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Nobuaki Tanaka, Yoshitaka Urashima, Hiromasa Nishikiori, and Tsuneo Fujii

Department of Environmental Science and Technology, Faculty of Engineering, Shinshu University, 4–17–1 Wakasato, Nagano 380–8553, Japan

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Ab initio and Density Functional Studies on Cyclopropanone Complexes with HF and HCl[#]

Nobuaki Tanaka,* Yoshitaka Urashima, Hiromasa Nishikiori, and Tsuneo Fujii

Department of Environmental Science and Technology, Faculty of Engineering, Shinshu University, 4–17–1 Wakasato, Nagano 380–8553, Japan

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Abstract

Motivation. Hydrogen bonding is an active topic of considerable interest. Hydrogen bonds play an important role in reactivity and chemical properties. Cyclopropanone possesses two possible sites for the hydrogen–bond formation, that is, a carbonyl group and a pseudo π C–C bond. How does the carbonyl substitution of cyclopropane affect the complex formation?

Method. The MP2 and B3LYP calculations are carried out for the geometry optimization and following frequency analysis of cyclopropanone complexes with HF and HCl. The cyclopropane–hydrogen halide complexes are also studied for comparison.

Results. Two stable conformers have been found: (I) the hydrogen–bond complex with a C=O···HX (X = F, Cl) interaction and (II) the C_{2v} complex where a HX molecule interacts perpendicularly with a C–C bond of cyclopropanone. The complex I is calculated to be more stable than the complex II. In complex I contacting H–X and C=O bonds are lengthened. In complex II a contacting H–X bond is lengthened while a C=O bond is shortened.

Conclusions. Natural bond orbital analysis revealed intermolecular charge transfers occur followed by intramolecular charge rearrangement. Large contributions from the n_O to the $\sigma^*_{H–X}$ in complex I and from the contacting $\sigma_{C–C}$ to the $\sigma^*_{H–X}$ in complex II are found.

Keywords. Cyclopropanone–HCl complex; cyclopropanone–HF complex; MP2; DFT; hydrogen bond; NBO.

Abbreviations and notations

B3LYP, Becke's three parameter hybrid exchange functional and the Lee–Yang–Parr correlation functional	DFT, density functional theory
CP, counterpoise	MP2, second order Møller–Plesset perturbation theory
CT, charge transfer	NBO, natural bond orbital

1 INTRODUCTION

Weakly bound hydrogen bonded complexes have been widely studied [1–3]. Of this category X–H···π type complexes have been investigated experimentally by Fourier transform microwave spectroscopy [4–9] and IR detection [10] and theoretically by *ab initio* and DFT calculations [11–

[#] Dedicated to Professor Nenad Trinajstić on the occasion of the 65th birthday.

* Correspondence author; phone: +81–26–269–5527; fax: +81–26–269–5550; E–mail: ntanaka@gipwc.shinshu–u.ac.jp.

15] where a hydrogen halide HX (X = F, Cl) acts as a proton donor and a phenyl ring or multiple bonds as an acceptor. Acetylene [4,5], ethylene [6,7], and cyclopropane [8,9] form complexes with HX in the manner a hydrogen atom of the HX points to a π bond or pseudo π bond perpendicularly. Cyclopropane is well known to have bent carbon–carbon bonds where bonding electrons lie principally outside the triangular internuclear lines [16] and have a π bond character [11]. In the present study, the properties of HF and HCl complexes with cyclopropanone as a proton acceptor have been investigated. There are two possible hydrogen–bonding sites for cyclopropanone, that is, a carbonyl group and a pseudo π C–C bond. Carbonyl group is a typical proton acceptor. Difference in the complexation properties will be considered using the NBO analysis. How the carbonyl substitution of cyclopropane ring affects the complex formation will be also discussed.

2 METHODS

Geometry optimizations were performed using the second–order Møller–Plesset theory (MP2) and Becke's three–parameter hybrid density functional [17] in combination with the Lee–Yang–Parr correlation functional (B3LYP) [18]. For weak bonding, both diffuse and polarization functions must be included in the basis set, so we used the Dunning's correlation consistent double and triple zeta basis set augmented with diffuse functions, aug–cc–pVXZ (X = D, T) [19,20]. Analysis of the charge distribution and charge–transfer processes was performed using the natural bond orbital (NBO) partitioning scheme [21] with the aug–cc–pVDZ basis set. The basis set superposition error (BSSE) was calculated according to the counterpoise (CP) method proposed by Boys and Bernardi [22]. All calculations were performed using Gaussian 98W [23].

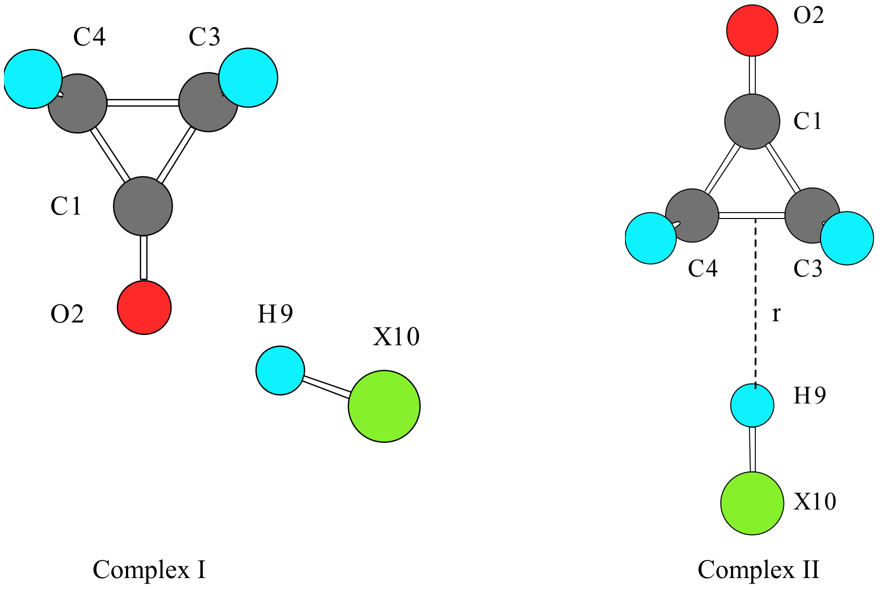

Figure 1. Optimized structures of the cyclopropanone–HX complexes, C_3H_4O–HX.

Table 1. Geometry parameters of the cyclopropanone–HX complexes computed at the MP2/aug–cc–pVDZ and B3LYP/aug–cc–pVTZ levels of theory. Changes in value from the corresponding monomer are given in parentheses.

Parameter [a]	MP2/aug–cc–pVDZ				B3LYP/aug–cc–pVTZ			
	HF		HCl		HF		HCl	
Complex I								
r_{C1O2}	1.221	(+0.0066)	1.221	(+0.0062)	1.203	(+0.0079)	1.202	(+0.0062)
r_{C1C3}	1.473	(–0.0080)	1.475	(–0.0065)	1.457	(–0.0086)	1.459	(–0.0063)
r_{C1C4}	1.473	(–0.0078)	1.475	(–0.0063)	1.457	(–0.0081)	1.459	(–0.0063)
r_{C3C4}	1.589	(–0.0001)	1.589	(–0.0004)	1.571	(–0.0003)	1.571	(–0.0008)
r_{CH}	1.093	(–0.0002)	1.093	(–0.0001)	1.083	(–0.0001)	1.083	(–0.0001)
r_{H9X10}	0.944	(+0.0188)	1.311	(+0.0230)	0.946	(+0.0222)	1.309	(+0.0250)
θ_{C1O2H9}	109.6		104.6		116.4		115.5	
$\theta_{O2H9X10}$	171.4		168.4		174.0		174.2	
$\phi_{C3C1O2H9}$	0.0		0.0		0.0		0.0	
$\phi_{C1O2H9X10}$	0.0		0.0		0.0		0.0	
Complex II								
r_{C1O2}	1.212	(–0.0023)	1.213	(–0.0019)	1.193	(–0.0023)	1.194	(–0.0015)
r_{C1C3}	1.480	(–0.0012)	1.481	(–0.0001)	1.465	(–0.0011)	1.465	(–0.0002)
r_{C3C4}	1.609	(+0.0195)	1.602	(+0.0124)	1.592	(+0.0205)	1.581	(+0.0096)
r_{CH}	1.094	(+0.0005)	1.094	(+0.0006)	1.083	(+0.0002)	1.083	(+0.0001)
r_{H9X10}	0.931	(+0.0059)	1.293	(+0.0052)	0.930	(+0.0059)	1.287	(+0.0031)
θ_{O2C1C3}	147.1	(–0.48)	147.3	(–0.29)	147.1	(–0.50)	147.3	(–0.23)

[a] Bond lengths and angles are in Å and degrees, respectively

3 RESULTS AND DISCUSSION

3.1 Conformation and Energetics

Optimization at the MP2 and B3LYP levels resulted in convergence on two conformations. Figure 1 shows the two optimized structures of the cyclopropanone–HX complexes. In complex I the n orbital of the oxygen atom of carbonyl group interacts with the hydrogen atom of HX. In complex II a HX molecule interacts perpendicularly with the C3–C4 bond with C_{2v} symmetry. Geometry parameters calculated at the MP2/aug–cc–pVDZ and B3LYP/aug–cc–pVTZ levels of theory are listed in Table 1. In complex I the C1–O2 and H9–X10 bonds participating in the hydrogen–bond are elongated, while other bonds shrink. In complex II the H9–X10 bond is less elongated in comparison with the complex I and the C1–O2 bond is contracted, in contrast with the complex I. As for the cyclopropanone moiety, the C3–C4 and C–H bond elongation and the C1–C3 and C1–C4 bond contractions are shown. In complex I the lengths of the four C–H bonds were calculated to be the same within the error limits and in complex II the four C–H bonds are equivalent. Therefore, the lengths of the four C–H bonds are represented by r_{CH}. The trend of geometry changes from the corresponding monomer has a similarity between the results obtained with the MP2 and B3LYP methods. However, the influence of methods is reflected on intermolecular distances as compared in Table 2. For the complex I a hydrogen–bond distance O2···H9 calculated by the MP2 method is longer than that by the B3LYP method with the same basis set, while for the complex II an intermolecular distance defined by *r* in Figure 1 calculated by the B3LYP method is longer except the HF complex using the 6–311++G(d,p) basis set.

Table 2. Intermolecular distances (Å) for the cyclopropanone–HX complexes

	Complex I (O2···H9)		Complex II (*r*)	
	HF	HCl	HF	HCl
MP2/6–311++G(d,p)	1.755	1.922	2.162	2.349
MP2/aug–cc–pVDZ	1.725	1.830	2.084	2.229
B3LYP/6–311++G(d,p)	1.714	1.867	2.151	2.459
B3LYP/aug–cc–pVDZ	1.690	1.808	2.119	2.471
B3LYP/aug–cc–pVTZ	1.694	1.847	2.141	2.497

Table 3. BSSE corrected interaction energies (kJ mol^{-1}) of the cyclopropanone–HX complexes

	Complex I		Complex II	
	HF	HCl	HF	HCl
MP2/6–311++G(d,p)	–29.5	–18.7	–6.7	–4.5
MP2/aug–cc–pVDZ	–34.2	–25.8	–8.7	–7.4
B3LYP/6–311++G(d,p)	–38.0	–23.6	–6.4	–1.4
B3LYP/aug–cc–pVDZ	–39.0	–25.2	–6.4	–1.6
B3LYP/aug–cc–pVTZ	–42.4	–26.7	–9.9	–4.7

Calculated interaction energies including BSSE correction for two complexes are listed in Table 3. It is seen the complex I is more stable than the complex II irrespective of the calculation levels. Dipole moments of cyclopropanone, HF, and HCl are calculated to be 3.03, 1.81, and 1.12 D, respectively, at the B3LYP/aug–cc–pVTZ level. The complexation gave dipole moments of 5.41 and 0.42 D for the HF complexes I and II, respectively, and 4.89 and 1.41 D for the HCl complexes I and II, respectively. The calculated rotational constants are shown in Table 4. There are quite differences in A_0 values between the complexes I and II. Therefore the structure will be determined experimentally. The rotational constants A_0 of complex II are close to the corresponding values of cyclopropanone, 19.953 and 20.335 GHz calculated at the MP2/aug–cc–pVDZ and B3LYP/aug–cc–pVTZ levels, respectively, due to the C_{2v} symmetry.

Table 4. Calculated rotational constants (GHz) for the cyclopropanone–HX complexes

	Complex I		Complex II	
	HF	HCl	HF	HCl
MP2/aug–cc–pVDZ				
A_0	10.786	9.256	19.551	19.690
B_0	2.336	1.507	1.712	1.009
C_0	1.972	1.319	1.609	0.972
B3LYP/aug–cc–pVTZ				
A_0	11.993	10.943	19.898	20.118
B_0	2.200	1.297	1.693	0.920
C_0	1.906	1.177	1.593	0.890

Table 5. Intermolecular distances (Å), BSSE corrected interaction energies, *E* (kJ mol^{-1}), and frequency shifts (cm^{-1}) of the cyclopropane complexes with HF and HCl

	MP2/aug–cc–pVDZ				B3LYP/aug–cc–pVTZ			
	r^a	r_x	**E**	$\Delta\nu$	r^a	r_x	**E**	$\Delta\nu$
HF	2.031	2.966	–17.1	–231.4	2.073	3.007	–17.1	–225.5
HCl	2.167	3.465	–13.5	–140.5	2.354	3.645	–8.7	–106.4

[a] Distance between the H atom and the center of the contacting C–C bond

For comparison, geometry optimization of the cyclopropane–HX complex, corresponding to the complex II, was carried out at the MP2/aug–cc–pVDZ and B3LYP/aug–cc–pVTZ levels of theory. Selected properties are listed in Table 5. Interaction energies are about two times larger than those of the cyclopropanone–HX complexes II. Calculated geometry parameters are in good agreement with those reported experimentally [8,9] and theoretically [12,14]. Dipole moments for the HF and HCl complexes are calculated to be 2.74 and 1.89 D, respectively. The distances (r_x) between the X atom and the center of the contacting C–C bond of cyclopropane were experimentally obtained to be 3.021 and 3.567 Å for the HF [8] and HCl [9] complexes, respectively. Calculated vibrational frequency shifts of HF and HCl are in good agreement with the experimentally observed shifts of 201 and 97 cm^{-1}, respectively [24]. On the basis of these results, the properties of the HF complex are well reproduced at both calculation levels. However, the HCl complex is more sensitive to the calculation levels. In the C_{2v} complex, a donor H–X molecule interacts with electrons in a pseudo π orbital. From the electrostatic considerations, one of the reasons of the difference in interaction energies between the cyclopropane–HX complexes and cyclopropanone–HX complexes II may be attributed to the difference in the negative charge of the acceptor orbital.

3.2 Vibrational Spectra

Vibrational analysis is performed by the density functional and *ab initio* correlated methods. As the DFT frequencies are known to be in better agreement with the experimental values than those of the MP2 calculations, we discuss the frequency shifts based on the results by the B3LYP calculation. Cyclopropanone belongs to the C_{2v} point group symmetry and hence the three A_2 symmetry vibrations are infrared inactive. In complex II, the corresponding vibrations are still inactive while in complex I, these vibrations gains the intensities because the C_{2v} symmetry is broken by the complexation. At the B3LYP/aug–cc–pVTZ level, the stretching vibrational frequencies of HF and HCl monomers are calculated to be 4070.2 and 2935.8cm^{-1}, respectively. For cyclopropanone monomer, the calculated C=O stretching vibrational frequency is 1921.3 cm^{-1}.

Table 6. Unscaled harmonic vibrational frequencies (cm^{-1}) and intensities (km mol^{-1}) calculated at the B3LYP/aug–cc–pVTZ level of theory. Changes in values from the corresponding monomer are given in parentheses.

	Complex I				Complex II			
	ν		I		ν		I	
HF								
$\nu_{C=O}$	1903.7	(–17.5)	424.8	(+64.2)	1931.1	(+9.8)	364.7	(+4.1)
ν_{HF}	3579.0	(–491.2)	1280.0	(+1168.5)	3925.7	(–144.5)	547.0	(+435.6)
ν^a	221.1		14.5		103.9		1.3	
HCl								
$\nu_{C=O}$	1901.8	(–19.5)	481.0	(+120.4)	1926.7	(+5.5)	389.2	(+28.6)
ν_{HCl}	2599.6	(–336.2)	1092.1	(+1051.3)	2889.1	(–46.7)	213.2	(+172.4)
ν^a	142.3		23.8		51.1		0.8	

[a] Intermolecular stretching

Table 6 shows the selected unscaled vibrational frequencies and infrared intensities of the complexes calculated at the B3LYP/aug–cc–pVTZ level. Frequency changes well reflect the geometry changes. Significant changes in frequency and intensity take place in the H–X stretching vibration. The HF and HCl vibrations of the complex I are found to absorb at 3579.0 and 2599.6 cm^{-1}, respectively. Frequency shifts in the HX moiety of the complex I from corresponding monomer are greater than those of the complex II. As the magnitude of the shift in HX stretching vibrational frequency is known to represent a measure of the intermolecular interaction, the difference in frequency is in good agreement with that in interaction energy. As compared with the cyclopropane–HX complexes (HF: 3844.7 cm^{-1}, HCl: 2829.4 cm^{-1}), the H–X frequency shifts of the complex II are smaller, indicating weaker interaction. As for the cyclopropanone moiety, the C=O stretching vibrational frequencies show the red shifts for the complex I and contrarily the blue shifts for the complex II. Intermolecular stretching vibrational frequencies are ranging from 51.1 to 221.1 cm^{-1}.

Table 7. Natural atomic charges of monomers and changes in natural atomic charges of the cyclopropanone–HX complexes

Atom	Δq / e				q / e
	Complex I		Complex II		Monomer
	HF	HCl	HF	HCl	
C1	23.2	15.6	8.8	8.4	0.70237
O2	–46.8	–27.8	17.1	12.9	–0.61769
C3	10.7	9.0	–34.6	–24.4	–0.51324
C4	7.6	7.9	–34.6	–24.4	–0.51324
H5	9.8	9.0	11.5	8.0	0.23545
H6	9.8	9.0	11.5	8.0	0.23545
H7	7.3	6.2	11.5	8.0	0.23545
H8	7.3	6.2	11.5	8.0	0.23545
H9	24.5		10.6		0.57564
F10	–53.4		–13.2		–0.57564
H9		38.4		0.3	0.28256
Cl10		–73.5		–5.0	–0.28256

3.3 Charge Distribution

To clarify the nature of the complexation, the NBO analysis was carried out. Table 7 gives the natural atomic charges (q) for monomers and the changes in natural atomic charges (Δq) for the complexes calculated with the aug–cc–pVDZ basis set. In complex I, the in–contact O2 and X10 atoms gain charges. In complex II, the O2 atom loses charge while the in–contact C3 and C4 atoms gain charges. The net CT was evaluated to be from cyclopropanone to HX by 29.0 and 2.6 me for the HF complexes I and II, respectively, and 35.1 and 4.6 me for the HCl complexes I and II, respectively. In case of the cyclopropane–HX complexes the changes in natural atomic charges for in–contact C atoms and halogen atom are –40.3 and –24.5 me, and –29.8 and –22.0 me for the HF and HCl complexes, respectively. The net CT values are 4.9 and 7.6 me for the HF and HCl complexes, respectively.

Table 8. Charge transfer interactions in the cyclopropanone–HX complexes. The changes in the orbital population are given in me.

Parameter [a]	Complex I		Complex II	
	HF	HCl	HF	HCl
intermolecular				
$E^{(2)}$ $n_{1\ O2} \rightarrow \sigma^*_{\ H9–X10}$	22.0	20.7		
$E^{(2)}$ $n_{2\ O2} \rightarrow \sigma^*_{\ H9–X10}$	65.2	67.7		
$E^{(2)}$ $\sigma_{\ C3–C4} \rightarrow \sigma^*_{\ H9–X10}$			10.7	11.5
intramolecular				
$\Delta E^{(2)}$ $\sigma_{\ C3–C4} \rightarrow \sigma^*_{\ C1–O2}$	+7.0	+7.3	–3.8	–1.7
$\Delta n_{1\ O2}$	–7.4	–7.8	0.0	–0.1
$\Delta n_{2\ O2}$	–4.0	–12.6	–2.8	–2.5
$\Delta\sigma^*_{\ C3–C4}$	–1.4	–0.9	+3.4	+2.4
$\Delta\sigma^*_{\ C1–O2}$	+2.7	+2.6	–1.9	–1.3
$\Delta\pi^*_{\ C1–O2}$	+6.6	+5.8	–0.9	–1.1
$\Delta\sigma_{\ H9–X10}$	–1.2	–1.7	–1.2	–1.2
$\Delta\sigma^*_{\ H9–X10}$	+29.3	+34.8	+4.9	+6.7

[a] The second–order perturbation energies are given in kJ mol^{-1}

Table 8 gives the second–order perturbation energies ($E^{(2)}$) and the changes in electron density in the orbitals. The distinctive intermolecular CT interactions for the complexes I and II are $n_{O2} \rightarrow \sigma^*_{H9–X10}$ and $\sigma_{C3–C4} \rightarrow \sigma^*_{H9–X10}$, respectively. The corresponding $E^{(2)}$ values for $\sigma_{C–C} \rightarrow \sigma^*_{H–X}$ of the cyclopropane–HX complexes are calculated to be 10.3 and 11.6 kJ mol^{-1} for the HF and HCl complexes, respectively. The population decreases in $\sigma_{H9–X10}$ orbital and increases in $\sigma^*_{H9–X10}$ orbital lead to elongations of the H9–X10 bond and red shifts of the H9–X10 stretching vibrational frequencies. The opposite changes in C=O bond lengths of the complexes I and II are easily explained. The $\sigma^*_{C1–O2}$ and $\pi^*_{C1–O2}$ orbitals gain population in complex I and lose population in complex II. The following features may contribute to the complex formation and make the cyclopropane–HX complexes more stabilized than the cyclopropanone–HX complexes II. Complexation resulted in the charge rearrangement in the components. Each component of the cyclopropane–HX complexes becomes more polarized than that of the cyclopropanone–HX complexes II. Dipole–induced dipole interaction is great in the former complexes. The $\sigma_{C–C}$ orbital populations for cyclopropane and cyclopropanone are 1.9675 and 1.9411 e, respectively. There are also differences in the magnitude of bond bending, that is, deviation of highest electron density from the line of nuclear centers. For cyclopropane and cyclopropanone the values are calculated to be 23.0 and 25.8 degrees, respectively.

4 CONCLUSIONS

Cyclopropanone complexes with HF and HCl have been studied by *ab initio* and DFT calculations. Two types of complexes exist according to whether the H atom of HX interacts with the C=O n orbital or C–C π like orbital of cyclopropanone. The former complex is more stabilized than the latter. HX molecules are good probe for the magnitude of the interaction. The stronger the interaction energy, the longer the bond length and the lower the stretching vibraional frequency. NBO analysis reveals that the intermolecular CT from cyclopropanone to HX takes place followed by the intramolecular charge rearrangement. Large contributions from the n_O to the $\sigma^*_{H\text{–}X}$ in complex I and from the contacting $\sigma_{C\text{–}C}$ to the $\sigma^*_{H\text{–}X}$ in complex II are found.

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