HeI Photoelectron Spectroscopy and Theoretical Study of Trichloromethanesulfenyl Acetate, $CCl_3SOC(O)CH_3$, and Trichloromethanesulfenyl Trifluoroacetate, $CCl_3SOC(O)CF_3$

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Two novel species, trichloromethanesulfenyl acetate, $CCl_3SOC(O)CH_3$, and trichloromethanesulfenyl trifluoroacetate, $CCl_3SOC(O)CF_3$, have been generated in situ by the heterogeneous reactions between trichloromethanesulfenyl chloride, CCl_3SCl, and corresponding silver salts, silver acetate ($AgOC(O)CH_3$) and silver trifluoroacetate ($AgOC(O)CF_3$), respectively. Photoelectron spectroscopy and quantum chemical calculations are performed to investigate these two molecules, together with their precursor, CCl_3SCl. Both of these two compounds may exist in the gas phase as a mixture of gauche and trans conformations. As for the dihedral angles $\delta_{RSOR'}$ of the gauche conformers, 107.0° and 108.5° are derived by theoretical calculations (at the B3LYP/6-311+G(3df) level) for $CCl_3SOC(O)CH_3$ and $CCl_3SOC(O)CF_3$, respectively. The first vertical ionization energies of $CCl_3SOC(O)CH_3$ and $CCl_3SOC(O)CF_3$, which have been determined by photoelectron spectroscopy, are 9.67 and 10.34 eV, respectively. According to the experimental results and theoretical analysis, the first ionization energy of these two molecules both come from the ionization of the lone pair electron of S atom.

Introduction

For a long period of time, species of the general formulas ROOR′, RSSR′, and RSOR′ have attracted considerable interest in chemistry. The most interesting feature in the structures of these species in general is the dihedral angles $\delta_{ROOR'}$, $\delta_{RSSR'}$, and $\delta_{RSOR'}$, respectively.

As the parent compound of peroxides ROOR′, HOOH possesses an equilibrium dihedral angle of 111.8°, which has been derived from spectroscopic data.[1] The interaction between the $n\sigma$ lone pairs of the two oxygen atoms and anomeric effects between the p-shaped lone pairs with the opposite σ^*(O−R) bonds make the substituents of R and R′ favor a gauche orientation. The dihedral angles $\delta_{ROOR'}$ of unstrained peroxides are between about 80° and 130°. But with very bulky substituents, bis(*tert*-butyl) peroxide and bis(trimethylsilyl) peroxide have the dihedral angles of 166(3)° and 144(6)°, respectively, which have been derived by gas electron diffraction (GED).[2]

HSSH, the parent compound of disulfanes RSSR′, has a dihedral angle of 90.76(6)° and 90.34°.[3,4] Because S−S bond length is larger than O−O bond, the steric repulsion between the substituents is reduced in disulfanes. The reported dihedral angles of CH_3SSCH_3,[5] *t*-Bu−SS-*t*-Bu,[6] FSSF,[7] FC(O)SSC(O)F,[8] $CH_3OSSOCH_3$[9] are 85.3(37)°, 128.2(27)°, 87.7(4)°, 82.2(19)°, 91(4)°, respectively. Very recently, dihedral angles $\delta_{RSSR'}$ of chlorosulfanyl thiocyanate, ClSSCN (87°)[10] and bis(trifluoroaceto) disulfide, $CF_3C(O)OSSOC(O)CF_3$ (95.1°)[11] were reported by our research group.

Thioperoxides, whose parent compound is HSOH, are less stable than peroxides and disulfanes. HSOH was studied recently by microwave spectroscopy and high-level ab initio calculations (CCSD(T)/cc-pCVQZ),[12] which predicted its dihedral angle of 91.3°. Lone pair−lone pair interactions in unsymmetrical systems, RSSR′ vs RSOR′, were discussed by means of semiempirical MO calculations.[13] RSSR′ and RSOR′ were theoretically predicted to exhibit comparable equilibrium geometries and to undergo conformational transformation with qualitatively similar energy requirements. The structural characteristics of thioperoxides are much similar to those for disulfanes than to those for peroxides. Many thioperoxides were found to be quite unstable,[13] so very little was known about the structural properties of these compounds before. Penn et al. studied the conformational features of methanesulfenic acid, CH_3SOH, by microwave spectroscopy.[14] The dihedral angle δ_{CSOH} is determined to be 93.9(1)°, which is very close to its parent compound, HSOH. Gas electron diffraction (GED) studies for dimethoxy sulfide,[15] CH_3OSOCH_3, and dimethoxy disulfide,[9] $CH_3OSSOCH_3$, show that the dihedral angles of δ_{OSOC} and δ_{SSOC} are 84(3)° and 74(3)°, respectively.

Recently, several studies have been performed to illustrate the structure of RSOR′. A new compound trifluoroacetylsulfenyl trifluoroacetate, $CF_3C(O)SOC(O)CF_3$, has been synthesized, in which the substituents on S−O bond are identical.[16] The calculated torsional angle around the S−O bond, δ_{CSOC}, of the most stable conformer is smaller than 80°. Oberhammer et al. studied the molecular structures and conformational properties of trifluoromethanesulfenyl acetate, $CF_3SOC(O)CH_3$, and trifluoromethanesulfenyl trifluoroacetate, $CF_3SOC(O)CF_3$, thereafter.[6] The dihedral angles of the most stable conformers, which were determined by GED, are 100(4)° and 101(3)°, respectively. They also found that both compounds existed in gas phase as a mixture of two conformers. The prevailing component possesses a gauche structure around the S−O bond. This result of GED is consistent with quantum chemical calculations.

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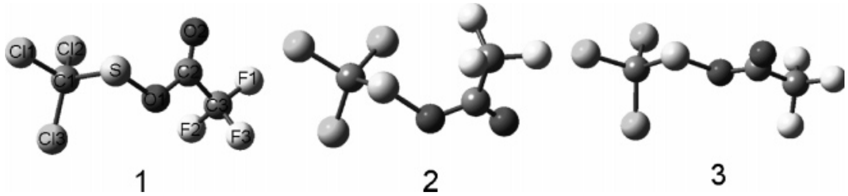

Figure 1. Schematic representation of stable conformers of $CCl_3SOC(O)CF_3$. (1 for gauche−syn structure, 2 for gauche−anti structure, 3 for trans−syn structure).

S-(fluoroformyl)*O*-(trifluoroacetyl)thioperoxide, $FC(O)SOC(O)CF_3$, was also investigated by Oberhammer et al. with GED, matrix isolation infrared spectroscopy, and quantum chemical calculations.[17] The most stable conformer shows a dihedral angle δ_{CSOC} of 75(3)°, which is much smaller than $CF_3SOC(O)CF_3$. Zeng et al. investigated bis(trifluoroaceto) disulfide, $CF_3C(O)OSSOC(O)CF_3$, by Raman, photoelectron spectroscopy (PES), and theoretical calculations.[11] The most stable conformer of this molecule shows a gauche conformation with both C=O groups cis to the S−S bond. They also find that the ground cationic-radical form of $CF_3C(O)OSSOC(O)CF_3^{\bullet+}$, which is generated after the ionization of the molecule, adopts a trans planar main atom structure ($\delta_{OSSO} = 180°$ and $\delta_{OCOS} = 0°$) with C_{2h} symmetry. This result is similar to that of Li et al.,[18] who conclude that the cationic-radical form of $CH_3SSCH_3^{\bullet+}$ adopts a planar conformation.

In the present study, we report a combined experimental and theoretical investigation of two sulfenic acid derivatives, trichloromethanesulfenyl acetate, $CCl_3SOC(O)CH_3$, and trichloromethanesulfenyl trifluoroacetate, $CCl_3SOC(O)CF_3$. Photoelectron spectroscopy (PES) and quantum chemical calculations were performed to investigate the structural and conformational properties of these two molecules. Also, the first vertical ionization energies of these two species, as well as the reaction precursor, trichloromethanesulfenyl chloride, CCl_3SCl, are determined by PES for the first time.

Experimental Section

Generation of $CCl_3SOC(O)CH_3$ and $CCl_3SOC(O)CF_3$. In the literature, $Cl_{3-n}F_nCSOC(O)CF_3$ ($n = 1,2,3$) were synthesized by $Cl_{3-n}F_nCSCl$ and $AgOC(O)CF_3$ at 20 °C.[19] In this work, CCl_3SCl and $AgOC(O)CF_3$ were used to generate $CCl_3SOC(O)CF_3$ (actually when $n = 0$) for the first time. Similarly, $CCl_3SOC(O)CH_3$ was generated from CCl_3SCl and $AgOC(O)CH_3$ following the same way. The reaction route is illustrated as below:

$$CCl_3SCl\ (g) + AgOC(O)CH_3\ (s) \rightarrow CCl_3SOC(O)CH_3\ (g) + AgCl\ (s)$$

$$CCl_3SCl\ (g) + AgOC(O)CF_3\ (s) \rightarrow CCl_3SOC(O)CF_3\ (g) + AgCl\ (s)$$

The products were generated at room temperature of 20 °C through gas−solid reactions by passing CCl_3SCl vapor over finely powdered $AgOC(O)CH_3$ and $AgOC(O)CF_3$, respectively, and in situ photoelectron spectrum of the gas-phase products were recorded. The precursor CCl_3SCl (97%), which was purchased from Alfa Aesar, was distilled in vacuum under room temperature to remove the slight impurities before use, and its purity was checked by photoionization mass spectroscopy. $AgOC(O)CH_3$ (99%) and $AgOC(O)CF_3$ (98%) were also purchased from Alfa Aesar. Before reaction, both silver salts were dried in vacuum (1×10^{-4} Torr) for 2 h.

Photoelectron Spectroscopy. As described elsewhere,[10,11] the photoelectron spectrum was recorded on a double-chamber UPS-II instrument, which has been proved to be effective apparatus for detecting unstable species. The resolution of the instrument is about 30 meV as indicated by the $Ar^+(^2P_{2/3})$ photoelectron band. During the experiments, small amounts of Ar and CH_3I were added to the sample flow to calibrate the experimental vertical ionization potentials.

Quantum Chemical Calculations. Gaussian 03[20] was used for the theoretical calculations of the two molecules, $CCl_3SOC(O)CH_3$ and $CCl_3SOC(O)CF_3$. All the conformers of these two molecules were optimized at HF/6-31+G*, B3PW91/6-31+G*, B3LYP/6-31+G*, and B3LYP/6-311+G(3df) theoretical levels, respectively. The vertical ionization energies for all conformers were calculated at the ab initio level according to Cederbaum's outer valence Green's function (OVGF)[21] method at 6-31G basis set. Besides, the geometry of CCl_3SCl was optimized with the method and basis set of B3LYP/6-311+G(3df), and the vertical ionization energies were calculated with OVGF/6-31G*.

Results and Discussion

Geometry of $CCl_3SOC(O)CH_3$ and $CCl_3SOC(O)CF_3$. As previously reported,[6,16,17] lone pair interactions make thioperoxides of the type RSOR′ prefer gauche conformations. According to the results of GED at 298 K, the most stable conformer of $FC(O)SOC(O)CF_3$ adopts gauche conformation, of which the dihedral angle δ_{CSOC} is 75(3)°.[17] Similar phenomenon was found in $CF_3C(O)SOC(O)CF_3$,[16] $CF_3SOC(O)CH_3$, and $CF_3SOC(O)CF_3$.[6] So the starting geometry of the gauche conformers of $CCl_3SOC(O)CH_3$ and $CCl_3SOC(O)CF_3$ for quantum chemical calculations were based on the structure of gauche conformers of $CF_3SOC(O)CH_3$ and $CF_3SOC(O)CF_3$ measured by GED. Besides, unexpected conformers of trans structure around the S−O bond were found in $CF_3SOC(O)CH_3$ and $CF_3SOC(O)CF_3$,[6] and similar structure may exist in $CCl_3SOC(O)CH_3$ and $CCl_3SOC(O)CF_3$. The trans structures around S−O bond were also optimized of $CCl_3SOC(O)CH_3$ and $CCl_3SOC(O)CF_3$, among which the different conformers of $CCl_3SOC(O)CF_3$ were shown in Figure 1. The structure of $CCl_3SOC(O)CH_3$ is similar.

To search for other possible conformers with different dihedral of δ_{CSOC}, relax scans of the potential energy surface were performed by rotating the torsional dihedral angle δ_{CSOC} in steps of 10° with HF/6-31G* and B3LYP/6-31G* approximation, while keeping the structure of CCl_3 and $CF_3C(O)$ moieties optimized. Figures 2 and 3 show the potential curves for dihedral angles δ_{CSOC} from 60° to 300° of $CCl_3SOC(O)CH_3$ and $CCl_3SOC(O)CF_3$, respectively.

As seen from Figure 2, at both levels, there are 3 minima of the calculated potential curves, which implies that besides the gauche structures with δ_{CSOC} around 110° and 250° (both with C=O syn of S−O bond), a trans structure with $\delta_{CSOC} = 180°$ probably exists as a stable conformer. According to the results of HF/6-31G* level, the energy of the trans conformer is slightly

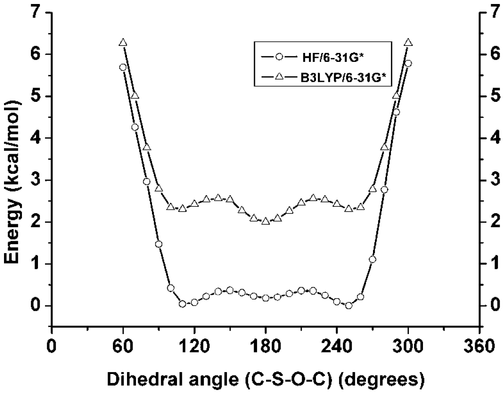

Figure 2. Calculated potential curves for internal rotation around the S−O bond in $CCl_3SOC(O)CH_3$ at the HF/6-31G* and B3LYP/6-31G* levels. The curve of B3LYP/6-31G* level is shifted by 2 kcal/mol.

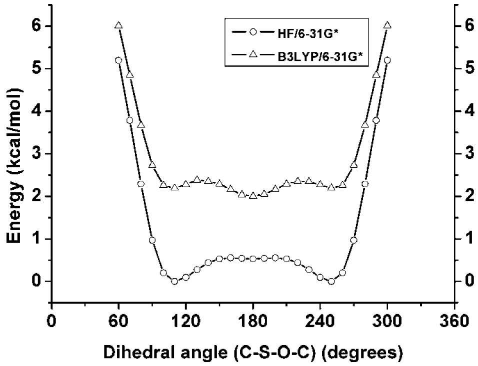

Figure 3. Calculated potential curves for internal rotation around the S−O bond in $CCl_3SOC(O)CF_3$ at the HF/6-31G* and B3LYP/6-31G* levels. The curve of B3LYP/6-31G* level is shifted by 2 kcal/mol.

higher (0.18 kcal/mol) than the gauche conformer. However, when the level of B3LYP/6-31G* is used, energy of the trans conformer is 0.31 kcal/mol lower than the gauche conformer. The situation of $CCl_3SOC(O)CF_3$ in Figure 3 is similar, which also shows that a trans conformer may exist. At the level of HF/6-31G*, the energy of the trans conformer is 0.53 kcal/mol higher than gauche conformer, while at B3LYP/6-31G* level, the energy of trans conformer is 0.19 kcal/mol lower. The energy differences are very small, so both the gauche and trans conformers may exist in the gas phase of the title compounds.

When considering the relative orientation of C═O and S−O bond, another two conformers with C═O anti of S−O bond should be taken into account. Only the gauche conformers with C═O anti of S−O bonds were found to be stable conformers of $CCl_3SOC(O)CH_3$ and $CCl_3SOC(O)CF_3$ by calculations, whose structures were also shown in Figure 1. All the three stationary points of each compound (Figure 1) were verified as local minima by vibrational analysis. After optimization, the relative Gibbs free energies calculated at 298 K for the conformers of $CCl_3SOC(O)CH_3$ and $CCl_3SOC(O)CF_3$ with different levels of theory are listed in Table 1. From Table 1 we can see, for both molecules, the differences of Gibbs free energy between the corresponding gauche−syn conformer and trans−syn conformer are less than 1.6 kcal/mol at all the theoretical levels. So both the gauche−syn and trans−syn conformers may exist in the gas phase, which is similar to the situation of $CF_3SOC(O)CH_3$ and $CF_3SOC(O)CF_3$. Our discussion of the geometry and electronic structure mainly focuses on the gauche−syn conformer of the title molecules. The optimized geometric parameters for the gauche−syn conformers of $CCl_3SOC(O)CH_3$ and $CCl_3SOC(O)CF_3$ are given in Supporting Information.

TABLE 1: Calculated Relative Gibbs Free Energies[a] (kcal/mol, $T = 298$ K) of Different Conformers of $CCl_3SOC(O)CH_3$ and $CCl_3SOC(O)CF_3$

	HF/ 6-31+G*	B3PW91/ 6-31+G*	B3LYP/ 6-31+G*	B3LYP/ 6-311+G(3df)
$CCl_3SOC(O)CH_3$				
gauche−syn	0	0	0	0
gauche−anti	6.79	5.16	5.22	4.46
trans−syn	0.45	−0.13	−0.01	0.31
$CCl_3SOC(O)CF_3$				
gauche−syn	0	0	0	0
gauche−anti	8.19	6.78	6.40	5.93
trans−syn	0.44	1.54	1.54	−0.94

[a] Includes different multiplicities ($m = 1$ for trans and $m = 2$ for gauche).

TABLE 2: S−O Bond Lengths and Dihedral Angles $\delta_{RSOR'}$ in Known Thioperoxides[a]

RSOR′	r_{SO}	$\delta_{RSOR'}$	method
HSOH[12]	1.662	91.3	CCSD(T)/cc-pCVQZ
$FSOCF_3$[22]	1.574	81.9	SINDO1
CH_3SOH[14]	1.658(2)	93.9(1)	microwave spectroscopy
CF_3SOCF_3[23]	1.677	105.0	B3LYP/ 6-311++G(3df,3pd)
$CF_3SOC(O)CH_3$[6]	1.659(4)	100(4)	GED
$CF_3SOC(O)CF_3$[6]	1.663(5)	101(3)	GED
$CCl_3SOC(O)CH_3$[b]	1.675	107.0	B3LYP/6-311+G(3df)
$CCl_3SOC(O)CF_3$[b]	1.694	108.5	B3LYP/6-311+G(3df)
CH_3OSOCH_3[15]	1.625(2)	84(3)	GED
$CH_3OSSOCH_3$[9]	1.653(3)	74(3)	GED
$FC(O)SOC(O)CF_3$[17]	1.647(5)	75(3)	GED
$CF_3C(O)SOC(O)CF_3$[16]	*c*	77	B3LYP/6-31G*
$CF_3C(O)OSSOC(O)CF_3$[11]	1.755	91.8	B3LYP/6-311G*

[a] Distances in Å, angles in deg. [b] This work. [c] No data available.

S−O bond lengths r_{SO} and dihedral angles $\delta_{RSOR'}$ of known thioperoxides RSOR′ are summarized in Table 2. The calculated S−O bond lengths of $CCl_3SOC(O)CH_3$ and $CCl_3SOC(O)CF_3$ are 1.675 and 1.694 Å (B3LYP/6-311+G(3df)), respectively, which are longer than most of the thioperoxides listed in Table 2. Oberhammer et al. suggested a simple electrostatic model to rationalize qualitatively of the trends of S−O bond length in thioperoxides.[6] The S−O bond in these molecules is expected to be highly polar, S^+-O^-. If the electronegativity of substitute R at S atom increases, the polarity of the bond is increased and the bond shortens. So the S−O bond in $CCl_3SOC(O)CH_3$ and $CCl_3SOC(O)CF_3$ are longer than those in $CF_3SOC(O)CH_3$ and $CF_3SOC(O)CF_3$, respectively. If the electronegativity of substitute R′ at O atom increases, the polarity of the bond is decreased and the bond lengthens. This explains the trend between $CF_3SOC(O)CH_3$ (1.659(4) Å) and $CF_3SOC(O)CF_3$ (1.663(5) Å), and $CCl_3SOC(O)CH_3$ (1.675 Å) and $CCl_3SOC(O)CF_3$ (1.694 Å).

Besides S−O bond length, another important structural parameter for thioperoxides is the dihedral angle of $\delta_{RSOR'}$, which can influence the overall structure of the molecules greatly. Because of the lone pair−lone pair interactions between S and O atoms, thioperoxides adopt gauche conformation as the most stable structure. In general, when the substitutes R and R′ are larger, the dihedral angle of $\delta_{RSOR'}$ tends to increase. For example, when the moiety of CF_3 in $CF_3SOC(O)CH_3$ is replaced by CCl_3, the dihedral angle changes from 100(4)° to 107.0°. This could be illustrated by the steric effect of the moieties.

Photoelectron Spectrum of CCl_3SCl. CCl_3SCl is a remarkable compound for synthesis of its derivatives for a long period.[24−26] Its infrared and Raman spectra were thoroughly

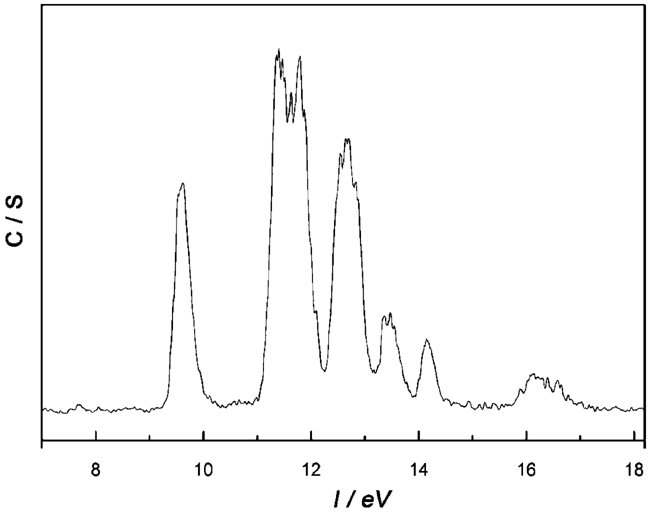

Figure 4. HeI photoelectron spectrum of CCl_3SCl.

TABLE 3: Experimental Vertical Ionization Energies (IP in eV), Computed Vertical Ionization Energies (E_v in eV) by OVGF/6-31G* Calculations, and Molecular Orbital Characters for Trichloromathanesulfenyl Chloride, CCl_3SCl

exptl IP	calcd E_v[a]	MO	character
9.61	9.64 (0.91)	45	n_S, n_{Cl}
11.33	11.29 (0.90)	44	n_{Cl}
	11.50 (0.90)	43	σ_{CS}, n_{Cl}
11.62	11.66 (0.90)	42	n_{Cl}
11.78	11.69 (0.90)	41	n_{Cl}
12.63	12.36 (0.90)	40	$n_{Cl(CCl3)}$, $n_{Cl(SCl)}$
	12.51 (0.90)	39	n_{Cl}
	12.65 (0.90)	38	n_{Cl}
13.36	13.16 (0.89)	37	n_{Cl}
14.10	13.94 (0.89)	36	σ_{SCl}
16.13	16.27 (0.88)	35	σ_{CCl}

[a] Pole strength in parentheses.

investigated and a point group of C_1 was proposed.[27] However, there was no photoelectron spectroscopy investigation before. So in the present study, the photoelectron spectrum of CCl_3SCl was measured before its reactions. The HeI photoelectron spectrum of the precursor, CCl_3SCl, is shown in Figure 4. OVGF calculations were performed to obtain the ionization energies for assigning the spectrum of CCl_3SCl. The experimental vertical ionization potentials, theoretical vertical ionization energies (OVGF/6-31G*), molecular orbitals (MO), and corresponding characters of outer valence shells for CCl_3SCl are listed in Table 3. Drawings of the first 12 HOMOs for CCl_3SCl are given in Supporting Information.

As seen from Figure 4, the HeI photoelectron spectrum of CCl_3SCl exhibits several ionization bands in the low-energy region (<14.5 eV). The experimental values are in good agreement with the calculated ionization energies with OVGF method. The first band, which centered at 9.61 eV, is mainly due to the ionization of electron from sulfur lone pair n_S, and partly from n_{Cl} of SCl moiety. The n_S lone pair is easier to be ionized in the molecule of CCl_3SCl, which is similar to other sulfur(II)-containing compounds, such as H_2S (10.48 eV), CH_3SH (9.46 eV), CH_3CH_2SH (9.36 eV), and CH_3SCH_3 (8.72 eV).[28] In all these molecules, the ionization of n_S lone pair results in the first ionization energies. The second band is localized at 11.33 eV, while the corresponding results of calculation show two very close values of 11.30 and 11.49 eV. The photoelectron spectrum shows only one band by experimental measurement. This band is caused by n_{Cl} from both CCl_3 moiety and SCl moiety. In the photoelectron spectrum of CCl_3CCl_3, the first ionization energy caused by n_{Cl} is 11.22 eV,[28] which is very close to the experimental value of CCl_3SCl at 11.33 eV. As to the third band of 11.62 eV, it is also close to the fourth one of 11.78 eV, both of which are due to the ionization of chlorine lone pair at the moiety of CCl_3. The ionization energy of 3p electron at nonbonding orbitals of Cl atoms are expected to be in the range of 11−14 eV. The ionization energies discussed above, which are caused by the ionization of n_{Cl}, are all within this range. The fifth band of the photoelectron spectrum of CCl_3SCl is probably also caused by the ionization of 3p electron from nonbonding orbitals of different Cl atoms in the molecule. The bands at higher energy of 13.36 and 14.10 eV are due to the ionization of electron from Cl atom at SCl moiety and the bonding orbital of S−Cl bond, respectively.

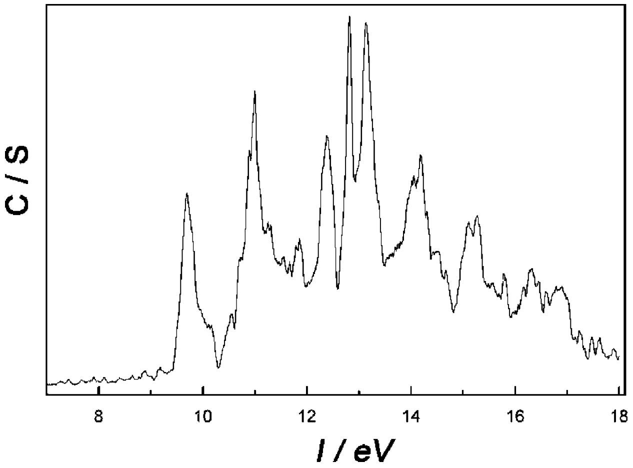

Figure 5. HeI photoelectron spectrum of $CCl_3SOC(O)CH_3$.

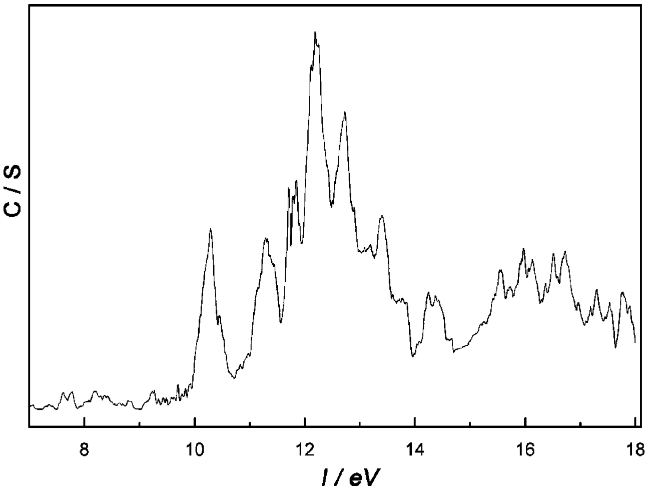

Figure 6. HeI photoelectron spectrum of $CCl_3SOC(O)CF_3$.

Photoelectron Spectra of $CCl_3SOC(O)CH_3$ and $CCl_3SOC(O)CF_3$. Before assigning the spectra, OVGF calculations were carried out to obtain the ionization energies for the theoretically stable conformers of $CCl_3SOC(O)CH_3$ and $CCl_3SOC(O)CF_3$ (the three conformers of $CCl_3SOC(O)CF_3$ are shown in Figure 1). The optimized structures (B3LYP/6-311+G(3df)) are used to perform OVGF calculations, and the ionization energies of the six conformers are given in the Supporting Information. Our discussion of the electronic structures and photoelectron spectra are based on the gauche conformers with C=O syn to S−O bond. The HeI photoelectron spectra of $CCl_3SOC(O)CH_3$ and $CCl_3SOC(O)CF_3$ are shown in Figures 5 and 6, respectively. The experimental vertical ionization potentials, theoretical vertical ionization energies (OVGF/6-31G), molecular orbitals,

TABLE 4: Experimental Vertical Ionization Energies (IP in eV), Computed Vertical Ionization Energies (E_v in eV) by OVGF/6-31G Calculations, and Molecular Orbital Characters for the Gauche−Syn Conformer of $\mathrm{CCl_3SOC(O)CH_3}$

exptl IP	calcd E_v[a]	MO	character
9.67	9.57 (0.91)	52	n_S
10.99	11.01 (0.90)	51	n_Cl
	11.02 (0.92)	50	n_O
	11.06 (0.91)	49	σ_CS, n_Cl
11.77	11.45 (0.92)	48	n_Cl
	11.52 (0.91)	47	n_Cl
12.38	12.22 (0.91)	46	n_Cl, π_CO
	12.37 (0.91)	45	n_Cl, n_O
12.78	12.54 (0.90)	44	n_Cl
13.15	13.22 (0.90)	43	σ_SO
14.18	14.17 (0.91)	42	π_CH3

[a] Pole strength in parentheses.

TABLE 5: Experimental Vertical Ionization Energies (IP in eV), Computed Vertical Ionization Energies (E_v in eV) by OVGF/6-31G Calculations, and Molecular Orbital Characters for the Gauche−Syn Conformer of $\mathrm{CCl_3SOC(O)CF_3}$

exptl IP	calcd E_v[a]	MO	character
10.34	10.34 (0.92)	64	n_S
11.32	11.42 (0.92)	63	n_Cl
11.73	11.66 (0.92)	62	n_Cl, σ_CS
11.90	11.93 (0.92)	61	n_Cl
	11.95 (0.92)	60	n_Cl
12.26	12.25 (0.90)	59	n_O
12.63	12.68 (0.91)	58	n_Cl
	12.72 (0.91)	57	n_Cl
13.41	13.39 (0.89)	56	n_O, π_CO
14.26	14.27 (0.90)	55	σ_SO

[a] Pole strength in parentheses.

and corresponding characters of outer valence shells for the gauche−syn conformers of $\mathrm{CCl_3SOC(O)CH_3}$ and $\mathrm{CCl_3SOC(O)CF_3}$ are listed in Table 4 and 5, respectively.

Drawings of the first 12 HOMOs for $\mathrm{CCl_3SOC(O)CH_3}$ is given in Supporting Information. As for the photoelectron spectrum of $\mathrm{CCl_3SOC(O)CH_3}$, the ionization energies of different bands are in good agreement with the calculated values derived from OVGF method. The molecular orbitals associated with each ionization band are assigned according to their atomic and bonding characters. It is well-known that ionization of lone pair electrons always leads to a sharp peak and results in lower ionization potentials. The band with longer vibrational progressions should be related to ionization of antibonding or bonding orbital electrons, and the broad band without vibrational fine structure should usually be attributed to ionization of stronger antibonding or bonding orbital electrons.

The first sharp band of $\mathrm{CCl_3SOC(O)CH_3}$, which located at 9.67 eV, is attributed to the ionization of the lone pair electron of S atom. It is similar to its precursor, $\mathrm{CCl_3SCl}$, of which the first ionization energy (9.61 eV) also comes from the ionization of n_S lone pair. However, the first vertical ionization energy of $\mathrm{CCl_3SOC(O)CH_3}$ is slightly (0.06 eV) bigger than $\mathrm{CCl_3SCl}$ as determined by photoelectron spectrum. According to the results of theoretical calculations, the second band (10.99 eV) with high intensity is composed of three possible peaks, which could not be clearly distinguished on account of the resolution of the instrument. With the aid of OVGF calculations (Table 4), the second band could be attributed to the ionization processes of $\{51\mathrm{a}(n_\mathrm{Cl})\}^{-1}$, $\{50\mathrm{a}(n_\mathrm{O})\}^{-1}$, and $\{49\mathrm{a}(\sigma_\mathrm{CS}, n_\mathrm{Cl})\}^{-1}$. The third band at 11.77 eV is due to the ionization of an electron from a 3p nonbonding orbital of Cl atom in $\mathrm{CCl_3}$ moiety. The band at 12.38 eV comes from the ionization processes of $\{46\mathrm{a}(n_\mathrm{Cl}, \pi_\mathrm{CO})\}^{-1}$ and $\{45\mathrm{a}(n_\mathrm{Cl}, n_\mathrm{O})\}^{-1}$. The $\mathrm{CCl_3}$ group in $\mathrm{CCl_3SOC(O)CH_3}$ is a characteristic functional group, and some observed photoelectron bands have come from the ionization of n_Cl electron of $\mathrm{CCl_3}$. The sharp band centered at 12.78 eV is definitely coming from the ionization of chloride lone pair electron, and the ionization energy of electron from the σ bond of S−O is 13.15 eV. These two bands could be clearly distinguished, although the energy difference between them is relatively small. As for the band at 14.18 eV, it could be attributed to ionization of electron from the pseudo π orbital of the methyl group.[28,29] The bands in high ionization energy region (>15 eV) are not attributed because the ionization processes are more complicated and the spectrum is not as clearly as in low-energy region.

The similar analysis can be used to the assignment of the HeI photoelectron spectrum of $\mathrm{CCl_3SOC(O)CF_3}$. Drawings of the first 12 HOMOs for $\mathrm{CCl_3SOC(O)CF_3}$ is given in Supporting Information. Combined with theoretical calculations, the assignment of the bands in the photoelectron spectrum of $\mathrm{CCl_3SOC(O)CF_3}$ could be easily done. Similar to $\mathrm{CCl_3SOC(O)CH_3}$, the first ionization energy of $\mathrm{CCl_3SOC(O)CF_3}$ (10.34 eV) is also caused by the ionization of lone pair electron of S atom. However, when $\mathrm{CH_3}$ moiety in $\mathrm{CCl_3SOC(O)CH_3}$ is replaced by $\mathrm{CF_3}$ moiety, the first ionization energy increases 0.67 eV, which means that the lone pair electron of S atom tends to be more difficult to ionize in $\mathrm{CCl_3SOC(O)CF_3}$. This is probably caused by the electron-withdrawing effect of the $\mathrm{CF_3}$ moiety with high electronegativity. From Table 5, we can see the experimental vertical ionization energies, and the calculated values agree very well. As for the second band at 11.32 eV, it could be attributed to the ionization of an electron from a 3p nonbonding molecular orbital of the $\mathrm{CCl_3}$ moiety. The third band is composed of two overlapping peaks (11.73 and 11.90 eV), which is caused by the ionization processes of $\{62\mathrm{a}(n_\mathrm{Cl}, \sigma_\mathrm{CS})\}^{-1}$, $\{61\mathrm{a}(n_\mathrm{Cl})\}^{-1}$, and $\{60\mathrm{a}(n_\mathrm{Cl})\}^{-1}$. The strongest peak of 12.26 eV can be attributed to the ionization of nonbonding electron $n_{\mathrm{O(C{=}O)}}$. The ionization energy from $n_{\mathrm{O(C{=}O)}}$ is quite different from $\mathrm{CCl_3SOC(O)CH_3}$ (10.99 eV). The $\mathrm{CF_3}$ moiety has very high electronegativity, the electron of $n_{\mathrm{O(C{=}O)}}$ tends to be more difficult to ionize in $\mathrm{CCl_3SOC(O)CF_3}$. The peak centered at 12.63 eV comes from the 3p nonbonding electron ionization of Cl atom at $\mathrm{CCl_3}$ moiety. The peak at 13.41 eV could be attributed to the electron ionization of n_O at S−O bond, together with the π bonding electron of C═O bond. The ionization energy of electron from σ_SO is 14.26 eV in $\mathrm{CCl_3SOC(O)CF_3}$, which is 1.11 eV higher than in $\mathrm{CCl_3SOC(O)CH_3}$ (13.15 eV). The change of substituent brings an obvious difference to the ionization energy of electron from σ_SO. The ionization energies of $\mathrm{CCl_3SOC(O)CF_3}$ at the high-energy region have not been attributed.

In a word, the outer molecular orbital structure of $\mathrm{CCl_3SOC(O)CH_3}$ and $\mathrm{CCl_3SOC(O)CF_3}$ are investigated combined with photoelectron spectroscopy and quantum chemical calculations for the first time. The nonbonding electron from Cl atom and the lone pair electron of S atom lead to many typical characters of the photoelectron spectra of both compounds. In the corresponding gauche−syn conformers, the dihedral angles $\delta_{\mathrm{RSOR}'}$ of $\mathrm{CCl_3SOC(O)CH_3}$ and $\mathrm{CCl_3SOC(O)CF_3}$ are theoretically determined to be 107.0° and 108.5° (B3LYP/6-311+G(3df)), respectively.

Conclusion

The compounds of $\mathrm{CCl_3SOC(O)CH_3}$ and $\mathrm{CCl_3SOC(O)CF_3}$ are generated in situ in the gas phase for the first time. The geometry of both molecules is optimized with DFT and ab initio methods. The gaseous products are detected and characterized by HeI photoelectron spectroscopy with the help of OVGF calculations. The combination of experimental and theoretical results proves the formation of $CCl_3SOC(O)CH_3$ and $CCl_3SOC(O)CF_3$. The dihedral angles δ_{CSOC} of the gauche−syn conformers are given in this work by theoretical calculations. The first ionization energies of $CCl_3SOC(O)CH_3$ and $CCl_3SOC(O)CF_3$ are determined to be 9.67 and 10.34 eV, respectively. The first HOMOs correspond to the electron mainly localized on the sulfur lone pair MOs: $\{52a(n_S)\}^{-1}$ and $\{64a(n_S)\}^{-1}$ for $CCl_3SOC(O)CH_3$ and $CCl_3SOC(O)CF_3$, respectively.

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Supporting Information Available: Optimized geometrical parameters for the gauche−syn conformers of $CCl_3SOC(O)CH_3$ and $CCl_3SOC(O)CF_3$; theoretical ionization energies for the six conformers of $CCl_3SOC(O)CH_3$ and $CCl_3SOC(O)CF_3$ by OVGF calculations; drawings of the first twelve HOMOs for CCl_3SCl, the gauche−syn conformers of $CCl_3SOC(O)CH_3$ and $CCl_3SOC(O)CF_3$, respectively. This material is available free of charge via the Internet at http://pubs.acs.org.

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