SeH$ is dominated by the strong ν(Se−H) band[8] that appears at 2332 cm^{-1}.

Although the theoretical calculations presented below predict an equilibrium between two conformers, however, because of the predicted small isomeric shift of the vibrational bands it is difficult to verify the presence of two stereoisomers at ambient temperatures by the IR and Raman spectra presented in Figure 1. Matrix-isolation spectroscopy appears thus as an alternative tool to explore the existence of a conformational equilibrium.

Table 1. Experimental and Calculated Vibrational Wavenumbers (in cm^{-1}) of $CF_3C(O)SeH$ (Relative Intensities Are Given in Parentheses)

experimental			MP2/6-311++G**		
vapor IR	liquid Raman	Ar-matrix	syn−anti	anti−syn	assignment
		2308.3		2543.0 (3)	ν(Se−H) a−s
2340	2332	2306.0	2536.9 (2)		ν(Se−H) s−a
		1749.7		1755.3 (96)	ν(C═O) a−s
1759	1738	1748.3	1750.3 (80)		ν(C═O) s−a
1277	1276	1277.9	1313.5 (35)		ν(C−C) s−a
		1274.3		1310.0 (44)	ν(C−C) a−s
		1220.0		1239.7 (68)	ν(C−F) a−s
1215	1213	1210.9	1226.1 (76)		ν(C−F) s−a
1188	1172	1181.1	1209.4 (100)		$\nu_{as}(CF_3)$ s−a
		1169.8		1180.3 (100)	$\nu_{as}(CF_3)$ a−s
		940.8	969.4 (64)		δ(OCC) a−s
937	935	935.9		968.6 (48)	δ(OCC) s−a
		779.8		822.2 (12)	δ(HSeC) a−s
	768	766.3	816.2 (9)		δ(HSeC) s−a
		733.9		739.6 (17)	$\delta_a(CF_3)_{wag}$ a−s
730	732	728.3	735.7 (21)		$\delta_a(CF_3)_{wag}$ s−a
		674.9		678.6 (<1)	δ_{oop}(CO) a−s
668		667.3	674.9 (<1)		δ_{oop}(CO) s−a
560	562	562.0	568.9 (6)		$\delta(CF_3)$ s−a
		560.1		566.3 (4)	$\delta(CF_3)$ a−s
503			507.7 (1)	510.3 (1)	$\delta(CF_3)$ s−a
452	458		464.6 (1)		ν(C−Se) s−a
	350		344.2 (3)	349.6 (<1)	τ(HseCO) s−a
	294		287.3 (2)	288.4 (1)	δ(CCF) s−a
	233		237.1 (<1)	209.6 (2)	$\rho(CF_3)$ s−a
	160		166.9 (<1)	167.3 (<1)	δ(SeCC) s−a

The IR spectrum of $CF_3C(O)SeH$ isolated in Ar matrix presented in Figure 2 shows a complex pattern for most of the absorptions. To distinguish between matrix and conformational splitting, the $CF_3C(O)SeH$/Ar mixtures were directed through a heated quartz capillary prior to deposition. Increasing the temperature several weak absorptions observed at ambient temperature grow simultaneously at the expense of the strong bands arising from the more stable *syn-anti* form. This behavior was used to assign the absorptions to each of the two conformers in Table 1. Experimental molar ratios of both the conformers were estimated for different temperatures from integrated intensities of the most intense absorptions using calculated absorption coefficients (Table 2).

Thermolysis Experiments. The low-pressure thermolysis at 310 °C of $CF_3C(O)SeH$ with subsequent matrix isolation of the products not only increased the features assigned to the less-stable anti−syn conformer; in addition new bands appeared at 3962.0, 2138.5, 2009.0, 1274.1, 1250.6, 1195.7/1195.1, and 1146.3 cm^{-1}.

The bands at 2138.5 and 2009.0 cm^{-1} were readily associated with CO (2138.0)[20] and OCSe (2009.0),[21] respectively. The presence of OCSe indicates the formation of CHF_3, which is confirmed by the appearance of the 1146.3 cm^{-1} band (Figure 3, reported at 1146.0 cm^{-1} in solid Ar[22]).

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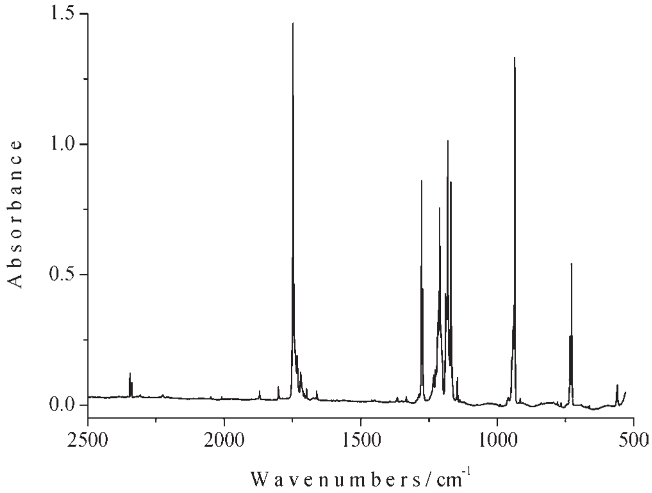

Figure 2. FTIR spectrum of $CF_3C(O)SeH$ isolated in solid Ar.

Table 2. Experimental and Calculated Molar Ratios and Relative Energies of the syn−anti and anti−syn Rotamers of $CF_3C(O)SeH$

	298 K		583 K		ΔE^a	$\Delta G^{\circ a}$
	% sa	% as	% sa	% as	[kJ/mol]	[kJ/mol]
Ar-matrix[b]	82.5	17.5	74.0	26.0		
MP2/6-311++G**	83.1	16.9	69.3	30.7	2.47	3.93
B3LYP/6-311++G**	69.0	31.0	60.1	39.9	2.47	1.97

[a] Relative energy of the *anti-syn* rotamers with respect to the most stable syn−anti. [b] Experimental values are obtained from integrated intensities of the ν(C=O) absorptions in the Ar-matrix IR spectra corrected by calculated absorption coefficients at the B3LYP/6-311++G** level.

Although the elimination of CO from $CF_3C(O)SeH$ suggests the concomitant formation of CF_3SeH, no features could be assigned to this species. Instead, bands at 1274.1 and 1195.7/1195.1 cm^{-1} (Figures 3 and 4) were attributed to $CF_2{=}Se$ (1275.0 [ν_1] and 1196.0 [ν_4] cm^{-1})[23] while the 3962.0 cm^{-1} band is associated with the formation of HF (3953.8 cm^{-1}).[24] The presence of the CF_3 radical is confirmed by an absorption at 1250.6 cm^{-1} (Figure 4) by comparison with the 1250 cm^{-1} value reported for the most intense absorption of this radical isolated in Ar matrix.[25]

The experimental results indicates two different thermal decomposition pathways of $CF_3C(O)SeH$, which are presented in Scheme 2. Although the CF_3SeH molecule was not detected in the spectrum, it is reasonable to assume that $CF_2{=}Se$ and HF were formed from a thermolabile CF_3SeH intermediate. The CF_3 radical is assumed to be involved in both decomposition routes.

Photochemistry of Matrix-Isolated $CF_3C(O)SeH$. $CF_3C(O)SeH$ displayed a rich photochemistry when it was subjected to light in the wavelengths range $200 \leq \lambda \leq 800$ nm of a high pressure mercury lamp. After 8 min of photolysis, the compound was completely decomposed, while several new absorption appeared, which are listed in Table 3 and depicted in Figures 5, S10, and S11.

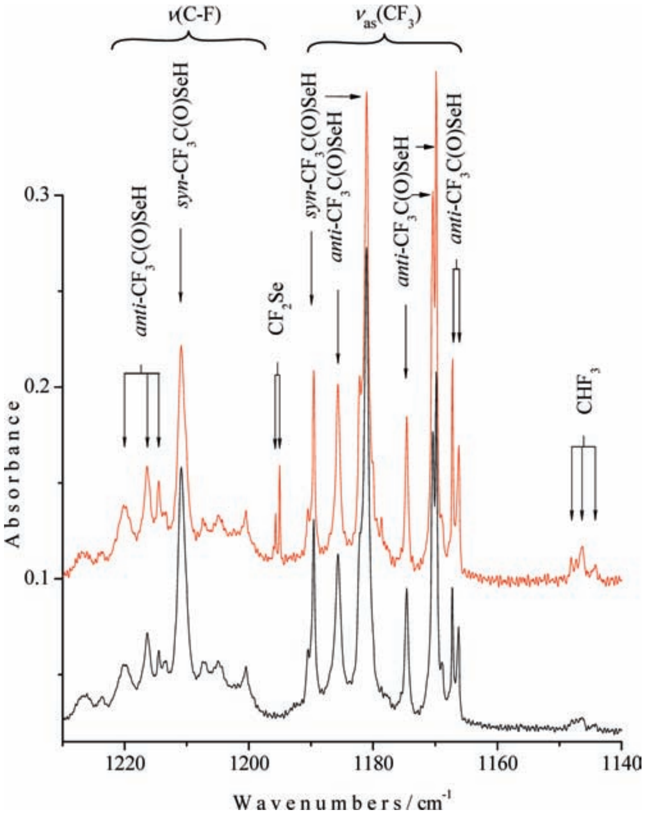

Figure 3. Section of the FTIR spectra in the range from 1230 to 1140 cm^{-1} of a solid deposit obtained at 15 K from Ar/$CF_3C(O)SeH$ mixtures with the spray-on nozzle held at room temperature (bottom) and at 310 °C (top).

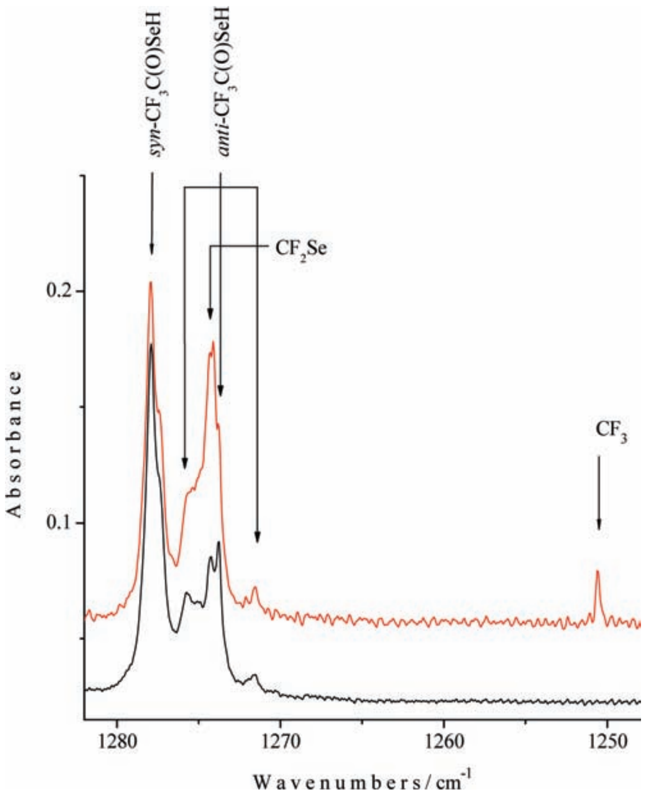

Figure 4. Section of the FTIR spectra in the range from 1282 to 1248 cm^{-1} of solid deposits obtained at 15 K from Ar/$CF_3C(O)SeH$ mixtures with the spray-on nozzle held at room temperature (bottom) and at 310 °C (top).

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Scheme 2. Proposed Low-Pressure Pyrolysis Mechanisms for $CF_3C(O)SeH$

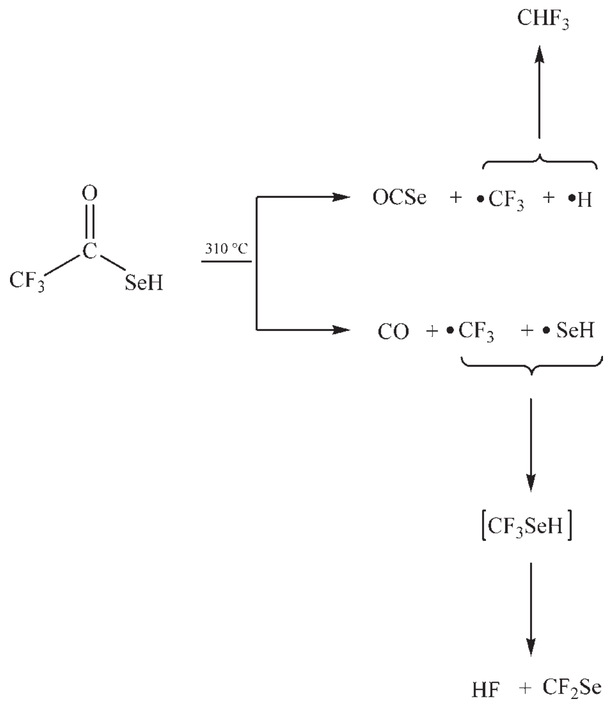


Table 3. Band Positions (in cm^{-1}) and Assignments of the IR Absorptions Appearing after Photolysis of $CF_3C(O)SeH$ Isolated in Solid Ar

Ar-matrix	molecule	vibrational mode	wavenumber reported prerviously
2147.8	CO	ν(C=O)	2138.0[a]
2009.0	OCSe	ν_1/ν(C=O)	2009.0[b]
1279.5	CF_3SeH	$\nu_2 + \nu_5$	1270[c]
1247.2	CF_3	$\nu_3/\nu_a(CF_3)$	1250[d]
1171.3	CF_3SeH	$\nu_4/\nu_a(CF_3)$	1170[c]
1146.3	CHF_3		1146[e]
1137.2	CHF_3		1134[e]
1112.0	CF_3SeH	$\nu_1/\nu_s(CF_3)$	1125[c]
1085.8	CF_3	$\nu_1/\nu_s(CF_3)$	1084[d]
1076.6	CF_3SeH	$\nu_2 + \nu_3$	1080[c]
785.3	CF_3SeH	ν_8/δ(CSeH)	785[c]
746.4	CF_3SeH	$\nu_2/\delta_a(CF_3)$	748[c]

[a] Reference 20. [b] Reference 21. [c] Reference 28. [d] Reference 25. [e] Reference 22.

The set of absorptions that appeared near 2140 cm^{-1} was attributed to CO, probably perturbed by other photoproducts formed in the same matrix cage. The possible formation of perfluoroketene, $F_2C{=}C{=}O$, which also exhibits absorptions in this spectral region, was discarded on the basis of the $\nu(^{13}C{=}O)$ band, that was shown to be useful to distinguish between CO and the ketene[26] and, also due to the absence of other bands attributable to this species.[27] In contrast to the results of the thermolysis experiments, CF_3SeH was identified as the main photoproduct by comparison of its absorptions with the values reported for gaseous CF_3SeH.[28]

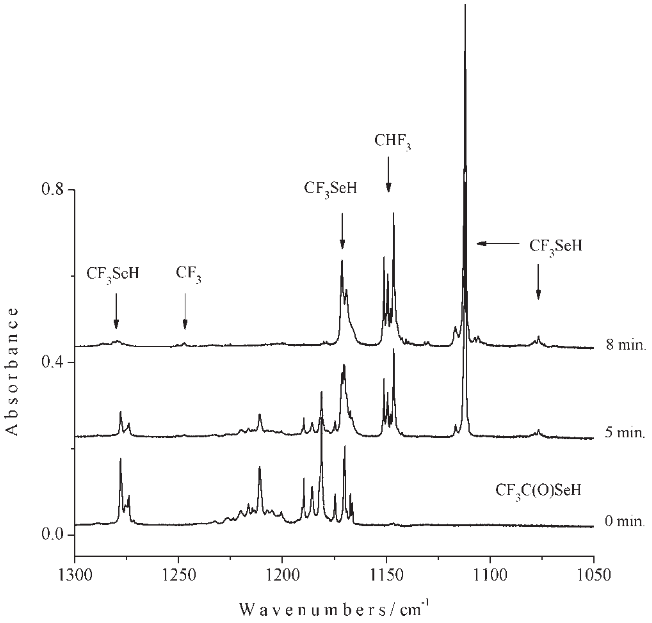
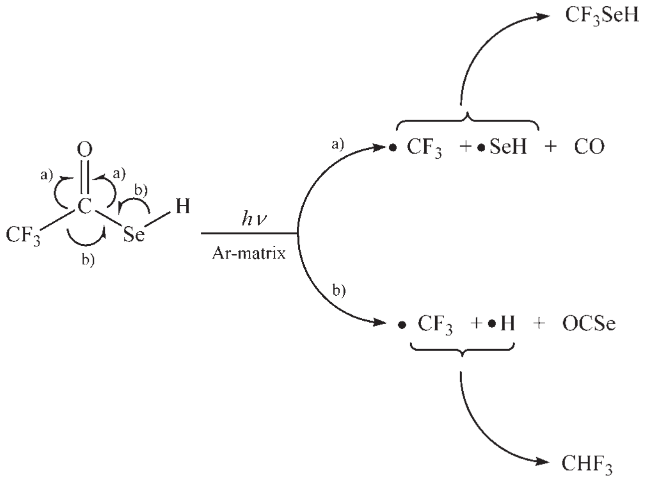


Figure 5. Section of the FTIR spectra of $CF_3C(O)SeH$ isolated in solid Ar in the 1300−1050 cm^{-1} region prior (bottom) and after 5 and 8 min of photolysis.

Scheme 3. Proposed Photolysis Mechanisms for $CF_3C(O)SeH$ Isolated in Solid Ar



In addition the photolysis of matrix-isolated $CF_3C(O)$-SeH yield OCSe,[21] CHF_3,[22] and CF_3 radicals.[25] As with the thermal decomposition, the photolysis products also suggest two different photodecomposition pathways of $CF_3C(O)SeH$, which are outlined in Scheme 3.

Theoretical Calculations. The conformational properties of $CF_3C(O)SeH$ were explored using the DFT/B3LYP and the ab initio MP2 methods in combination with the 6-311++G** basis set. Two stable structures, syn−anti and anti−syn depicted in Figure 6, were found on the potential energy surface. The geometrical parameters are compiled in Table S1. In the most stable syn−anti form the Se−H single bond is *syn* with respect to the C=O double bond while one of the C−F single bonds is anti with respect to the C=O double bond. Computed relative energies and standard Gibbs free energy differences for the two conformers are listed in Table 2, together with the Boltzmann distribution at two different

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(26) Romano, R. M.; Della Védova, C. O.; Downs, A. J. *J. Phys. Chem. A* **2002**, *106*, 7235–7244.
(27) Kötting, C.; Sander, W.; Senzlober, M.; Bürger, H. *Chem.—Eur. J.* **1998**, *4*, 1611–1615.
(28) Marsden, C. J. *J. Fluorine. Chem.* **1975**, *5*, 401–422.

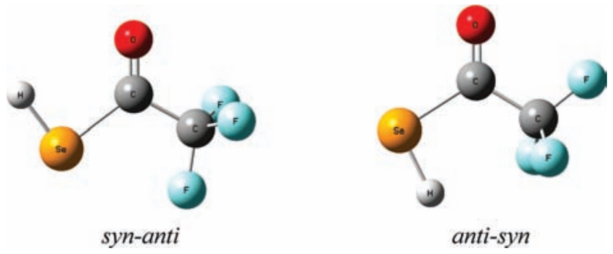

Figure 6. B3LYP/6-311++G** molecular models for the syn−anti (left) and anti−syn (right) conformers of $CF_3C(O)SeH$.

temperatures. The syn−syn and anti−anti forms correspond to transition states.

The assignment of the spectra obtained from matrix-isolation experiments were guided by computed vibrational spectra of the two stable conformers. The calculated wavenumbers for the syn−anti and anti−syn conformers are listed in Table 1.

Theoretical calculations predict the following trend for the gas phase acidity: $CF_3C(O)SeH > CF_3C(O)SH > CF_3C(O)OH$. The energies, enthalpies, and Gibbs free energies at 298 K of deprotonation of syn trifluorochalcogenoacetic acids $CF_3C(O)EH$ (E = O, S and Se) calculated with the MP2/6-311+G* approximation are placed as Supporting Information (Table S2).

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Supporting Information Available: Tables of selected geometrical parameters, energies, enthalpies, and Gibbs free energies and figures showing vapor pressure, Claussis−Clapeyron plot, GC/chemical-ionization mass spectrum, proposed mass fragmentation pattern, ^1H, ^{19}F, ^{77}Se, and ^{13}C NMR spectra, gas-phase UV−vis spectra, and FTIR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.