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# Intramolecular hydrogen-atom tunneling and photoreaction mechanism of 4-bromo-2-chloro-6-fluorophenol in low-temperature argon matrices

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#### ABSTRACT

Infrared spectra of 4-bromo-2-chloro-6-fluorophenol in low-temperature argon matrices were measured with an FTIR spectrometer. Despite that an F-type geometrical isomer, which has an intramolecular hydrogen bond of OH···F, is as stable in the CCl<sub>4</sub> solution at room temperature as a Cl-type geometrical isomer, which has that of OH···Cl, no infrared bands of the F-type were observed in an argon matrix at 20 K. This implied that the F-type changed to the more stable Cl-type by hydrogen-atom tunneling in the argon matrix. To confirm the tunneling isomerization, similar experiments on the deuterated species were performed, resulting in that an O–D stretching band of the F-type appeared as well as that of the Cl-type. This finding suggested that a deuterium is inhibited from the tunneling migration. The UV-induced photoreaction pathways of 4-bromo-2-chloro-6-fluorophenol were additionally examined, resulting in that 2-fluoro-4-bromocyclopentadienylidenemethanone was produced from the Cl-type by Wolff rearrangement after dissociation of the H atom in the OH group and the Cl atom. However no cyclohexadienone derivative, which is analogous to a photoproduct of a parent molecule, 2-chloro-6-fluorophenol, was produced upon UV irradiation. It is concluded that the bromine atom located at the 4th position disturbs the intramolecular migration of the Cl atom.

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# 1. Introduction

Recently we have investigated the stable conformational isomers, intramolecular hydrogen-atom tunneling, and UV-induced photoreaction mechanisms of a series of 2-halogenophenols in low-temperature rare-gas matrices [1-8]. It was concluded that only the syn isomer, which has an intramolecular hydrogen bond of OH···X, exists in the low-temperature rare-gas matrices. In addition, the intermediates and final products yielded from 2-halogenophenols upon UV irradiation were identified with an aid of density-functional-theory (DFT) calculations. For example, an infrared (IR) spectrum of 2-hydroxyphenyl radical (HPR) produced by detachment of the iodine atom from 2-iodophenol was first observed and assigned [1]. As for 2-chlorophenol [4] and 2-bromophenol [2], two photoreaction pathways were confirmed; one product is a five-membered ring ketene, 2,4-cyclopentadiene-1-ylidenemethanone (CPYM), via a ketocarbene by Wolff rearrangement immediately after capture of the H atom in the OH group by a halogen atom X, as shown in Scheme 1, where X = Cl or Br. The other product is 4-halogeno-2,5-cyclohexadienone (4X-CHD) yielded by migration of a halogen atom X to the 4th position and the H atom in the OH group to the 2nd position. The branching ratio of the two photoreaction pathways depends on the kind of halogen atoms, i.e., 2-bromophenol prefers 4X-CHD, whereas 2-chlorophenol prefers CPYM [2,4].

On the other hand, 2.6-heterodihalogenophenols have two stable isomers having an intramolecular hydrogen bond of OH···X or  $OH \cdots Y$ . The energy difference between the two isomers is so small that they co-exist in the gas phase and in the CCl<sub>4</sub> solution [9]. However, we observed an IR spectrum of only one isomer of 2-chloro-6-fluorophenol in low-temperature matrices [7]. In addition, the UV-induced photoproducts of only the Cl-type were obtained by detachment or intramolecular migration of H and Cl atoms, but no photoproducts of the F-type were observed. To explain this notable finding, we assumed the tunneling isomerization of the H atom in the OH group from the F type, which has an intramolecular hydrogen bond of OH···F, to the more stable Cl-type geometrical isomer, which has an intramolecular hydrogen bond of OH. Cl. This assumption was confirmed by a similar experiment on the deuterated species, where two O-D stretching IR bands for the both isomers were observed even in a low-temperature matrix by inhibition of deuterium tunneling migration.

In the present study, 4-bromo-2-chloro-6-fluorophenol (4Br-2Cl-6F-Phe) has been chosen as a target molecule. This molecule is expected to have two stable isomers of the Cl-type and the F-type like 2-chloro-6-fluorophenol. We examine the influence of the bromine atom located at the 4th position on tunneling





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isomerization by using normal and deuterated isotope species. We also examine the influence of the bromine atom on photoreaction pathways and conclude that the intramolecular migration of the Cl atom to the 4th position to produce a CHD derivative is disturbed by the bromine atom.

## 2. Experimental and calculation methods

A sample of 4Br-2Cl-6F-Phe was purchased from Wako Pure Chemical Industries and used after vacuum distillation. The solid sample was put in a way of a vacuum line, on the surface of which argon gas (Taiyo Toyo Sanso, 99.9999% purity) was flowed to vaporize the solid sample. After mixing the sample/argon gas with pure argon gas, introduced through another vacuum line so as to get the satisfaction for the isolation, the mixed gas was deposited on a CsI plate in a vacuum chamber, which was cooled to about 20 K by a closed-cycle helium-refrigeration unit (CTI Cryogenics, Model SC). A deuterated sample, in which the H atom in the OH group was replaced with a D atom, was prepared as follows: The solid sample of 4Br-2Cl-6F-Phe (0.5 g) was solved in heavy water,  $D_2O$  (purity > 99.8%, 20 ml); the solution was stirred for 1 week; the solid sample obtained by vacuum filtration was dried in a desiccator for 5 days. The deuteration ratio (D/H) was estimated from the IR band intensities in an argon matrix to be about 0.19/1. IR spectra of the matrix samples were measured with an FT-IR spectrometer (JEOL, Model JIR-7000). The band resolution was 0.5 cm<sup>-1</sup> and the number of accumulation was 64. UV radiation from a superhigh-pressure mercury lamp (Ushio, SX-UI-500HQ) was used to induce photoreaction, where a water filter was used to remove thermal reactions and a cut-off optical filter, UV25 (HOYA), to choose irradiation wavelength ( $\lambda > 240$  nm). Other experimental details were reported previously [10,11].

An IR spectrum of 4Br-2Cl-6F-Phe in CCl<sub>4</sub> solution was measured with the same spectrometer. A liquid cell composed of KBr crystal plates with a space of a thickness of 100  $\mu$ m was used. The solvent of CCl<sub>4</sub> (purity > 99.8%) was purchased from Wako



Fig. 1. Two stable isomers of 4Br-2Cl-6F-Phe.

Pure Chemical Industries, and the concentration of the solution was 48 mg/mL. The spectral resolution was  $4 \text{ cm}^{-1}$ .

DFT calculations were carried out with the 6-31++G<sup>\*\*</sup> basis set using the Gaussian03 program [12]. Beck's three-parameter hybrid density functional [13], in combination with the Lee–Yang–Parr correlation functional (B3LYP) [14], was used to optimize the geometrical structures and to obtain relative energies and IR spectral patterns. A linear scaling formula of 0.9894–1.04 × 10<sup>-5</sup>  $v_{calcd}$  proposed in our previous study [15] was used to reproduce the observed wavenumbers in the wide range of 600 and 4000 cm<sup>-1</sup>.

### 3. Results and discussion

#### 3.1. IR spectra and conformation of the reactant

As shown in Fig. 1, 4Br-2Cl-6F-Phe has two stable isomers. Since there are neither experimental nor theoretical reports on the energy difference between the two isomers, to our knowledge, we measured an IR spectrum of the sample in CCl<sub>4</sub> solution at room temperature before the matrix-isolation experiments.

The O–H stretching region of the solution is shown in Fig. 2, where two strong bands appear around 3574 and 3542 cm<sup>-1</sup>. The former is assignable to the F-type, while the latter to the Cl-type, judging from the calculation results obtained by the DFT method, as described later, and by comparison with the previous studies on other heterodihalogenophenols in CCl<sub>4</sub> solution by IR spectroscopy [9]. The absorption ratio for the observed two IR bands is 0.85, from which the energy difference between the two isomers can be approximately estimated to be 0.99 kJ mol<sup>-1</sup>, according to the Boltzmann's distribution law at 300 K, if the ratio of the absorption coefficients for the IR bands obtained by the DFT method, 43:34, is true. We also calculated the energy difference between the isomers by the DFT method, resulting in that the Cl-type is more stable than the F-type by 0.05 kJ mol<sup>-1</sup> after zero-point-energy (ZPE) correction. The calculated value is smaller than that of our experimental result. Though IR spectral patterns calculated by the DFT method can reproduce the corresponding observed matrix IR spectra satisfactorily, it is known that the quantum-chemical calculations are difficult to reproduce the small energy difference between isomers, depending on the calculation methods and the size of basis sets [16].

Though the population ratio of isomers in the gas phase at room temperature before deposition may be changed to some extent in the low-temperature matrix by conformational cooling [17], IR bands of the two isomers of 4Br-2Cl-6F-Phe could be observed in



**Fig. 2.** An observed IR spectrum in the O–H stretching region of 4Br-2Cl-6F-Phe in  $CCl_4$  solution measured at room temperature: The concentration is 48 mg/mL.



**Fig. 3.** Observed and calculated IR spectra of 4Br-2Cl-6F-Phe: (a) Observed spectrum measured in an argon matrix at 20 K and spectral patterns of (b) Cl-type and (c) F-type, calculated at the DFT/B3LYP/6-31++G<sup>\*\*</sup> level. A linear scaling formula of 0.9894–1.04  $\times$  10<sup>-5</sup>  $\nu_{calc}$  is used [15].

the matrix as well as in the CCl<sub>4</sub> solution. However, only one band was observed at  $3556 \text{ cm}^{-1}$  in the O–H stretching region between 3400 and 3800  $\text{cm}^{-1}$ , as shown in Fig. 3. This implies that the less stable isomer changed to the more stable isomer through the hydrogen-atom tunneling isomerization around the C-OH bond. As a result, the population ratio of the two isomers changed to be less than 0.01, which was calculated at the matrix temperature of 20 K using the energy difference of 0.99 kJ mol<sup>-1</sup> obtained from the relative intensity of the IR bands in the CCl<sub>4</sub> solution at room temperature. The barrier to interconversion is estimated to be at least 21 kJ mol<sup>-1</sup>, which is the sum of the rotational barrier of phenol [18], 14 kJ mol<sup>-1</sup>, and the stabilizing energy due to hydrogen bonding of 2-chlorophenol [7], 7 kJ mol<sup>-1</sup>. Then, our assumption is reasonable because the barrier to interconversion is too high for thermal equilibrium to be approached at 20 K without tunneling isomerization [17].

To confirm which isomer exists in the matrix, we calculated the spectral patterns of the Cl-type and the F-type by the DFT method and compared them with the observed IR spectrum. As shown in Fig. 3, the spectral patterns of the two isomers in the spectral region between 800 and 1800 cm<sup>-1</sup> are similar to each other. However, the wavenumber of the O–H stretching band for the F-type,  $3608 \text{ cm}^{-1}$ , is different from that of the Cl-type,  $3576 \text{ cm}^{-1}$ . Since the latter is close to the observed wavenumber,  $3556 \text{ cm}^{-1}$ , we assumed that the species existing in the matrix is only the Cl-type, which is more stable than the F-type in the CCl<sub>4</sub> solution at room temperature by 0.99 kJ mol<sup>-1</sup>. This is consistent with the fact that only the Cl-type for 2Cl-6F-Phe exists in an argon matrix [7]. The observed and calculated wavenumbers and relative intensities are compared in Table 1. Since most of the bands show splitting, one may claim that both the Cl-type and the F-type co-exist in the matrix. However, our assignment is credible because only one O-H stretching band is observed. Then we assume that the band splitting is due to the matrix effect.

To confirm the tunneling isomerization, we carried out a similar experiment using the deuterated species. In contrast to the result for the normal species, two IR bands were observed at 2627 and 2659 cm<sup>-1</sup> in the O–D stretching region, as shown in Fig. 4, implying that the deuterium tunneling isomerization is inhibited. Since the calculated wavenumbers for the Cl-type and the F-type are 2632 and 2656 cm<sup>-1</sup>, respectively, the observed bands of 2627 and 2659 cm<sup>-1</sup> are assignable to the Cl-type and the F-type, respectively. The intensity of the Cl-type band is much stronger than that of the F-type band. The ratio of the intensities is estimated to be 0.58, which is inconsistent to some extent with the result observed in the CCl<sub>4</sub> solution shown in Fig. 2, probably because

Table 1

Observed and calculated wavenumbers and relative intensities for 4Br-2Cl-6F-Phe.

Obsd.		Calcd. <sup>a</sup> (Cl-Type)		Calcd. <sup>a</sup> (F-Type)	
v/cm <sup>-1</sup>	Int. <sup>b</sup>	$v/cm^{-1}$	Int. <sup>c</sup>	v/cm <sup>-1</sup>	Int. <sup>c</sup>
3556 (2659	S	3576	34	3608 2656	43 23) <sup>d</sup>
(2627		2632	17) <sup>d</sup>		,
1623	w	1602	3	1602	1
1607 m 1599 m	m	1585	21	1584	23
$\begin{bmatrix} 1490\\ 1482 \end{bmatrix}$	VS	1481	100	1482	100
$\begin{bmatrix} 1424 \\ 1415 \end{bmatrix}$	m	1409	14	1406	20
1330	S	1334	13	1340	13
$1290 \\ 1280 \end{bmatrix}$	m	1281	12	1277	16
1250 1246 1242	S	1236	54	1234	36
$\begin{bmatrix} 1222\\ 1206 \end{bmatrix}$	S	1221	6	1208	18
1157	S	1143 1055	29 4	1138 1052	17 5
922 920	m	904	18	900	38
<sup>849</sup> 842 ] m	m	838	6	843	6
=0.4		743	8	750	9
$\binom{721}{718}$	m	713	25	716	21

aCalculated at DFT/B3LYP/6-31++G^\*\* level. A linear scaling formula of 0.9894–  $1.04\times 10^{-5}\nu_{calc}$  is used.

<sup>b</sup>Letters represent relative intensities; vs, s, m, and w denote very strong, strong, medium, and weak, respectively.

<sup>c</sup>Relative intensities.

<sup>d</sup>O-D stretching mode of deuterated species in an argon matrix.



**Fig. 4.** Observed and calculated IR spectra of deuterated species in the O–D stretching region. See the caption of Fig. 3.

the gas-phase molecules were frozen gradually with thermal isomerization on the cold plate during sample deposition by conformational cooling. If this is true, the thermal equilibrium temperature in deposition can be estimated to be 140 K from the population ratio of the IR bands, according to Boltzmann's distribution law using the energy difference of 0.99 kJ mol<sup>-1</sup>.

#### 3.2. Photoproducts by UV irradiation

When the matrix sample was exposed to UV light coming from a superhigh-pressure mercury lamp, spectral changes were



**Fig. 5.** Observed spectral changes and calculated IR spectral patterns: (a) Difference spectrum of 2Cl-6F-Phe between spectra measured after minus before 60-min UV irradiation ( $\lambda > 240$  nm), (b) difference spectrum of 4Br-2Cl-6F-Phe between spectra measured after minus before 60-min UV irradiation ( $\lambda > 240$  nm), and calculated spectral patterns of (c) O-Complex, (d) F-Complex, and (e) Br-Complex between 4Br-2Cl-6F-Phe and HCl. A linear scaling formula of 0.9894–1.04 × 10<sup>-5</sup> $\nu_{calc}$  is used [15]. See Fig. 6 for the structures of the complexes. A band with a symbol of \* is due to CO<sub>2</sub> in atmosphere.

observed. Fig. 5b shows a difference spectrum between the spectra measured before and after 2-min UV irradiation ( $\lambda > 240$  nm). The decreasing and increasing bands are due to a reactant and a photoproduct, respectively. A weak band appearing at 2858 cm<sup>-1</sup> is due to HCl, suggesting that the H atom in the OH group and the Cl atom were dissociated upon UV irradiation. The strongest band around 2150 cm<sup>-1</sup> is characteristic for the C=C=O stretching mode of ketene derivatives. Since similar strong bands were observed in the photolysis of other 2-halogenophenols [1–8], the 2150 cm<sup>-1</sup> band is assignable to a five-member-ring ketene, i.e., 4-bromo-2-fluoro-CPYM (4Br-2F-CPYM). Neither bands of the F-type before UV irradiation nor a band of HF after the irradiation were observed, leading to the conclusion that 4-bromo-2-chloro-CPYM (4Br-2Cl-CPYM) was not produced by detachment of HF from the F-type upon UV irradiation.

In the case of 2CI-6F-Phe, another product, 4CI-2F-CHD, was obtained upon UV irradiation by migration of the Cl atom to the 4th position and the H atom in the OH group to the 2nd position besides 2F-CPYM [7]. The difference spectrum of 2CI-6F-Phe is redrawn in Fig. 5a, where the C=O stretching mode of 4CI-2F-CHD appears at 1694 cm<sup>-1</sup>. If a similar photoreaction occurs in the present sample of 4Br-2CI-6F-Phe, 4Br-4CI-2F-CHD could be produced by migration of the Cl and H atoms. However, no character-



Fig. 6. Structures of three possible complexes between 4Br-2Cl-6F-Phe and HCl.

istic band due to the C=O stretching mode was observed around 1700 cm<sup>-1</sup>, as shown in Fig. 5b, Therefore we conclude that 4Br-4Cl-2F-CHD was not produced because the bromine atom located at the 4th position disturbs recombination of the Cl atom detached by UV irradiation. A photoreaction mechanism of 4Br-2Cl-6F-Phe is summarized in Scheme 2.

In the production of 4Br-2F-CPYM, the detached HCl band that appeared at 2858 cm<sup>-1</sup> was shifted from the argon matrix value of the isolated monomer at 2888 cm<sup>-1</sup> [19], implying that HCl interacts with 4Br-2F-CPYM. There are three possible complexes between 4Br-2F-CPYM and HCl, i.e., O-complex, where HCl interacts at the part of C=C=O, and F-complex and Br-complex, as shown in Fig. 6. To determine which complex was produced in the matrix upon UV irradiation, we calculated the spectral patterns of the three complexes and compared them with the observed spectrum in Fig. 5. The spectral patterns of 4Br-2F-CPYM in the three complexes are nearly equal to one another, implying that there is little influence of the position on the intermolecular interaction. On the other hand, the wavelengths of HCl are totally different from one another, being calculated to be 2812, 2786, and 2689 cm<sup>-1</sup> for the O-complex, the F-complex, and the Br-complex, respectively, reflecting the strength of intermolecular hydrogen bonds. Since the wavenumber of the O-complex corresponds to that of the observed band, we conclude that HCl interacts with 4Br-2F-CPYM at the part of C=C=O. This result is consistent with those of 2Cl-6F-Phe [7] and 2-chlorophenols [4].

Our assignment can be supported by the analysis of the C=C=O stretching mode. The calculated wavenumbers of the O-complex,



#### Table 2

Observed and calculated wavenumbers and relative intensities for 4Br-2F-CPYM-HCl complexes.

Obsd.		Calcd. <sup>a</sup>							
		O-Complex <sup>b</sup>		F-Complex <sup>b</sup>		Br-Complex <sup>b</sup>			
$v/cm^{-1}$	Int. <sup>c</sup>	v/cm <sup>-1</sup>	Int. <sup>d</sup>	v/cm <sup>-1</sup>	Int. <sup>d</sup>	v/cm <sup>-1</sup>	Int. <sup>d</sup>		
2858	m	2812	10	2786	12	2689	31		
2177	w								
2157	w			2151	100	2153	100		
2145	VS	2142	100						
1591	m	1582	13	1576	14	1576	14		
1488	w	1494	2	1490	3	1491	4		
1436	w	1426	4	1432	5	1431	5		
1320	w	1301	3	1303	5	1304	4		
1289	w	1273	4	1273	5	1280	4		
1284									
1186	m	1174	0	1174	0	1175	0		
1120	w	1095	2	1090	4	1100	2		
1106	w	1054	2	1058	2	1057	1		
889	w	915	1	951	2	905	2		
877	w	867	1	869	1	865	2		
788	w	770	0	776	0	770	0		
739	w	734	3	731	4	734	3		
		687	2	692	2	678	2		
		660	0	660	0	659	0		

 $^a$  Calculated at DFT/B3LYP/6-31++G\*\* level. A linear scaling formula of 0.9894–1.04  $\times$  10  $^{-5}$   $\nu_{calc}$  is used.

<sup>b</sup> Structures are defined in Fig. 6.

<sup>c</sup> Letters represent relative intensities; vs, m, and w denote very strong, medium, and weak, respectively.

<sup>d</sup> Relative intensities.

the F-complex, and the Br-complex are 2142, 2151, and 2153 cm<sup>-1</sup>, respectively. It is found in Table 2 that the wavenumber of the O-complex is very close to the observed value among the three complexes, though the difference is small. In the higher-wavenumber side of the C=C=O stretching band, a few very weak bands appeared, which may be due to other complexes. We calculated the relative energies of the three complexes by the DFT method, resulting in that the most stable complex is the Br-complex whereas the least stable one is the O-complex, though the relatively small energy difference of isomers is not so credible, as described before. This finding implies one possibility that the HCl molecule generated from the H atom in the OH group and the Cl atom stays near the C=C=O part and immediately forms the O-complex before migration to the distant Br and F atoms in an argon cage.

### 4. Summary

An IR spectrum of 4Br-2Cl-6F-Phe in the CCl<sub>4</sub> solution was measured at room temperature, where two O—H stretching bands were observed and assigned to Cl-type and F-type isomers. Only the IR band of the Cl-type was observed in the argon matrix at 20 K, suggesting that the less stable F-type changed to the more stable Cl-type by intramolecular hydrogen-atom tunneling. This was supported by a similar experiment of the deuterated species, where two O—D stretching IR bands for the both isomers were observed by inhibition of the hydrogen-atom tunneling. When the matrix sample was exposed to UV light ( $\lambda > 240$  nm), 2F-4Br-CPYM was produced from the Cl-type by Wolff rearrangement after dissociation of the H atom in the OH group and the Cl atom. The HCl molecule was found to interact with 2F-4Br-CPYM at the C=C=O part. The absence of another product, 4Br-4Cl-2F-CHD, which could be produced by migration of the Cl atom to the 4th position and the H atom to the 2nd position, is interpreted as that the Br atom located at the 4th position disturbs the migration of the Cl atom.

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