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doi: 10.3866/PKU.WHXB201410311

www.whxb.pku.edu.cn

FC(O)SNCO 的电子结构和光电离解离过程

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摘要: 由于拥有一C(O)S—和一NCO基团, FC(O)SNCO的分子和电子结构是非常有趣的. 利用FC(O)SCI和AgNCO制备了FC(O)SNCO, 并利用HeI光电子能谱(PES)、光电离质谱(PIMS)以及理论计算研究了其分子和电子结构. 通过将实验、理论计算以及自然键轨道(NBO)分析结合起来, 获得了FC(O)SNCO的最稳定分子构型. 利用外壳层格林函数(OVGF)方法以及与相似化合物的比较, 对其光电子能谱进行了指认. 理论计算表明, 对于中性分子最稳定的构型为syn-syn非平面构型, 而电离后的离子最稳定构型为syn-syn平面构型. 实验结果表明, 第一电离能来自于S的孤对电子轨道, 为10.33 eV. 第二至第六电离能分别为12.03、13.23、13.77、14.78、15.99 eV, 并对这些电离能进行了指认. 在光电离质谱中产生了六个质谱峰, 分别为SN⁺、FC(O)⁺、SNCO⁺、FC(O)SN⁺、C(O)SNCO⁺、FC(O)SNCO⁺, 其中FC(O)SNCO⁺的峰是最强峰. 结合HeI光电子能谱和理论计算, 对PIMS进行了分析, 并研究了可能的电离和解离过程并对其进行了讨论.

关键词: 结构; HeI光电子能谱; 光电离质谱; 理论计算; 电离和解离过程

中图分类号: O641

Electronic Structure and Photoionization Dissociation Process of FC(O)SNCO

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Abstract: (Fluorocarbonyl) sulfenyl isocyanate (FC(O)SNCO) contains —C(O)S— and —NCO groups, so has an interesting electronic and molecular structure. FC(O)SNCO was prepared by the metathesis of FC(O)SCI and AgNCO. HeI photoelectron spectroscopy (PES), photoionization mass spectrometry (PIMS), and theoretical calculations were used to study the molecular and electronic structure of FC(O)SNCO. The experimental, theoretical calculations, and NBO results indicated the most stable conformer of FC(O)SNCO. In addition to the outer-valence Green's function calculation, the PES spectrum was assigned from analogous studies of similar molecules. The syn-syn non-planar conformer ($\delta_{\text{FCSN}}=180^\circ$) with C_1 symmetry was favored by the neutral molecule, and changed to the syn-syn planar structure with C_s symmetry after ionization. The experimental first vertical ionization potential mainly from the S lone pair orbital was 10.33 eV. The second to sixth ionization potentials of FC(O)SNCO were 12.44, 13.23, 13.77, 14.78, and 15.99 eV, respectively, and were also assigned. The FC(O)⁺, SN⁺, FC(O)SN⁺, SNCO⁺, C(O)SNCO⁺, and FC(O)SNCO⁺ peaks were observed in the PIMS spectrum, the highest intensity of which was FC(O)SNCO⁺. The PIMS data were analyzed based

Received: September 3, 2014; Revised: October 30, 2014; Published on Web: October 31, 2014.

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The project was supported by the Strategic Priority Research Program (B) of the Chinese Academy of Sciences (XDB05010400), National Natural Science Foundation of China (41105085, 21073051), and Natural Science Foundation of Hebei Province, China (B2010000368)

中国科学院战略性先导专项B (XDB05010400), 国家自然科学基金(41105085, 21073051)及河北省自然科学基金(B2010000368)资助项目

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on the PES and theoretical results. Possible ionization and dissociation processes are discussed.

Key Words: Structure; HeI photoelectron spectroscopy; Photoionization mass spectroscopy; Theoretical calculation; Ionization and dissociation processes

1 Introduction

A wide series of studies on thiol ester compounds have been carried out because of their close relation to many biomolecules. For instance, acetyl CoA, is well known as a biological acetylating reagent, leading to a reductive scission of the S—S linkage of 6,8-thioctic acid to form a dithiol.¹ It is also of great importance in biochemistry as a condensing agent. Due to the important role against free radicals, the S-acyl-CoA and reduced glutathione GSH are also seen as important intermediates in the metabolism of acidic drugs. Some thiol esters also represent as latent medicine which can be reactivated through hydrolysis.² Needless to say, at present it is difficult to explain all the biological activity distinctly. Some significant aspects of them, however, may be examined by the investigation of simple model compounds, such as sulfenyl carbonyl compounds, XC(O)SY (X, Y: halogen). XC(O)SY compounds containing —C(O)S— are an interesting family of many theoretical and experimental investigations. Haas and Reinke³ reported the preparation of the first such compound in 1966, namely ClC(O)SCl. Since then, several other members of this type of compounds have been characterized, e.g., FC(O)SCl,⁴⁻⁷ FC(O)SBr,⁸⁻¹⁰ and ClC(O)SBr.^{10,11} Recently, the X, Y in XC(O)SY represent not only halogen but also pseudohalogen and other substituent groups, e.g., FC(O)SSCN,¹² CH₃OC(O)SNCO,¹³ FC(O)SOC(O)CH₃¹⁴ and so on. The essentially planar nature of the XC(O)SY skeleton gives rise to syn and anti conformational options. Gas electron diffraction,⁴ vibrational analysis,⁵ and calculations⁶ demonstrated that FC(O)SCl exists as a mixture of two planar forms with the energy of anti conformation (C=O bond anti with respect to the S—Cl bond) being higher than that of the syn conformer. In all the reported cases, the syn conformation represents the most stable structure.^{8,10,15}

Isocyanates as one of the pseudohalide derivatives are important precursors in the synthesis of polymer materials.¹⁶ The production is based on a nucleophilic addition reaction which takes place *via* the nucleophile's attack on the carbon of the NCO group. The synthetic procedure gives high yields and exhibits no side reactions. Pseudohalides are examples of distorted linear triatomic systems. It was difficult to predict the conformational stability of simple isocyanates and may also be different in different aggregation states. Several studies have been carried out on the conformational and spectroscopic properties of organoisocyanate molecules. For example, in methoxycarbonylsulfenyl isocyanate, CH₃OC(O)SNCO,¹³ the C=O double bond syn-periplanar with respect to the S—N single bond was the most stable form, which confirmed by Fourier transform infrared (FTIR) spectroscopy, ultraviolet visible (UV-Vis) spectroscopy, X-ray diffraction (XRD), Raman spectroscopy, and theoretical calculations. Gas-phase electron diffraction (GED), microwave,

calculations, and vibrational analysis were used to study the conformational and structural properties of acetylisocyanate CH₃C(O)NCO,¹⁷ all results predicted that in the gas phase and ambient temperature the *cis* conformer (isocyanate group *cis* to the carbonyl bond) was more stable than the *trans* conformer. The studies on conformational properties of CCl₃C(O)NCO were close to those of CH₃C(O)NCO.¹⁸ In the liquid phases the *cis* conformer was more stable than the *trans* conformer indicated by Raman and IR studies, while only the *cis* conformer was present for CF₃C(O)NCO in the solid phase.¹⁹

(Fluorocarbonyl) sulfenyl isocyanate, FC(O)SNCO, is a very meaningful molecule, which is one of the examples of the XC(O)SY compounds including isocyanate (NCO) group. The conformation of the gaseous FC(O)SNCO has been studied by GED, FTIR, and quantum chemical calculation.²⁰ In addition, the vibrational analysis and matrix-photochemical study have been reported.²¹ However, the electronic structure of FC(O)SNCO has never been studied. Our group has a long-term concern with the generation and electronic structures of unstable molecules.^{22,23} The HeI photoelectron spectroscopy (PES), together with theoretical calculation will play an important role in studying electronic structures of compounds. Comparing with the structure investigations, the electronic structures of these unstable molecules can be studied. In this work, the HeI photoelectron spectrum and photoionization mass spectrum (PIMS) of FC(O)SNCO were first reported. The electronic structure of the compound was analyzed based on the HeI photoelectron spectrum in combining with theoretical calculation and photoionization mass spectroscopy.

2 Experimental

2.1 Sample preparation

In the preparation of isocyanates, silver isocyanate (AgOCN, Alfa, >97%) was found to be a perfect precursor.²⁴ In this work, FC(O)SNCO was prepared by substitution reaction of FC(O)SCl and AgOCN at -80 °C for 12 h according to literature.²⁵ The reaction route was illustrated as below:

The reactant FC(O)SCl was prepared by ClC(O)SCl (97%, Alfa Aesar) and TIF (99%, Acrod, USA) referring to the previous report,²⁶ and its potential energy (PE) and IR spectra were identical to the reports previously.²⁷ AgOCN was all purchased from Alfa Aesar Company. Before reaction, AgOCN was dried for 2 h in vacuum (1.33×10^{-6} Pa). The IR spectrum of gaseous FC(O)SNCO was also obtained. Compared with the reported IR spectroscopy, it was verified that the synthetic compound was FC(O)SNCO.²¹

2.2 Instruments

A double-chamber UPS-II instrument was used to record the photoelectron spectrum as reported before.^{28,29} The instrument was specially designed to detect unstable species. A little of Ar gas and CH₃I were acceded to the sample flow tube to calibrate the experimental vertical ionization potentials during the experiments. The spectral resolution of HeI spectrum was about 30 meV. The mass spectrum was recorded by a time-of-flight mass spectrometer and mounted directly to the double-chamber UPS-II instrument. The soft ionization was supplied by single wavelength HeI radiation. The instrument was represented in detail in the previous paper.²⁹ Under identical conditions the photoelectron and photoionization mass spectra can be recorded within seconds of each other.

2.3 Theoretical computation

The geometry of the neutral ground state was optimized using MP2/6-311++G(*d,p*) and B3LYP/6-311++G(*d,p*). Harmonic vibrational frequencies were also calculated to check whether the optimized structure was a stationary point or a saddle point. The potential functions for internal rotation around the C—S were performed to search for other possible formers of FC(O)SNCO at the MP2/6-311++G(*d,p*), B3LYP/6-311++G(*d,p*), and HF/6-311++G(*d,p*) levels. At the B3LYP/6-311++G(3*df*,3*pd*) level, the natural bond orbital (NBO) calculations were calculated. To assign the photoelectron spectrum, the out-valence Green's function (OVGF) calculation, which included sophisticated correlation effects of the self-energy, was applied to the most stable conformers of FC(O)SNCO to give accurate results of the vertical ionization energies. Gaussian 03 program was used for calculations.³⁰ Three-dimensional molecular orbital (MO) plots were obtained with the Gauss View program, and each orbital displayed with the 0.06 isodensity value was oriented in a way that allowed for the best view. The Mulliken population analysis was applied to assign the charges for both neutral and cationic-radical forms.

3 Results and discussion

3.1 Molecular structure

In order to seek other possible conformers of FC(O)SNCO, the potential functions for internal rotation around the C—S were performed by rotating the torsional dihedral angle (δ_{FCSN}) in steps of 10° ranging from 0° to 360° at the MP2/6-311++G(*d,p*), B3LYP/6-311++G(*d,p*), and HF/6-311++G(*d,p*) levels (Fig.1). All these methods predicted that the syn-syn structure ($\delta_{\text{FCSN}}=180^\circ$) was the global minimum form. At the same time, a second minimum was anti-anti structure ($\delta_{\text{FCSN}}=0^\circ$). The structural optimization and vibrational analysis indicated that the syn-syn and anti-anti conformers of FC(O)SNCO were stable, which were shown in Fig.2. Relative Gibbs free energies (ΔG) for the two stable conformers of FC(O)SNCO at 298 K after optimization were calculated. The second stable form was anti-anti former with the energy gaps of 8.00, 7.29, and 10.84 kJ·mol⁻¹ based at the HF/6-311++G(*d,p*), B3LYP/6-311++G(*d,p*), and MP2/6-311++G(*d,p*) levels, respectively. All the computational methods predicted that the syn-syn conformer was the most stable. This can be explained by the sulfur lone-pair and steric interactions between FC(O) and

Fig.1 Relative energies of FC(O)SNCO with different dihedral angles (δ_{FCSN}) calculated at the HF/6-311++G(*d,p*), B3LYP/6-311++G(*d,p*), and MP2/6-311++G(*d,p*) levels

Fig.2 Schematic representation of FC(O)SNCO

NCO groups.

Probably the most interesting and contrasting results uncovered by the potential energy curves shown in Fig.1 are the very different rotational barriers obtained for the two studied compounds. Computed energy barriers E_a for the syn→anti internal rotation were derived from fully optimized transition state (TS) structures at B3LYP levels of theory. The TS (Fig.3) structures were verified by an intrinsic reaction coordinate calculation to connect the conformers along the reaction path for the normal coordinate of the imaginary frequency.

To gain some deep information on the stabilities of syn-syn and anti-anti conformations of FC(O)SNCO, NBO calculations were also performed on these two conformers. The most important orbital interactions occur between the two sulfur lone pairs relevant to the conformational properties, $\text{lp}_\sigma\text{S}(2)$ and $\text{lp}_\sigma\text{S}(1)$ [lp : lone pair; the $\text{lp}_\sigma\text{S}(1)$ orbital is parallel to the $\sigma^*(\text{C1}-\text{O1})$ bond, the $\text{lp}_\sigma\text{S}(2)$ orbital is parallel to the $\pi(\text{C1}=\text{O1})$ bond]. The occupancies of $\text{lp}_\sigma\text{S}(1)$ and $\text{lp}_\sigma\text{S}(2)$ are 1.98e and 1.79e, respectively. The lower occupancy of $\text{lp}_\sigma\text{S}(2)$ indicates its strong electron-donor capacity. The strongest interactions are due to donations from $\text{lp}_\sigma\text{S}(2)$ to the

Fig.3 Optimized structures, labeling of the atoms, and relative energies of the syn, anti conformations, and rotational transition state (TS) of FC(O)SNCO molecule at the B3LYP/6-311++G(*d,p*) level

unoccupied molecular orbits $\pi^*(\text{C}1=\text{O}1)$ [$\text{lp}_s(\text{S}2) \rightarrow \pi^*(\text{C}1=\text{O}1)$] and $\pi^*(\text{N}=\text{C}2)$ [$\text{lp}_s(\text{S}2) \rightarrow \pi^*(\text{N}=\text{C}2)$]. This is evidenced by high occupancy of the two antibonding orbitals $\pi^*(\text{C}1=\text{O}1)$ ($0.27e$), anti-anti form, which contributes to stabilization of an approximate planar structure for FC(O)SNCO by resonance (mesomeric effect). As shown in Table 1, these interactions contribute similarly to stabilization energies for both the syn-syn and anti-anti forms. However, delocalization of lp_sS reveals a strong conformational dependence. In account with the anomeric effect, the $\text{lp}_s(\text{S}1) \rightarrow \sigma^*(\text{C}1-\text{O}1)$ interaction stabilized the syn-syn form by $21.87 \text{ kJ} \cdot \text{mol}^{-1}$, while the corresponding delocalization in the anti-anti form is below the threshold for printing ($2.09 \text{ kJ} \cdot \text{mol}^{-1}$). On the other hand, the syn-syn form is favored through $\text{lp}_s(\text{S}1) \rightarrow \sigma^*(\text{C}1-\text{F})$ delocalization by $11.77 \text{ kJ} \cdot \text{mol}^{-1}$. Thus, considering the electronic contributions of both lone pairs at the sulfur atom, the syn-syn form is favored by $22.73 \text{ kJ} \cdot \text{mol}^{-1}$. Similar results were reported also for other sulfenylcarbonyl molecules.³¹

In the previous work, the conformational properties of FC(O)SNCO have been investigated by gas electron diffraction,²⁰ theoretical calculation, and matrix infrared spectra.²¹ Only a syn-syn conformation (carbonyl $\text{C}=\text{O}$ syn with $\text{S}-\text{N}$ and the NCO

Table 1 NBO stabilization energies for orbital interactions associated with sulfur lone pair (lp) in FC(O)SNCO calculated at the B3LYP/6-311++G(3df,3pd) level

Item	Value	
	syn-syn	anti-anti
$\text{lp}_s(\text{S}1) \rightarrow \sigma^*(\text{C}1-\text{F})$		11.77
$\text{lp}_s(\text{S}1) \rightarrow \sigma^*(\text{C}1=\text{O}1)$	18.80	
$\text{lp}_s(\text{S}2) \rightarrow \pi^*(\text{C}1=\text{O}1)$	138.84	125.61
$\text{lp}_s(\text{S}2) \rightarrow \pi^*(\text{N}=\text{C}2)$	52.21	49.74
$\Delta E_{\text{anomer}}/(\text{kJ} \cdot \text{mol}^{-1})$	7.03	
$\Delta E_{\text{conj}}/(\text{kJ} \cdot \text{mol}^{-1})$	15.70	
$\Delta E_{\text{total}}/(\text{kJ} \cdot \text{mol}^{-1})$	22.73	

ΔE : syn-syn and anti-anti energy difference. Note that positive value contributes to stabilization of the syn-syn rotamer. ΔE_{anomer} : anomeric interaction energy difference. ΔE_{conj} : conjugation interaction energy difference. $\Delta E_{\text{total}} = \Delta E_{\text{anomer}} + \Delta E_{\text{conj}}$

group syn to $\text{C}-\text{S}$) was confirmed to be the most stable conformer at ambient temperature. The result of our theoretical calculation agreed with the previous studies. Therefore, our calculations were all based on the syn-syn conformer.

Most of the series of compound used B3LYP method, such as $\text{CH}_2=\text{CHC}(\text{O})\text{NCO}$,³² $\text{FC}(\text{O})\text{SOC}(\text{O})\text{CH}_3$,¹⁴ $\text{CH}_3\text{OC}(\text{O})\text{SCH}_3$,¹³ FCOSSCN ,¹² $\text{FC}(\text{O})\text{SCN}$,³¹ and so on. For neutral and cationic FC(O)SNCO, full geometry optimizations and frequency calculations were performed on the syn-syn conformer at the B3LYP/6-311++G(*d,p*) basis set. Table 2 compared experimental and calculation geometric parameter of FC(O)SNCO. The structure obtained by theoretical calculations was in accordance with the GED results.²⁰ Fig.2 showed the geometric parameters of the ground cationic-radical form $\text{FC}(\text{O})\text{SNCO}^+ \cdot$, which were also calculated by the B3LYP approach at the same basis set. After the vibrational analysis, the most stable conformer of the cationic-radical form was *C*_s symmetry (Fig.2).

3.2 Photoelectron spectroscopy

In combination with theoretical calculations, PES with HeI resonance source (58.4 nm) is an effective method to investigate the electronic structure of unstable compounds and free radicals.³³ By HeI photoelectron energy analysis, the valence shell structure of the molecule can be obtained, especially for investigating similar molecules.³⁴ The HeI photoelectron spectroscopy spectrum of FC(O)SNCO is presented in Fig.4. Table 3 listed the experimental ionization potentials (IP in eV) and theoretical vertical ionization energies (E_v in eV) as well as corresponding characters of each occupied molecular orbital. The OVGf pole strengths in Table 4 are all larger than 0.85, which agrees with a one-electron depiction of ionization. If the OVGf pole strengths are smaller than 0.85, OVGf approach would be unapplicable because a severe breakdown of the orbital (or one-electron) picture of ionization should be expected.³⁵ To obtain the ionization energies for FC(O)SNCO, OVGf calculations were carried out before assigning the spectrum. All the calculations were based on the

Table 2 Experimental and calculated geometric parameters for syn-syn conformer of FC(O)SNCO^a

Parameter	Value		
	neutral		cation
	GED ^b	B3LYP	B3LYP
$r_{\text{C}1-\text{S}}/\text{nm}$	0.1748(5)	0.1775	0.1907
$r_{\text{C}1-\text{O}1}/\text{nm}$	0.1187(5)	0.1181	0.1168
$r_{\text{C}1-\text{F}}/\text{nm}$	0.1333(4)	0.1353	0.1298
$r_{\text{S}-\text{N}}/\text{nm}$	0.1669(3)	0.1681	0.1598
$r_{\text{N}-\text{C}2}/\text{nm}$	0.1208(8)	0.1216	0.1248
$r_{\text{C}2-\text{O}2}/\text{nm}$	0.1167(5)	0.1162	0.1139
$\alpha_{\text{SC}1\text{O}1}/(^{\circ})$	129.5(8)	128.8	121.8
$\alpha_{\text{SC}1\text{F}}/(^{\circ})$	107.3(5)	107.4	107.8
$\alpha_{\text{O}1\text{C}1\text{F}}/(^{\circ})$	123.2(10)	123.8	130.4
$\alpha_{\text{C}1\text{SN}}/(^{\circ})$	101.6(20)	101.5	100.5
$\alpha_{\text{SC}2\text{C}2}/(^{\circ})$	127.8(14)	136.0	139.2
$\alpha_{\text{SC}2\text{O}2}/(^{\circ})$	165.9(32)	172.1	171.0
$\delta_{\text{O}1\text{C}1\text{SN}}/(^{\circ})$	0.000	2.0	0.0
$\delta_{\text{C}1\text{SNCO}}/(^{\circ})$	17(6)	-22.3	0.0

^aatom numbering shown in Fig.2; ^btaken from Ref. 27

Fig.4 Photoelectron spectroscopy of FC(O)SNCO

Table 3 Experimental vertical ionization potentials (IP^{exp}), calculated vertical ionization potentials^a (IP^{calc}) as obtained by OVGF/6-311++G** and MO characters for FC(O)SNCO

IP^{exp}/eV	IP^{calc}/eV	MO	Character ^b
10.33	10.097(0.91)	30a	n_s
12.44	12.197(0.90)	29a	n_{O_1}, π_{SNCO}
13.23	13.259(0.90)	28a	n_{O_2}, π_{SNCO}
13.77	13.448(0.90)	27a	π_{SNCO}
14.78	15.218(0.88)	26a	$n_F, \pi_{C=O}$
15.99	15.463(0.89)	25a	σ, n_F

^apole strength in parentheses; ^bmolecular orbital corresponding to the assignment of ionization energy

Table 4 Atomic charges for the neutral (syn-syn) and cationic-radical (syn-syn) conformer of FC(O)SNCO as obtained by the B3LYP/6-311++G(d,p) level

	Atomic charge ^a /e							TAC ^b /e
	C1	S	O1	F	N	C2	O2	
FC(O)SNCO	0	0.34	-0.18	-0.07	-0.26	0.38	-0.21	0
FC(O)SNCO ⁺	0.06	0.62	-0.06	0.05	-0.10	0.44	-0.01	1
Δq^c	0.06	0.28	0.12	0.12	0.16	0.06	0.20	1

^aatom numbering, shown in Fig.2; ^btotal atomic charge;

^c $\Delta q = q(FC(O)SNCO^+) - q(FC(O)SNCO)$

most stable conformer syn-syn. Fig.5 shows the characters of the some occupied molecular orbitals of FC(O)SNCO.

It can be clearly seen from Table 3, the ionization energies of different bands are in consistent with the calculated values of OVGF method. Combining with band profiles, relative band intensities, comparison with the similar compounds, and theoretical method (OVGF calculation), the bands in the photoelectron spectra can be reliable assignments. The assignment of the photoelectron spectrum of FC(O)SNCO is obtained easily, because lone pairs generally display no fine structure.

In the photoelectron spectrum, the first ionization band of FC(O)SNCO was at 10.33 eV that can be contributed to the ionization process from the highest occupied molecular orbital (HOMO) [$n_s(S)$], which can be direct-viewing as a lone pair formally localized on the sulfur atom. This is similar to FC(O)SCL, its precursor.³⁶ The first ionization energy (10.7 eV) of FC(O)SCL also is from the ionization of lone pair of the sulfur atom. For FC(O)SNCO the first vertical ionization energy is slightly lower (0.37 eV) than FC(O)SCL in photoelectron spectrum. The reason was that the highly polar S^+-O^- of the S—O

Fig.5 Characters of the occupied molecular orbitals (MOs) for FC(O)SNCO

bond in sulfenic esters RSOR'. Because the electronegativity of F is larger than that of CH_3O , it results in more electrons on S lone pair of FC(O)SNCO. The first ionization of FC(O)SNCO is higher (0.77 eV) than that of $CH_3OC(O)SNCO$ (9.56 eV).¹³ The first band of $ClC(O)SCL$ ³⁷ is located at 10.36 eV, which can be assigned to the removal of an electron from the sulfur lone pair, the highest occupied molecular orbital (HOMO).

Fig.6 shows a diagrammatic representation of the experimentally determined IPs for some molecules formally containing the sulfenylcarbonyl group,^{13,36–40} which can also be known as $-C(O)S-$ containing compounds. Taking $CH_3OC(O)SNCO$ ¹³ as a reference, it can be observed a reduction of the IP values because of the substitution of the NCO by electron-releasing alkyl groups. On the other hand, substitution of the NCO or SCN groups by more electronegative groups can lead to higher IP values.

The $-C(O)S-$ compounds previously studied had the similar first ionization potential values, which can be assigned as a lone pair formally localized on the sulfur atom (Fig.6). For instance, the ionization potential values of $CH_3OC(O)SY$ series, $ClC(O)SY$ series and $FC(O)SY$ series, the strong inductive effect of Cl atom or F atom can raise the ionization energy of sulfur lone pair orbital n_s , with respect to the $CH_3OC(O)SY$ molecules. The electronegativity of F is the strongest, and CH_3 is the weakest. So the ionization potentials of FC(O)SY compounds are higher than

Fig.6 Correlation diagram of the IPs of $-C(O)S-$ containing compounds

The ionization energies of $CH_3OC(O)SCH_3$, $CH_3OC(O)SNCO$, $CH_3OC(O)SSCN$, $ClC(O)SCH_3$, $ClC(O)SCL$, $FC(O)SCL$, $FC(O)SSCN$ are taken from Refs. 13, 36–40.

those of $\text{CH}_3\text{C}(\text{O})\text{SY}$ compounds, and $\text{ClC}(\text{O})\text{SY}$ compounds are in the middle. Meanwhile, the electronegativity of $-\text{NCO}$ is between $-\text{CH}_3$ and $-\text{SCN}$. So the first ionization energy of $\text{FC}(\text{O})\text{SNCO}$ at 10.33 eV between those of $\text{CH}_3\text{OC}(\text{O})\text{SNCO}^{13}$ and $\text{FC}(\text{O})\text{SSCN}^{12}$ is very reasonable.

However, this effect must be interpreted in terms of delocalization effects, rather than as inductive effects of the substituents. This stabilization seems to be caused by the planar $\text{XC}(\text{O})\text{S}$ moiety around the $\text{C}(\text{sp}^2)$ and is independent of the nature of X. The first IP values of two model compounds $\text{CH}_3\text{OC}(\text{O})\text{SCH}_3^{38}$ and $\text{ClC}(\text{O})\text{SCH}_3^{39}$ are 9.46 and 10.11 eV, respectively.

In order to analyze the nature of the cation formed in the first ionization process, further calculations (B3LYP/6-311+G(*d,p*)) were performed. It demonstrated that the atomic charges were a palpable fraction localized at sulfur atoms, with delocalized all over the molecule (Table 4). Table 3 summarized the optimized structural parameters of the cationic-radical form. The adiabatic potential of $\text{FC}(\text{O})\text{SNCO}$ is 9.87 eV, which was derived from the different energies between the neutral and ground cationic-radical forms at B3LYP/6-311G(*d,p*) level of theory. Further vibrational calculations were performed for the cationic-radical form, which resulted in shift (128 cm^{-1}) of the wavenumber for $\nu_{\text{C=O}}$ toward higher values, as compared to the neutral molecular, while the $\nu_{\text{C-S}}$ wavenumber exhibits a shift of 23 cm^{-1} in the opposite direction. With the interruption of the mesomeric effect and a reinforced bond character in the $\text{C}=\text{O}$ bond and decreasing in the corresponding $\text{S}-\text{C}$ bond, the picture of an electron ionization mainly localized at the S atom.

The second band of $\text{FC}(\text{O})\text{SNCO}$ at 12.44 eV in the photoelectron spectrum, which is due to the electrons ionization from the orbital 29a (Fig.5), can be assigned to the oxygen lone pair n_{O} of the carbonyl group with some admixture out-of-plane non-bonding orbital on the NCO moiety. This value is consistent with the IPs of the oxygen lone pair orbitals in the correlative species. The second band of $\text{FC}(\text{O})\text{SCI}^{35}$ is at 12.1 eV which can be contribute to the removal of an electron from the lone pair electron of oxygen atom of the carbonyl group, and is higher than that of $\text{FC}(\text{O})\text{SNCO}$ by 0.34 eV. The forth IP of $\text{FC}(\text{O})\text{SSCN}^{12}$ at 12.73 eV is mainly due to the lone pair electron of oxygen atom. In contrast to $\text{FC}(\text{O})\text{SCI}$ and $\text{FC}(\text{O})\text{SSCN}$, the third ionization band of $\text{FC}(\text{O})\text{SC}(\text{O})\text{CH}_3^{41}$ is at 11.80 eV ($n_{\text{O}(\text{FC}(\text{O}))}$). The trend showed a clear dependence on the substituents attached to the sulfur atom. Therefore, in the series of $\text{FC}(\text{O})\text{SX}$ ($\text{X}=\text{NCO}$, SCN , $\text{C}(\text{O})\text{CH}_3$) species, the $\text{FC}(\text{O})\text{SNCO}$ molecule possessed higher stabilization of the oxygen lone pair.

The bands at 13.23 and 13.77 eV can be assigned of ionization electrons on the in-plane lone pair of carbonyl oxygen $\pi_{\text{C=O}}$ and the in-plane π'_{SNCO} . The orbit π'_{SNCO} consists the the in-plane of isocyanate and in-plane lone pair of sulfur. The fifth band originates from ionizations related to the $\text{FC}(\text{O})$ moiety. Interactions between the $\pi_{\text{C=O}}$ and n_{F} localized orbitals become effective in the planar geometry of the $\text{FC}(\text{O})$ moiety. Howere, it is impossible to have this interaction in the in-plane lone-pair orbital. From the above, the band at 14.78 eV may involve $\pi_{\text{C=O}}$ and n_{F} orbitals. The related

species had the similar ionization potentials of the $\text{C}=\text{O}$ group orbitals, such as $\text{CH}_3\text{OC}(\text{O})\text{SCH}_3^{38}$ (14.18 eV), $\text{FC}(\text{O})\text{SC}(\text{O})\text{CH}_3^{41}$ (14.10 eV), $\text{FC}(\text{O})\text{SCI}^{36}$ (14.9 eV), $\text{FC}(\text{O})\text{SSCH}_3^{36}$ (14.8 eV) and $\text{FC}(\text{O})\text{SSCN}^{12}$ (14.17 eV). The $\pi_{\text{C=O}}$ orbital is destabilized by the electron donating effect and stabilized by the resonance interaction with the fluorine non-bonding orbital.

The sixth band at 15.99 eV is just ascribed to the ionization of the orbital σ and n_{F} . The band at 15.36 eV of FCOSSCN is mainly due to the lone pair electron of fluorine atom. The corresponding bands in propynoyl fluoride and formyl fluoride were at 15.4 and 15.5 eV,¹² respectively, which exhibited remarkably similar shapes. The band at higher ionization region ($>16.00\text{ eV}$) can be attributed to the ionization of σ orbital, and can be attributed to the ionization of inner orbital of $\text{FC}(\text{O})\text{SNCO}$, which may be difficult to assign certainly.

3.3 Photoelectron mass spectrometry

The PIMS spectroscopy is depicted in Fig.7. Combining the PES and the theoretical results, the PIMS results can be analyzed. The assignments mainly depended on the mass number of the fragments. It shows six peaks: SN^+ ($m/z=46$), $\text{FC}(\text{O})^+$ ($m/z=47$), FCOSN^+ ($m/z=93$), $\text{C}(\text{O})\text{SNCO}^+$ ($m/z=102$), SCNO^+ ($m/z=74$) and the parent molecular ion $\text{M}^{+\bullet}$, among which the dominant features was the parent molecular ion $\text{M}^{+\bullet}$ peaks.

The energies of the identified fragments and the adiabatic ionization of $\text{FC}(\text{O})\text{SNCO}$ were computed, to confirm the level of electronic structure theory which is used in the energetics calculation of dissociation pathways. Table 5 shows the experimentally measured values and the calculated results. The experimental ionization energy data of the $\text{FC}(\text{O})\text{S}$, SNCO , $\text{C}(\text{O})\text{SNCO}$, and $\text{FC}(\text{O})\text{SN}$ radicals are not available. Since the experimental ionization energies are in very good agreement with the calculated ionization energies of the other fragments, the calculated ionization energies for these radicals can be used to estimate the actual values. Theoretical calculation was performed to estimate the energies of the dissociation pathway. These ionization energies are necessary to construct the energy diagrams of different pathways for the ionic dissociation of the parent ion shown in Fig.8.

3.4 Dissociation of fluorocarbonyl sulfenyl isocyanate

Fig.7 PIMS spectrum of $\text{FC}(\text{O})\text{SNCO}$

Table 5 Calculated and experimental ionization potentials of FC(O)SNCO and its fragments

Molecule	Energy/hartree	IP/eV	
		calcd. ^a	expt.
FC(O)SNCO	-779.542399	9.87	9.85 ^b
FC(O)SNCO ⁺	-779.179679		
FC(O)•	-213.161374	9.66	9.30±0.10 ⁴²
FC(O) ⁺	-212.806439		
FC(O)S•	-611.408511	11.27	—
FC(O)S ⁺	-610.994317		
SNCO•	-566.283010	10.13	—
SNCO ⁺	-565.910710		
NCO•	-168.044804	11.90	11.76±0.01 ⁴³
NCO ⁺	-167.546371		
SCO•	-511.590978	11.23	11.22 ⁴⁴
SCO ⁺	-511.178217		
CO•	-113.344011	14.20	14.1 ⁴⁵
CO ⁺	-112.822266		
C(O)SNCO•	-679.637398	8.90	—
C(O)SMCO ⁺	-679.310496		
F•	-99.760581	21.40	
F ⁺	-98.974241		
FC(O)SN•	-666.102722	9.62	—
FC(O)SN ⁺	-665.749312		
SN•	-452.901060	9.15	9.85±0.28 ⁴⁶
SN ⁺	-452.564669		
S•	-398.133071	10.51	10.5±0.3 ⁴⁷
S ⁺	-397.746958		

^aB3LYP/6/311++G(*d,p*); ^bthis work

Besides the studies of the PES and PIMS, the dissociation processes of FC(O)SNCO were also investigated in this work.

The neutral ground state of FC(O)SNCO possesses the C_1 symmetry with a non-planar conformer ($\delta_{\text{CSNC}} = -22.33^\circ$). But FC(O)SNCO⁺ has an interesting and important feature with C_s symmetry, with F and SNCO synperiplanar with C=O. In other

word, FC(O)SNCO⁺ is a planar conformer ($\delta_{\text{CSNC}} = 0^\circ$). Removing one electron from the HOMO, lone pair of sulfur atom can influence the geometric parameters. The change in bond lengths is obvious: the $r_{\text{C1-S}}$ bond elongates to 0.1907 nm. The occupancy of C1—S band also reduces from 1.97 e (electron charge) (neutral) to 0.98 e (cation). Therefore, these changes in the geometric parameters can strongly influence the removal of the $\sigma_{\text{C1-S}}$ bonding electrons. The strongest interaction describing a conjugation (mesomeric effect) between the lp_sS lone pair and the $\pi^*(\text{C1-O})$ bond [$\text{lp}_s\text{S}(2) \rightarrow \pi^*(\text{C1-O})$] is disappeared. All these changes can weaken the C1—S band. All these results demonstrate that the parent ion is easy to have a dissociation on the C1—S single bond to form the FC(O)⁺/SNCO• pair or the SNCO⁺/FC(O)• pair.

The possible dissociation pathways of FC(O)SNCO⁺ are shown in Fig.8. The dissociation of FC(O)SNCO⁺ into FC(O)⁺/SNCO• (2.46 eV) and SNCO⁺/FC(O)• (2.93 eV) are energetically favorable over most ways. However, the dissociation of FC(O)SNCO⁺ into FCOSN⁺/CO• (2.35 eV) is the easiest channel, which is lower than FC(O)⁺/SNCO• by 0.11 eV. The other two dissociation pathways are SNCO⁺/FC(O)• (2.93 eV) and C(O)SNCO⁺/F• (2.96 eV). Through the above four ways, we can obtain FC(O)SN⁺, FC(O)⁺, SNCO⁺, and C(O)SNCO⁺. Because SNCO⁺ can easily dissociate into SN⁺/CO•, FC(O)SN⁺ into SN⁺/FC(O)•, and F•/C(O)SNCO⁺ into F•/2CO•/SN⁺, which only need 0.05, 0.63, and 1.57 eV, respectively. This is why SN⁺ appeared in photoionization mass spectrum and had the second highest intensity. The energies of the dissociation into FC(O)⁺, SNCO⁺, FC(O)SN⁺, C(O)SNCO⁺ are very nearly, so the intensities of their bands are similar. Thus, the ion intensities observed in the photoionization mass spectrum can be explained by anticipating the dissociation pathways.

Fig.8 Schematic energy profile (eV) showing ionization and dissociation pathways of FC(O)SNCO calculated at the B3LYP/6-311++G(*d,p*) level

4 Conclusions

FC(O)SNCO was synthesized by the reaction between AgOCN and FC(O)SCl. The structural and electronic properties of FC(O)SNCO were studied by combination of experiment, theoretical studies, and NBO analysis, before characterizing by PES and PIMS. The result showed that the most stable conformer for the title molecule was the syn-syn form with C_1 symmetry. After ionization, the cationic-radical FC(O)SNCO^{•+} adopted syn-syn structure with C_1 symmetry and planar conformer. Combining with OVGF calculation, the PES spectrum was assigned. Because of the geometric change after ionization, the first vertical ionization energy (10.33 eV) was different from the first adiabatic ionization energy (9.87 eV). In the PIMS of FC(O)SNCO, there were six peaks: SN⁺, FC(O)⁺, SNCO⁺, FC(O)SN⁺, C(O)SNCO⁺, and FC(O)SNCO^{•+}. According to the calculated bond dissociation energies, the investigations of possible ionization and dissociation processes were presented. Our investigation on the electronic structure of fluorocarbonyl sulfonyl isocyanate may have further implications for the understanding the chemical behavior of FC(O)SNCO.

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第十八届全国电化学大会第一轮通知

由中国化学会主办、哈尔滨工业大学承办、黑龙江大学协办的第十八届全国电化学大会将于2015年8月7-11日在黑龙江省哈尔滨市举行,本届大会主题是“支撑未来能源发展的电化学”。

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会议预定时间:2015年8月7-11日

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