Acryloyl Chloride and Acryloyl Isocyanate ($CH_2{=}CHC(O)X$, X = Cl, NCO): A HeI Photoelectron Spectroscopy and Theoretical Study

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Acryloyl isocyanate $CH_2{=}CHC(O)NCO$ is quantitatively prepared by the metathesis reaction between $CH_2{=}CHC(O)Cl$ and AgNCO. Also, jointly with acryloyl chloride, their molecular and electronic structures have been investigated by photoionization mass spectroscopy (PIMS), HeI photoelectron spectroscopy (PES), and theoretical calculations. $CH_2{=}CHC(O)NCO$ was theoretically predicted to prefer the trans−cis (tc) conformation as the most stable conformer, with the C=O bond trans to the C=C bond and cis to the NCO moiety. IR and Raman spectra also suggest the presence of the trans−cis (tc) conformation only. Calculations of the cationic-radical form were carried out in order to compare their properties with those of the neutral molecules. It is worthwhile mentioning that both compounds retain planar structures after ionization. After structural optimizations, a theoretical study involving the calculation of the ionization energies using orbital valence Green's functional (OVGF) was performed. The ionization energies of different bands in the photoelectron spectrum are in good agreement with the calculated values from the OVGF method. The first vertical ionization energies of $CH_2{=}CHC(O)Cl$ and $CH_2{=}CHC(O)NCO$ are determined to be 10.97 and 10.68 eV, respectively. The HOMOs correspond to the ionization of electrons mainly localized on the $\pi_{C=C}$ or the π_{NCO} orbitals: $\{4a''(\pi_{C=C})\}^{-1}$ and $\{5a''(\pi_{NCO})\}^{-1}$, respectively.

Introduction

The α,β-unsaturated carbonyl compounds constitute interesting building blocks for further functionalization by various reactions in organic chemistry and have many important applications in the medical and biological fields.[1−3] They can undergo photoinduced cycloadditions and ring closure of the C=C−C=O moiety in the acyclic compounds. These reactions have been the subject of experimental and theoretical investigations.[4−6]

Acryloyl chloride ($CH_2{=}CHC(O)Cl$) serves as a simple α,β-unsaturated carbonyl compound, which is an important intermediate in the biomedicine and polymer fields.[6] Previous characterization of this molecule mainly focuses on its conformational properties by UV spectroscopy,[7] gas phase electron diffraction (GED),[8] vibrational spectroscopy (IR and Raman),[9] and theoretical calculations.[10] Two distinct conformers were identified: a more stable planar trans form and a less stable cis form. Both the chlorine and the oxygen atom of the carbonyl group play a competitive role in determining the conformational equilibrium that leads to a small energy difference between the stable conformers of the molecule.[11] The microwave spectra of the acryloyl chloride molecule were recorded for both rotational isomers but only interpreted for the more stable trans form.[12] The energy difference between the trans and cis forms was inferred to be less than 1.0 kcal mol^{-1}; the barrier to the cis−trans isomerization was estimated to be about 3.5 kcal mol^{-1}.[1] Arendt et al.[13] studied the emission spectroscopy of acryloyl chloride. The transition at 199 nm was identified by configuration interaction with single excitation (CIS) calculations as promotion of an electron into an orbital of $\pi^*(C{=}C)/\pi^*(C{=}O)$ character. It was suggested that photodissociation of $CH_2{=}CHC(O)Cl$ did not proceed through a single direct dissociation mechanism and that the excitation was initially to a predissociative state from which the dissociation channels were made possible. Pietri et al.[14] studied the photolysis of $CH_2{=}CHC(O)Cl$ at $\lambda \geq 310$ nm and $\lambda \geq 230$ nm in argon matrix at 10 K. At $\lambda > 310$ nm, isomerization to 3-chloro-1,2-propenone followed two subsequent dissociation pathways. At shorter wavelengths, $\lambda > 230$ nm, the isomerization rate was found to increase, and the resultant 3-chloro-1,2-propenone followed two subsequent dissociation pathways.[10]

As one of the pseudohalide derivatives of acryloyl chloride, acryloyl isocyanate has similar conformational properties. Isocyanates are interesting molecules for two reasons. First, isocyanates are important precursors in the synthesis of polymer materials.[15,16] 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. Second, pseudohalides are examples of distorted linear triatomic systems. The conformational stability of simple isocyanates has been difficult to predict and may also be different in different aggregation states. For example, in acetyl isocyanate, $CH_3C(O)NCO$, the main conformation changes from the gas to the liquid phase.[17] In the gas phase, the cis conformer (isocyanate group syn with respect to the C=O double bond) is more stable than the trans conformer by 1.28 kcal mol^{-1}. However, the trans conformer is more stable by 1.06 (0.17) kcal mol^{-1} in the liquid phase and remains the preferred conformation in the crystalline solid.[18] Furthermore, the conformational stability of the XC(O)NCO (X = F,[16,19]

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Cl,[20−22] Br,[23] CH_3,18·24 and $CF_3$25) molecules in the vapor state depends on the X substituent. Vinyl isocyanate[26] was predicted by DFT-B3LYP/6-311+G** calculations to exist in the planar cis and trans conformations. The trans barrier was calculated to be of 1.5 kcal/mol for vinyl isocyanate.[27] The conformational behavior of these molecules depends on the extent of the interaction between the substituent groups and both the lone pair of nitrogen and the π-system of the isocyanate group.[28]

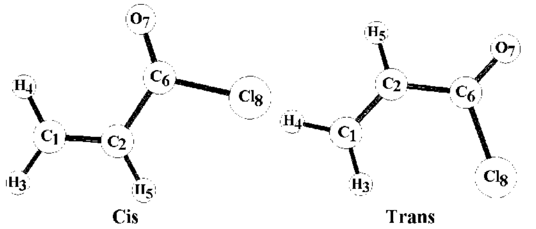
The electronic structure of pseudohalides is relevant for understanding their chemical behavior, so the compounds were investigated previously by UV photoelectron spectroscopy (UPS) and MO calculations. Few experimental data have been reported in the literature on the electronic structure of pseudohalides. The derivatives studied previously were alkyl pseudohalides,[29] methyl pseudohalides,[30,31] silicon pseudohalides,[32] halogen isocyanates,[33] and aromatic pseudohalides.[34] Considering the information that has been reported, we were interested in the electronic structure of acryloyl pseudohalides. In this work, we present the preparation of acryloyl isocyanate and its subsequent detection and characterization by ultraviolet photoelectron (PES), photoionization mass spectrometry (PIMS), FTIR, and Raman. Also, its precursor acryloyl chloride was investigated by PES and PIMS. For comparison with the experimental ionization values, a complete theoretical study involving structure calculations of stable conformers at different levels of theory was performed. MO analysis and ionization energy calculations were also carried out.

Experimental Section

Sample Preparation. The precursor acryloyl chloride was purchased from Alfa Aesar, and used without further purification after checking its photoionization mass spectrum. Silver isocyanate (AgOCN, Aldrich, 99%) was used from commercial sources and was dried in vacuum (1×10^{-4} Torr) for 2 h at 60 °C before used. Silver isocyanate is found to be the ideal precursor for the preparation of isocyanates.[15,35−38] Also, acryloyl isocyanate had been prepared by silver isocyanate and acryloyl chloride with paraffin oil as solvent.[23,39] In this work, acryloyl isocyanate, $CH_2{=}CHC(O)NCO$, was prepared by the heterogeneous reaction between $CH_2{=}CHC(O)Cl$ and AgOCN at room temperature. Briefly, 1.5 g of (10 mmol) AgNCO was loaded in a reaction vessel which was wrapped with light-avoiding material. After evacuation of the vessel, 0.6 g (6 mmol) of acryloyl chloride was condensed on the silver salt at −196 °C, and then the temperature of the vessel was warmed up to room temperature (20 °C) and held for 24 h. Under these conditions, the volatile product was slowly pumped and separated by trap-to-trap condensation to remove a minor impurity of acryloyl chloride. The yield is greater than 90%. The purity was checked by gas-phase infrared spectroscopy as well as mass spectrometry. The reaction route is as follows:

$$CH_2 = CHC(O)CI(g) + AgNCO(s) \rightarrow CH_2 = CHC(O)NCO(g) + AgCI(s)$$

IR and Raman Spectroscopy. Infrared spectra, recorded at 4 cm^{-1} resolution, were collected on a Thermo Nicolet 6700 interferometer equipped with a 20 cm single-pass gas cell. The cell, with KBr windows, gave a spectral range from 4000 to 400 cm^{-1}. All compounds had sufficient vapor and were pumped continuously through the cell using a rotary pump. The Raman was collected and focused into a spectrometer (SpectraPro-500i, Acton) equipped with a liquid nitrogen cooled CCD detection system (SPEC-10-400B/LbN, Roper Scientific). The sample in a 4 mm glass capillary was excited with 200 mW of Ar+ laser at 488 nm (Spectra-Physics Beam Lock).



Cis Trans

Figure 1. Schematic representation of cis and trans conformers of $CH_2{=}CHC(O)Cl$.

Photoelectron Spectroscopy. The PE spectra were recorded on a double-chamber UPS-II machine, which was designed specifically to detect transient species at a resolution of ≈30 meV as indicated by the $Ar^+(^2P_{2/3})$ photoelectron band.[40,41] Experimental vertical ionization energies (IPs in eV) were calibrated by simultaneous addition of a small amount of argon and methyl iodide to the sample. Mass analysis of ions is achieved by a time-of-flight mass analyzer mounted directly at the photoionization point. Ionization is provided by single-wavelength HeI radiation. PE and PIMS spectra, although not measured simultaneously, are recorded within seconds of each other under identical conditions; thus, it is assumed that for a given PE spectrum the subsequent PIMS is of the same compound.

Quantum Chemical Calculations. Electronic structure calculations were carried out by using the Gaussian series of programs.[42] Because the values and the order of the molecular orbital (MO) energies depend on the molecular geometry, the geometries of the neutral ground state and lowest-lying cationic state of $CH_2{=}CHC(O)Cl$ and $CH_2{=}CHC(O)NCO$ were optimized using density functional theory (B3LYP, B3P86, and B3PW91) at the 6-311++G(3df,3pd) basis set level. The single point energies of different conformers were calculated by an ab initio (MP2) method with the 6-311++G** basis set. The density functional calculations were previously employed for pseudohalides and had good performance.[17,35,36] The vibrational frequencies were computed analytically, and zero-point energy (ZPE) corrections were included in the calculation of relative energies. To assign the PE spectra, the out-valence Green's function (OVGF/6-311+G*) calculations, which include sophisticated correlation effects of the self-energy, were applied to the most stable conformer of each compound to give accurate results for the vertical ionization energies. The adiabatic energy was obtained according to the energy differences between the most stable conformer and the corresponding cationic-radical form. The Mulliken population analysis was applied to assign the charges for both neutral and cationic-radical forms. Three-dimensional MO plots were obtained with the Gauss View program by using the 0.06 isodensity.

Results and Discussion

(a) Geometry of $CH_2{=}CHC(O)Cl$ and $CH_2{=}CHC(O)NCO$. Acryloyl chloride adopts two conformations by rotation around the carbon−carbon single bond: the cis and trans conformers for which the dihedral angle C=C−C=O is equal to 0° and 180°, respectively (Figure 1). Earlier studies show that the most stable conformer of $CH_2{=}CHC(O)Cl$ possesses C_s symmetry with the C=C bond in trans position to the C=O bond. Studies of gas-phase electron diffraction (GED), MW, and IR and Raman spectra for acryloyl chloride in the ground state[8,9,43,44] showed that acryloyl chloride existed as a more stable

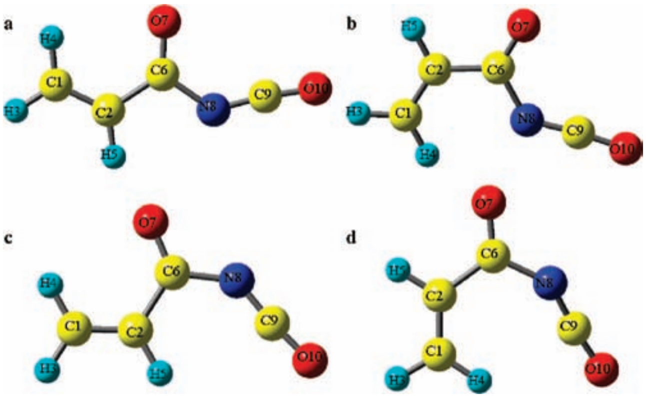


Figure 2. Schematic representation of the four conformers of $CH_2{=}CHC(O)NCO$: (a) cis−cis (cc); (b) trans−cis (tc); (c) cis−trans (ct); (d) trans−trans (tt).

planar trans form together with a less stable cis form. Due to a small energy difference between the cis and trans forms of acryloyl chloride, a small contribution of the cis form can be expected in the PE spectrum. However, theoretical calculations (OVGF/6-311+G*) for this form predict that the difference in the values of the ionization energies between the two conformers is negligible with respect to the experimental resolution.

The accuracy of the DFT method used was tested by calculating geometries for acryloyl chloride for which accurate experimental data are available. Full geometry optimizations and frequency calculations for neutral and cationic $CH_2{=}CHC(O)Cl$ were performed on the most stable structure determined by IR and GED using the three DFT methods (B3LYP, B3P86, and B3PW91) at the 6-311++G(3df,3pd) basis set.

The structure obtained by theoretical methods is in general agreement with the GED[8] experimental results (Table S1). From Table S1, we could see that the parameters calculated by the B3LYP approach were closer to the experimental values. So the geometric parameters of the ground cationic-radical form $CH_2{=}CHC(O)Cl^{\cdot+}$ were also calculated by the B3LYP approach at the same basis set. It is worth noting that obvious changes can be seen in bond lengths and angles between the neutral molecule and cationic-radical form; the most intensive change is the C=O bond length, which elongates from 1.185 to 1.233 Å after ionization. Contrary to this, the C−C bond length shortens by 0.043 Å. Besides, the OCCl angle changes from 119.4° to 106.6°. Furthermore, the cationic-radical form of acryloyl chloride retains the planar trans conformation with C_s symmetry, which is the same as that of the neutral molecule.

In the case of $CH_2{=}CHC(O)NCO$, no theoretical studies on its structural and spectroscopic properties have been reported so far. Generally, four conformations are feasible, depending on the orientation around the C−C and C−N single bonds (see Figure 2). The molecular structure and conformational properties for related $CH_2{=}CHC(O)Cl$ and $CH_2{=}CH{-}NCO$ had been studied by theoretical and experimental methods. According to these antecedents, structure for $CH_2{=}CHC(O)NCO$ with both synperiplanar orientation around the C−C and C−N single bonds were used as the initial forms in the calculations. To gain insight into the conformational preference of these two molecules, the potential energy functions for internal rotation around the $\Phi(C{=}C{-}C{=}O)$ and $\Phi(O{=}C{-}N{=}C)$ dihedral angles were calculated at the MP2/6-31+G* level, by allowing geometry optimizations with the respective dihedral angles Φ varying from 0° to 360° in steps of 10°. The potential energy curves are shown in Figure 3.

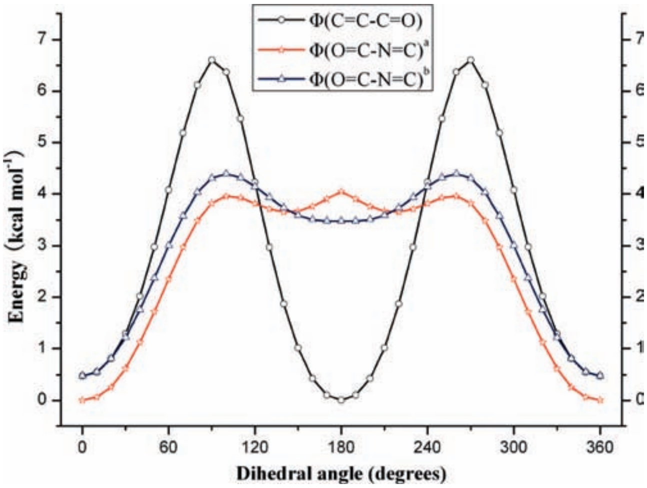


Figure 3. Potential energy curves of $CH_2{=}CHC(O)NCO$ by rotating the C−C and C−N bonds from 0° to 360° in steps of 10°: (a) $\Phi(C{=}C{-}C{=}O) = 180°$, (b) $\Phi(C{=}C{-}C{=}O) = 0°$.

TABLE 1: Calculated Relative Energies (kcal/mol) of Different Conformers of $CH_2{=}CHC(O)NCO$

level of theory	tc	cc	ct	tt
B3LYP/6-311++G(3df,3pd)	0.0	0.34	2.49	3.18
B3P86/6-311++G(3df,3pd)	0.0	0.45	2.44	3.03
B3PW91/6-311++G(3df,3pd)	0.0	0.40	2.40	3.09
MP2/6-311++G**	0.0	0.61	3.25	3.60

As expected for the $CH_2{=}CHC(O){-}$ moiety, a trans orientation of the $\Phi(C{=}C{-}C{=}O)$ dihedral angle is preferred, while the cis form is higher in energy. Likewise, four structures correspond to minima in the potential energy curve around the $\Phi(O{=}C{-}N{=}C)$ dihedral angle (Figure 3). Full geometry optimizations and frequency calculations for the four feasible conformers have been performed using three DFT methods (B3LYP, B3P86, and B3PW91) at the 6-311++G(3df,3pd) basis set, and the single point energies were calculated at the MP2/6-311++G** level. Relative ΔE energy values are listed in Table 1. The B3LYP method predicts that all four conformers correspond to stable structures with planar molecular skeletons, except for the tt form. In this conformer, the N=C=O group is above or below the molecular plane. All computational methods predict a structure with trans (C=C−C=O) orientation and cis (O=C−N=C) orientation to be the most stable conformer of $CH_2{=}CHC(O)NCO$ (tc). The second stable form, cc, corresponds to a conformer with cis orientation around both dihedral angles, and its energy is calculated to be about 0.61 kcal mol^{-1} higher than that of the tc form by the MP2/6-311++G** approach. A third conformer named cis−trans (ct) in Figure 2, with trans orientation of the C=O and N=C bonds, results in a minima in the potential hypersurface as well, located at 3.25 kcal mol^{-1} above the global minimum. The calculated energy of the fourth conformer with trans orientation of both dihedral angles (tt) is higher than 3.60 kcal mol^{-1} with respect to the minimum. The tc−cc rotational barrier was predicted to be 7.84 kcal mol^{-1} for $CH_2{=}CHC(O)NCO$.

Selected geometric parameters as obtained by the B3LYP/6-311++G(3df, 3pd) approach for the most stable conformer and the cationic-radical form for $CH_2{=}CHC(O)NCO$ are given in Table 2. Apparent changes can be found in bond lengths and angles between the neutral molecule and the cationic-radical form. For $CH_2{=}CHC(O)NCO$, the most intensive change is the C−N bond length, which shortens from 1.421 to 1.359 Å after ionization, while the bond length of C=O elongates by 0.041

TABLE 2: Calculated Geometric Parameters for the tc Conformer of CH_2=CHC(O)NCO[a] and for the Cationic-Radical Form CH_2=CHC(O)$NCO^{\cdot+}$

	neutral			cation
parameter	B3PW91	B3P86	B3LYP	B3LYP
r_{C1C2}	1.328	1.327	1.329	1.340
r_{C2C6}	1.471	1.469	1.474	1.437
r_{C6O7}	1.203	1.202	1.205	1.256
r_{C6N8}	1.416	1.415	1.421	1.359
r_{N8C9}	1.214	1.213	1.215	1.244
r_{C9O10}	1.157	1.156	1.158	1.137
α_{C1C2C6}	124.1	124.0	124.4	120.1
α_{C2C6O7}	123.3	123.3	123.2	122.9
α_{C2C6N8}	114.1	114.1	114.3	123.0
α_{O7C6N8}	122.6	122.6	122.5	114.1
α_{C6N8C9}	130.0	129.9	130.0	131.9
$\alpha_{N8C9O10}$	174.0	174.0	174.0	172.0
$\delta_{C1C2C6O7}$	180.0	180.0	180.0	180.0
$\delta_{O7C6N8C9}$	0.0	0.0	0.0	0.0
$\delta_{C6N8C9O10}$	180.0	180.0	180.0	180.0

[a] Distances in Å, angles in degrees. All the calculations were performed with the basis set of 6-311++G(3df,3pd). For atom numbering see Figure 2.

Å, and the angles of CCN and OCN change from 114.3° and 122.5° to 123.0° and 114.1°, respectively. It is interesting to compare acryloyl isocyanate with acetyl isocyanate:[17] the C—N bond length for the latter shortens from 1.428 to 1.346 Å and the C=O bond length elongates by 0.045 Å after ionization, and angles of CCN and OCN change from 112.2° and 122.4° to 121.7° and 118.2°, respectively. It seems that the substituents do not significantly affect the geometry of the —C(O)NCO moiety. Similar to acryloyl chloride, the cationic-radical form of acryloyl isocyanate retains the planar tc conformation with C_s symmetry. This behavior is similar to that of FC(O)SCl[45] as well.

(b) Vibrational Analysis. The infrared spectrum of CH_2=CHC(O)Cl has been reported by Katon and Durig et al.[9,44] in detail. However, for CH_2=CHC(O)NCO, only several spectroscopic data have been reported, with no spectrum.[23] Also, no detailed assignments, Raman spectrum, or theoretical calculations have been reported for CH_2=CHC(O)NCO. The IR (gas) and Raman (liquid) spectra of CH_2=CHC(O)NCO are shown in Figure 4. Experimental and calculated (B3LYP/6-311++G(3df,3pd)) frequencies and intensities are given as Supporting Information (Table S2). A tentative assignment of the observed bands was carried out by comparison with spectra of related molecules, specially CH_2=CHC(O)Cl,[44] CH_3C(O)NCO,[46] and CH_2=CH-NCO.[47] The molecules in their planar tc conformations possess the C_s symmetry. Thus, in the two molecules, the 24 normal modes of vibration correspond to an irreducible representation 17A′ + 7A″ for the in-plane and out-of-plane modes, respectively.

The general features of the vibrational spectra of CH_2=CHC(O)NCO are dominated by the more stable tc conformer. All stretching modes at high wavenumbers are characteristic and assignable. Generally, the ab initio and DFT harmonic vibrational frequencies are overestimated.[48] Since this overestimation is found to be consistent, the constant or exponential scaling method is often employed.[49] Furthermore, the carbonyl and NCO stretching vibrations give rise to three prominent infrared absorptions. The NCO antisymmetric stretching mode appears only as a very weak and broad line in the Raman spectra. The strong 2255−2275 cm^{-1} and 1400−1425 cm^{-1} infrared features are diagnostic of isocyanates, being rather insensitive to the nature of the substituents. Also, the characteristic vibrational frequencies of the vinyl group are well documented.[7,50] Seen from Figure 4, the most intense band is at 2257 cm^{-1}, which is somewhat lower than the calculated value 2322 cm^{-1} corresponding to the N=C=O antisymmetric stretching mode, and appears as a weak signal in the Raman spectrum. The most characteristic band at 1730 cm^{-1} can be attributed to the stretching mode of ν(C=O) undoubtedly. Other characteristic bands at 1631, 1412, 1198, and 980 cm^{-1} correspond to the ν(C=C) stretching, ν(NCO) symmetry stretching, ν(C—C) stretching, and the stretching of the C—N bond. The broad absorption at 624 cm^{-1} can correspond to the overlap of the NCO in-plane and out-of-plane bend, which is mainly based on the results of the theoretical calculation. The skeletal bending modes are strongly mixed, and the proposed assignment is arbitrary.

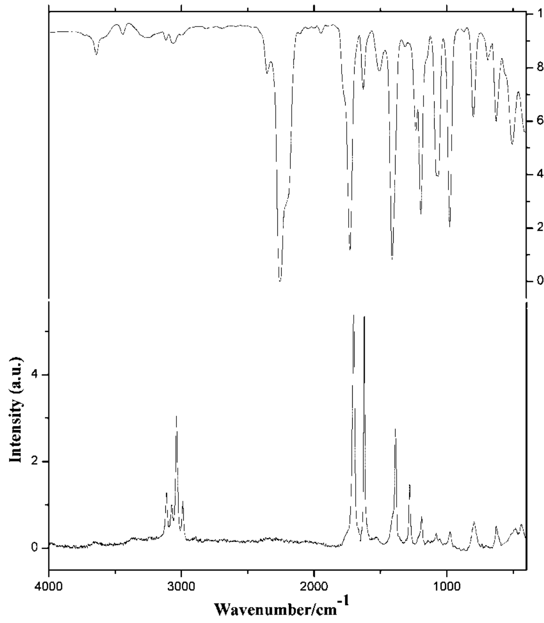


Figure 4. Infrared (gas phase) and Raman (liquid phase) spectrum of CH_2=CHC(O)NCO.

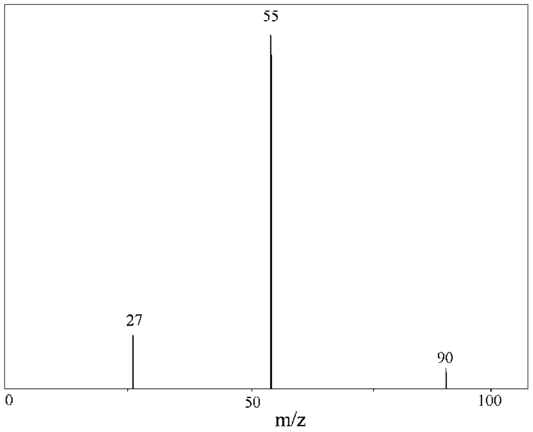


Figure 5. PIMS spectrum of CH_2=CHC(O)Cl.

(c) Photoionization Mass Spectroscopy. The HeI photoionization mass spectra of acryloyl chloride and acryloyl isocyanate are shown in Figures 5 and 6. The spectrum of acryloyl chloride is relatively simple. It shows three peaks: $C_2H_3^+$, $C_2H_3CO^+$, and the parent molecular ion M^+, with the dominant features being the $C_2H_3CO^+$ peaks. However, in the mass spectrum (70 eV),[51] the parent molecular ion M^+ was not visible. For acryloyl isocyanate, though it is unstable at room

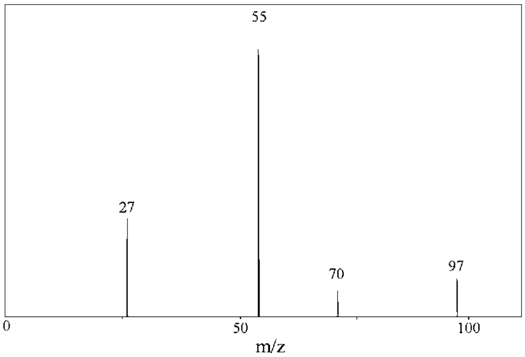


Figure 6. PIMS spectrum of $CH_2{=}CHC(O)NCO$.

temperature, the parent molecular ion peak is also distinct in the spectrum. Also similar to acryloyl chloride, the $C_2H_3CO^+$ peak is the most dominant feature in the spectrum of acryloyl isocyanate. Because there are no peaks of the acryloyl chloride in Figure 6, and no acryloyl chloride bands in the corresponding PE spectra, it can be concluded that the peaks $C_2H_3CO^+$ and $C_2H_3^+$ are fragments of acryloyl isocyanate. As seen from Figure 6, there are three dissociation paths for $CH_2{=}CHC(O)NCO^+$ (M^+). The first is C_2H_3 radicals with $CONCO^+$, the second is $C_2H_3CO^+$ with NCO radicals, and the third is $C_2H_3^+$ with CONCO radicals. According to the intensity of the peaks in the spectrum, it is distinct that the second path is the dominant dissociation way for acryloyl isocyanate.

(d) Photoelectron Spectra. Photoelectron spectroscopy with HeI resonance source (58.4 nm) is an effective method for investigating the electronic structure of unstable compounds and free radicals in combination with theoretical calculations. The valence shell structure of the molecule can be readily obtained by HeI photoelectron energy analysis, especially for studying similar molecules. Previously, photoelectron spectroscopic investigations on acetyl halides indicated that the first two occupied molecular orbitals (HOMOs) are the carbonyl oxygen lone pair (n_O) and the approximately nonbonding antisymmetric π_2 orbital. However, for isocyanates, the first two occupied molecular orbital (HOMOs) are the bonding π and nonbonding π orbitals on the NCO group.[17] These principles are of particular interest in connection with our present study.

As we know, within the HeI energy region (21.2 eV), the nonbonding and bonding π level (of the originally linear moieties) will give rise to four IPs in the linear molecule, viz. a″ (n.b.), a′ (n.b.), a″ (b), and a′ (b). One group of orbitals with a′ symmetry lies in the molecular plane, while the other group with a″ symmetry belongs to orbitals perpendicular to the plane. These orbitals are partially localized on the pseudohalide carbonyl group and the C=C. So the interpretation of the PE spectra of these molecules becomes straightforward when considering the similarities between them. Also, the vertical ionization energies and pole strengths derived from the Green's function calculations were calculated for $CH_2{=}CHC(O)Cl$ and $CH_2{=}CHC(O)NCO$. As for $CH_2{=}CHC(O)NCO$, no noticeable difference can be found between the orbital energies of the two stable conformers of tc and cc; therefore, our discussion is reduced to the analysis of the slightly more stable conformer tc.

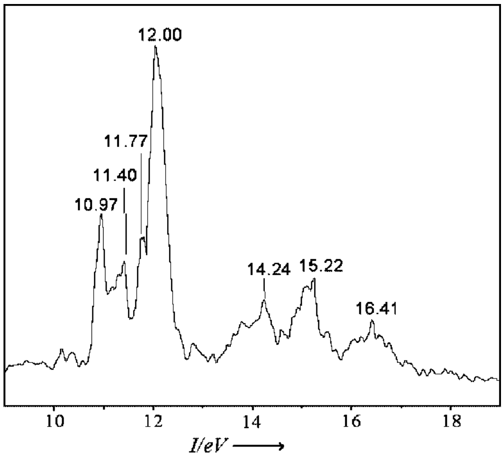


Figure 7. HeI photoelectron spectrum of $CH_2{=}CHC(O)Cl$.

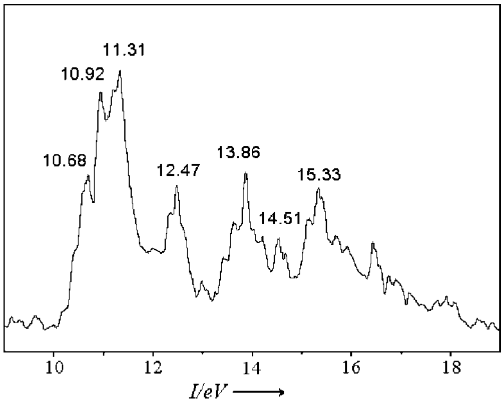


Figure 8. HeI photoelectron spectrum of $CH_2{=}CHC(O)NCO$.

TABLE 3: Experimental Vertical Ionization Energies (IP in eV) and Computed Vertical Ionization Energies (Ev in eV) as Obtained by OVGF/6-311+G* Calculation for the Trans $CH_2{=}CHC(O)Cl$ and the tc $CH_2{=}CHC(O)NCO$[a,b]

exptl IP	calcd Ev	MO	character
	$CH_2{=}CHC(O)Cl$		
10.97	10.94(0.89)	4a″	$\pi_{C=C}$
11.40	11.35(0.90)	19a′	n_O, n_{Cl}
11.77	11.67(0.90)	3a″	$n_{Cl}(\pi)$
12.00	11.77(0.91)	18a′	n_{Cl}
14.24	14.15(0.89)	17a′	$\sigma_{C=C}$
15.22	15.28(0.85)	2a″	$\pi_{C=O}$
	15.51(0.89)	16a′	σ
16.41	16.76(0.87)	15a′	σ
	$CH_2{=}CHC(O)NCO$		
10.68	10.81(0.88)	4a″	$\pi_{C=C}$
10.92	11.07(0.90)	3a″	π_{NCO}, n_O
11.31	11.56(0.88)	21a′	n_O
12.47	12.59(0.88)	20a′	π'_{NCO}
13.86	13.93(0.90)	19a′	$\sigma_{C=C}$
14.51	14.87(0.86)	2a″	$\pi_{C=O}$
15.33	15.64(0.88)	18a′	σ

[a] Pole strength between parentheses. [b] Geometry optimized at the B3LYP/6-311++G(3df,3pd) level of approximation.

The HeI PE spectra of acryloyl chloride and acryloyl isocyanate in the gas phase are shown in Figures 7 and 8. The experimentally determined and theoretical ionization energies, molecular orbitals, and characters are summarized in Table 3. Drawings of six MOs for these two molecules are given in Figures 9 and 10. Seen from Figure 7, seven distinct ionization bands are observed in the region 10−18 eV, and four bands with high intensity in the low ionization region (<13.0 eV), while the other three bands in the high ionization region overlap seriously. In comparison to the PE spectra of $CH_3C(O)Cl$[52] and $CH_2{=}CHC(O)H$,[53] the present spectrum of $CH_2{=}CHC(O)Cl$ can be reasonably assigned. For $CH_2{=}CHC(O)H$, the outermost orbital is mainly of oxygen nonbonding type with some

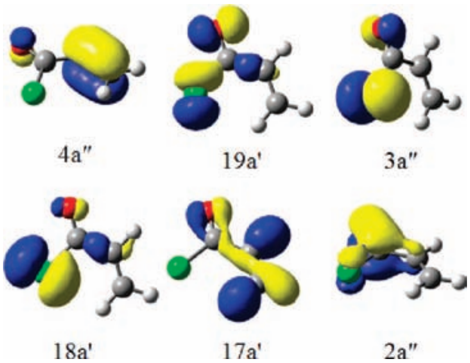


Figure 9. Drawings of selected occupied MOs of $CH_2{=}CHC(O)Cl$.

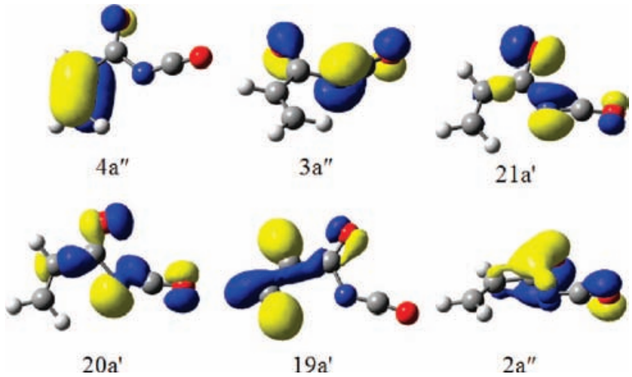


Figure 10. Drawings of selected occupied MOs of $CH_2{=}CHC(O)NCO$.

admixture of vinyl and formal group orbitals. Different from $CH_2{=}CHC(O)H$, the first band of acryloyl chloride has a vertical IP of 10.97 eV, which can be ascribed to ionization of a C=C π electron. This band is similar to the second IP of acrolein,[53] where it is assigned to ionization of electrons from a π MO. Unlike the case of butadiene where resonance interaction between the two terminal groups is very large, the calculations indicate that resonance interaction between the C=C and the C=O π electrons of acryloyl chloride is rather small; this weak resonance interaction can be attributed to the large energy difference between the C=C π and C=O π orbitals. Because of the strong inductive effect caused by the strong electronegative chlorine atom, it will exert an inductive effect which will draw electron density from the carbons. This inductive effect will also stabilize the C=C π orbital and destabilize the nonbonding orbital. The bonding between carbon with chlorine looks like some double bond character. Two factors should be noted about this assignment. First, the ordering of the n and π is changed compared to that of acrolein, and second, the C=C π orbitals are stabilized by 0.84 eV when compared to those of acrolein.[53] The calculated first vertical ionization energy of acryloly chloride is 10.94 eV, which agrees well with the experimental value 10.97 eV.

Further calculations (UB3LYP/6-311++G(3df,3pd)) were performed in order to analyze the nature of the cation formed in the first ionization process. The results demonstrate that the atomic charges are delocalized all over the molecule, with an appreciable fraction localized at the chlorine and the carbonyl oxygen atoms (Table 4). The optimized structural parameters of the cationic-radical form are summarized in Table 1. In a similar way, the C=O and C−Cl bonds and the OCCl angle are the geometric parameters most influenced by ionization. The planar form, with anti orientation of the C=C and C=O bonds, is retained after ionization. The values of the adiabatic IP derived from these calculations are 10.46 eV in the UB3LYP/6-311++G(3df,3pd) approximations. Further vibrational calculations performed for the cationic form result in shifts of 213 and 192 cm^{-1} of the wavenumbers for v(C=O) and v(C=C) toward lower values, as compared to the neutral form. These results agree with the picture of an electron ionization mainly localized at the C=C, with a reinforced bond character in the C−C and C−Cl bonds and the decrease in the corresponding C=C and C=O bonds.

As for $CH_2{=}CHC(O)NCO$, there are four separate bands that appeared in the low ionization region (10−13 eV). The first band at 10.68 eV can be attributed to the process of an electron ionized from the HOMO, the antibonding $\pi_{C=C}$ orbital; it is similar to the first ionization process of $CH_2{=}CHC(O)Cl$ and $CH_2{=}CHNCO$.[54] Because of the stronger inductive effect of chlorine as compared to that of the NCO group, the first ionization potential of the latter shifted to the lower energy region by 0.29 eV. This assignment is in agreement with both the OVGF/6-311+G(d) calculation and with the results obtained by a charge analysis (UB3LYP/6-311++G(3df,3pd)) for the cationic-radical $CH_2{=}CHC(O)NCO^{\cdot+}$, which shows that the positive charge is mainly localized at the C_1 atom, with a great proportion of the NCO oxygen atom (see Table 5). A value of IP^{ad} = 10.08 eV is derived from the difference between the energies of the neutral and the cationic-radical form.

The second band in the photoelectron spectrum of acryloyl chloride at 11.40 eV is the result of the ionization of electrons in the orbital 19a′, composed by in-plane oxygen lone pair n_O with some admixture of the in-plane chlorine lone pair n_{Cl}. It is similar to the first IP of $CH_3C(O)Cl$ (11.03 eV)[52] {16a′(n_O, n_{Cl})}.

TABLE 4: Atomic Charge for the Molecular and Cationic-Radical Form of $CH_2{=}CHC(O)Cl$ Calculated with the UB3LYP/6-311++G(3df,3pd) Approximation

atom[a]	C1	C2	H3	H4	H5	C6	O7	Cl8	TAC[b]
$CH_2{=}CHC(O)Cl$	−0.312	0.722	0.030	0.024	0.060	0.127	−0.539	−0.111	0
$CH_2{=}CHC(O)Cl^{\cdot+}$	−0.195	0.894	0.052	0.072	0.091	0.070	−0.250	0.266	1
Δq^c	0.117	0.172	0.022	0.048	0.031	−0.057	0.289	0.377	1

[a] For atom numbering, see Figure 1. [b] Total atomic charge. [c] $\Delta q = q(CH_2{=}CHC(O)Cl^{\cdot+}) - q(CH_2{=}CHC(O)Cl)$.

TABLE 5: Atomic Charge for the Molecular and Cationic-Radical Form of $CH_2{=}CHC(O)NCO$ Calculated with the UB3LYP/6-311++G(3df,3pd) Approximation

atom[a]	C1	C2	H3	H4	H5	C6	O7	N8	C9	O10	TAC[b]
$CH_2{=}CHC(O)NCO$	−0.205	0.323	0.021	0.051	0.039	0.814	−0.690	−0.916	1.192	−0.629	0
$CH_2{=}CHC(O)NCO^{\cdot+}$	−0.029	0.406	0.044	0.101	0.071	0.856	−0.327	−0.864	1.232	−0.490	1
Δq^c	0.176	0.083	0.023	0.050	0.032	0.042	0.363	0.052	0.040	0.139	1

[a] For atom numbering, see Figure 2. [b] Total atomic charge. [c] $\Delta q = q(CH_2{=}CHC(O)NCO^{\cdot+}) - q(CH_2{=}CHC(O)NCO)$.

Different from that of $CH_2{=}CHC(O)Cl$, the second band in the photoelectron spectrum of acryloyl isocyanate at 10.92 eV agrees well with the calculated value 11.07 eV, which originated from the ionization of the 3a″ orbital. Compared with HNCO[55] and $CH_3C(O)NCO$,[17] it can be unambiguously assigned to the ionization of electrons from the out-of-plane antibonding π_{NCO} orbital, and the lone pair on the carbonyl oxygen atom n_O also shows some contribution. The spectrum of HNCO[55] contains a pair of bands (11.62 and 12.30 eV, respectively); the primary characters are one for the out-of-plane π orbital on the NCO moiety with a″ symmetry, and another for the in-plane π type orbital on the same moiety but with a′ symmetry. In the spectrum of $CH_3C(O)NCO$,[17] the band at 11.33 eV is mainly the ionization of electrons on the orbital 4a″, composed by out-of-plane π_{NCO}, while the band at 12.48 eV is the result of ionization of electrons on the orbital 17a′, the main character being in-plane π'_{NCO}. Due to the inductive effect of the $CH_2{=}CH$ group, the ionization of $CH_2{=}CHC(O)NCO$ shifts to the higher ionization energy region by 0.70 eV compared with that of HNCO,[55] and 0.41 eV compared with that of $CH_3C(O)NCO$.[17]

The next two bands in the low ionization region of $CH_2{=}CHC(O)Cl$ at 11.77 and 12.00 eV, which originated from the presence of a Cl atom and can be assigned to ionization processes arising from the n_{Cl} out-of-plane and n_{Cl} in-plane orbitals, respectively, which is consistent with the Franck−Condon principle that the sharp and narrow bands correspond to the ionization from strongly localized nonbonding orbitals. However, in the spectrum of $CH_2{=}CHC(O)NCO$, these two bands at 11.31 and 12.47 eV can be assigned to the ionization of the in-plane oxygen lone pair n_O and the in-plane π'_{NCO}. The vertical ionization energies from the ionization process of orbitals ($\sigma_{C=C}$, $\pi_{C=O}$, and σ) in $CH_2{=}CHC(O)Cl$ are 14.24, 15.22, and 16.41 eV, respectively. However, the responding ionization energies of the latter are 13.86, 14.51, and 15.33 eV, respectively. The broad bands left in higher ionization energies may be attributed to the ionization of inner orbitals which can not be assigned with certainty.

3. Conclusions

Acryloyl isocyanate was synthesized by the reaction between acryloyl chloride and AgNCO, and together with acryloyl chloride both compounds were investigated by HeI photoelectron spectroscopy and photoionization mass spectra, and combined with theoretical calculations. The results show that the most stable conformer for acryloyl isocyanate is the tc (trans−cis) form, the C═C bond at trans orientation with respect to the C═O bond, with the C═O bond at cis orientation with respect to the NCO group. The first vertical ionization potentials of them are 10.97 and 10.68 eV, respectively. Also, both of them can be attributed mainly to the ionization of the $\pi_{C=C}$ orbital. In order to understand the nature of the first ionization processes, the cationic-radical forms of acryloyl isocyanate were also studied, with the structures of them changed with the geometry retained after ionization. From the more general point of view of reactivity, our investigation on the electronic structure of acryloyl chloride and acryloyl isocyanate may have further implications for the understanding of their chemical behavior.

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Supporting Information Available: Experimental and calculated geometric parameters for the trans conformer of $CH_2{=}CHC(O)Cl$ and for the cationic-radical form ($CH_2{=}CHC(O)Cl^{\cdot+}$) combined with assignments of the IR and Raman spectra of acryloyl isocyanate. This information is available free of charge via the Internet at http://pubs.acs.org.

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