

# Matrix Isolation and Computational Study on the Photolysis of $\text{CHCl}_2\text{COCl}$

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Received 24 May 2014; revised 20 June 2014; accepted 15 July 2014

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## Abstract

UV light photolysis of dichloroacetyl chloride ( $\text{CHCl}_2\text{COCl}$ ) has been investigated by infrared spectroscopy in cryogenic Ar, Kr, Xe, and  $\text{O}_2$  matrices. The formation of  $\text{CHCl}_3$  and CO was found to be the dominant process over the ketene formation. The C-C bond cleaved products  $\text{CHCl}_2$  and COCl were also observed. As the number of the chlorine atom substitution to methyl group of acetyl chloride increased, the C-C bond cleaved product yield in the triplet state increased, which can be attributed to an internal heavy-atom effect where the intersystem crossing rate was enhanced.

## Keywords

Dichloroacetyl Chloride, Photolysis, Cryogenic Matrix

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## 1. Introduction

Dichloroacetyl chloride ( $\text{CHCl}_2\text{COCl}$ ) is known to be produced in the oxidation of chlorinated ethenes [1]-[4]. In the chlorine atom initiated oxidation of chlorinated ethenes, relatively high product yields of chlorinated acetyl chloride were reported by Hasson and Smith [5]. Conformations of  $\text{CHCl}_2\text{COCl}$  were studied by vibrational spectroscopy [6]-[9], electron diffraction [10], and theoretical method [11]. Two conformers exist in the  $\text{CHCl}_2$  internal rotation potential: *syn* conformer having an H-C-C=O dihedral angle of  $0^\circ$  and *gauche* conformer having a non-zero value of the dihedral angle. As for the photolysis of chlorinated acetyl chloride in rare gas matrix, one chlorine atom substitution to methyl group of acetyl chloride opened the additional reaction paths in the  $T_1$  state [12] [13]. Without chlorination the ketene...HCl complex was exclusively produced in the  $S_0$  state after the internal conversion from the  $S_1$  state [14] [15]. In the  $\text{CCl}_3\text{COCl}$  photolysis in an Ar matrix, the C-C bond cleavage was found to be the major reaction path [16].

In the present study, the UV light photolysis of  $\text{CHCl}_2\text{COCl}$  was investigated in cryogenic Ar, Kr, Xe, and  $\text{O}_2$

matrices with the aid of the calculation using the B3LYP and MP2 methods to clarify how the two chlorine atom substitutions affect the reaction mechanism.

## 2. Experimental

Light irradiation was performed using a low pressure mercury arc lamp (HAMAMATSU L937-04,  $\lambda > 253.7$  nm). IR spectra were measured in the range 4000 - 700  $\text{cm}^{-1}$  with 1.0  $\text{cm}^{-1}$  resolution by a SHIMADZU 8300A Fourier transform IR spectrometer with a liquid-nitrogen-cooled MCT detector. Each spectrum was obtained by scanning over 128 times. A closed-cycle helium cryostat (Iwatani M310/CW303) was used to control the temperature of the matrix.

Argon (Nippon Sanso, 99.9999%), krypton (Taiyo Sanso), xenon (Nippon Sanso), and  $\text{O}_2$  (Okaya Sanso) were used without further purification. Dichloroacetyl chloride (Wako Pure Chemicals) was used after freeze-pump-thaw cycling at 77 K. Chloroform (Wako Pure Chemicals) was used as an authentic sample for product identification. Samples were deposited on a CsI window at 6 K.

For product identification and energetic consideration, molecular orbital calculation was utilized. Geometry optimizations were performed using the second-order Møller-Plesset theory (MP2) and density functional theory (B3LYP [17] [18], CAM-B3LYP [19], and M06-2X [20]) with the 6-311++G(3df,3pd) and aug-cc-pV(T+d)Z basis sets. Harmonic vibrational frequency calculation was performed to confirm the predicted structures as local minima and to elucidate zero-point vibrational energy corrections (ZPE). The vertical transition energy was calculated at the SAC-CI/D95+(d,p) level based on the structures optimized at the CCSD/D95+(d,p) level. All calculations were performed using Gaussian 09 [21].

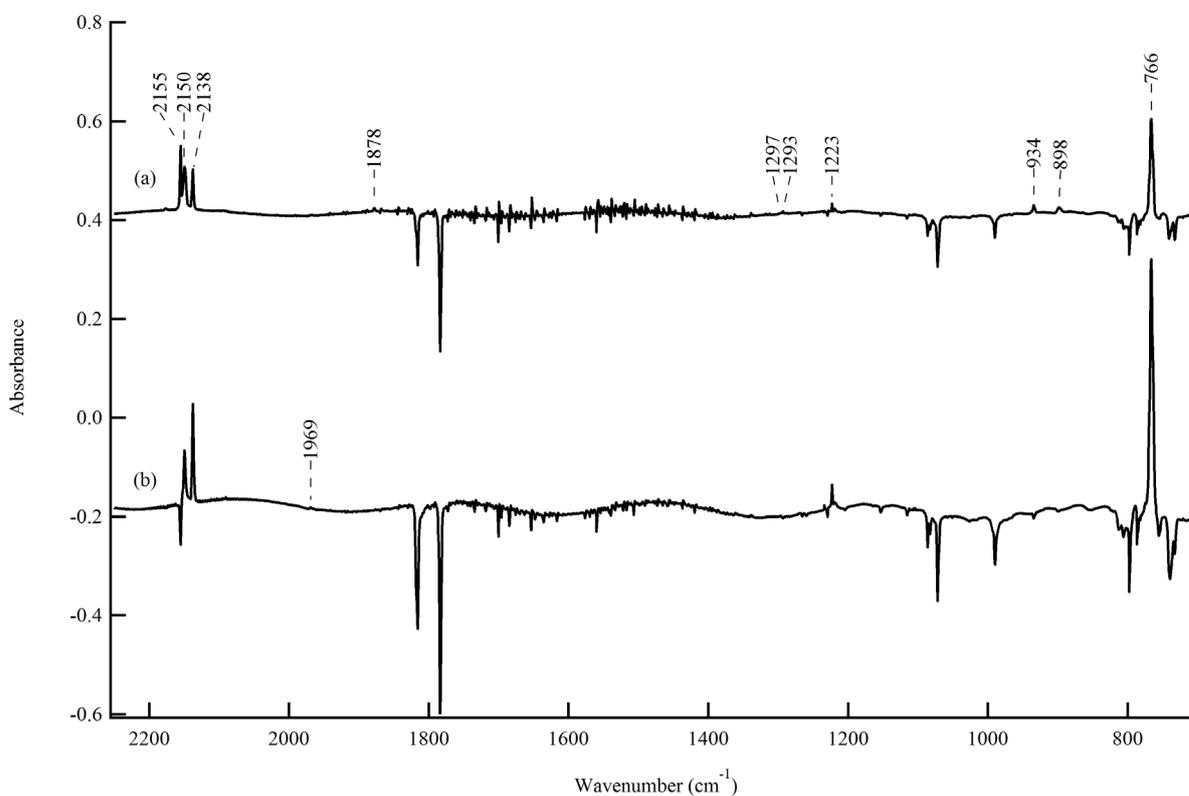
## 3. Results and Discussion

### 3.1. $\text{CHCl}_2\text{COCl}/\text{Ar}$

A mixture of  $\text{CHCl}_2\text{COCl}/\text{Ar}$  was deposited on a CsI window with a ratio of  $\text{CHCl}_2\text{COCl}/\text{Ar} = 1/1000$ . In the infrared spectrum obtained after deposition, two conformers, *gauche*- and *syn*- $\text{CHCl}_2\text{COCl}$  were distinguished by the C=O stretching vibration bands at 1816 and 1784  $\text{cm}^{-1}$ , respectively [8] [9]. **Figure 1(a)** shows the infrared difference spectrum obtained upon  $\lambda > 253.7$  nm irradiation of a matrix  $\text{CHCl}_2\text{COCl}/\text{Ar}$  for 60 min. The positive and negative bands indicate the growth and depletion, respectively, during the irradiation period. **Table 1** lists the observed wavenumbers of the growth bands. In the CO stretching region, a strong band observed at 2138  $\text{cm}^{-1}$  assignable to the CO stretching continued to grow during the prolonged irradiation period. A band at 2155  $\text{cm}^{-1}$  showed growth and decay behavior accompanied with the bands at 1293 and 934  $\text{cm}^{-1}$ , whose frequencies are consistent with those of  $\text{CCl}_2=\text{C}=\text{O}$  observed in the  $\text{CCl}_3\text{COCl}$  photolysis in Ar [16]. The bands at 2844 and 2836  $\text{cm}^{-1}$  were assigned to the stretching vibration of HCl complexed with the  $\text{CCl}_2=\text{C}=\text{O}$ . With the different growth rate from those of CO and  $\text{CCl}_2=\text{C}=\text{O}$ , three bands at 2150, 1297 and 1113  $\text{cm}^{-1}$  showed continuous growth which are assignable to the C=O stretching, C=C stretching, and C-H in-plane bending vibrations of  $\text{CHCl}=\text{C}=\text{O}$ , respectively [12]. The C-Cl stretching band observed in the photolysis of  $\text{CH}_2\text{ClCOCl}$  in Ar was difficult to be discerned due to the overlapping with the strong depletion band of *syn*- $\text{CHCl}_2\text{COCl}$ . A band at 1878  $\text{cm}^{-1}$  was assigned to the CO stretching vibration of COCl [22]. Photolysis counterpart of COCl,  $\text{CHCl}_2$ , showed the C-H bending and  $\text{CCl}_2$  antisymmetric stretching vibrations at 1219 and 898  $\text{cm}^{-1}$ , respectively [23]. Prolonged irradiation caused the depletion in intensities of the bands due to  $\text{CCl}_2=\text{C}=\text{O}$  as shown in **Figure 1(b)**. A band at 1969  $\text{cm}^{-1}$  showing an induction period was assigned to the CO stretching vibration of CCO [24]. A band at 766  $\text{cm}^{-1}$  grew continuously to be the strongest in the spectrum after 360 min irradiation, which was assigned to the C-Cl stretching vibration of  $\text{CHCl}_3$ . The C-H bending vibration of  $\text{CHCl}_3$  was observed at 1223  $\text{cm}^{-1}$ .

### 3.2. $\text{CHCl}_2\text{COCl}/\text{Kr}$ , $\text{CHCl}_2\text{COCl}/\text{Xe}$

**Figure 2** shows the infrared difference spectra obtained upon  $\lambda > 253.7$  nm irradiation of the matrix  $\text{CHCl}_2\text{COCl}/\text{Xe}$ . In Kr, similar results were obtained. In addition to the photolysis products in Ar, the products of  $\text{Kr}_2\text{H}^+$  and  $\text{Xe}_2\text{H}^+$  were observed in Kr and Xe, respectively [25]. The growth bands at 1814, 1262, 987, and 740  $\text{cm}^{-1}$  in Kr and 1809, 1259, 984, and 736  $\text{cm}^{-1}$  in Xe were assigned to the C=O stretching, CH bending, C-C stretching, and  $\text{CCl}_2$  symmetric stretching vibrations of *gauche*- $\text{CHCl}_2\text{COCl}$ , respectively [9]. It is controversial



**Figure 1.** Infrared difference spectra upon  $\lambda > 253.7$  nm irradiation of the matrix  $\text{CHCl}_2\text{COCl}/\text{Ar} = 1/1000$ . (a) 60 - 0 min and (b) 360 - 60 min.

which of the two conformers is more stable [11]. **Table 2** compares the relative electronic energies calculated at the several calculation levels. The barrier height for the conversion from the *syn* to *gauche* rotamer is calculated to be approximately  $1200\text{ cm}^{-1}$  in the  $S_0$  ground state indicating that the conversion between the *syn* and *gauche* rotamers is not expected to occur at 7 K in the absence of UV irradiation. UV irradiation yielded an increase of the population of the less stable rotamer.

### 3.3. $\text{CHCl}_2\text{COCl}/\text{O}_2$

In order to clarify the route of the ketenes and  $\text{CHCl}_3$  formation *i.e.* the radical or concerted mechanism, the reactive  $\text{O}_2$  matrix was used. **Figure 3** shows the infrared difference spectrum obtained after 480 min irradiation of  $\text{CHCl}_2\text{COCl}$ . The product bands were assigned by comparison with the spectrum observed in the photolysis of the matrix  $\text{CCl}_3\text{COCl}/\text{O}_2$ . Due to the photolysis in  $\text{O}_2$  at 253.7 nm, ozone formation is prominent at  $1038\text{ cm}^{-1}$  ( $\nu_3$ ) [26]. Other  $\text{O}_3$  absorption bands were observed at  $2107$  ( $\nu_1 + \nu_3$ ) and  $1101\text{ cm}^{-1}$  ( $\nu_1$ ) [26] [27]. The  $2342$  and  $2276\text{ cm}^{-1}$  bands are assigned to  $\nu_3$  vibrations of  $^{12}\text{CO}_2$  and  $^{13}\text{CO}_2$ , respectively. The  $2037\text{ cm}^{-1}$  band is attributed to  $\text{CO}_3$  complexed with Cl [16]. A broad band at  $1436\text{ cm}^{-1}$  was assigned to  $\text{ClOO } \nu_1$  [28]. In  $\text{O}_2$ , compared with the ratio of  $\text{CHCl}_3$  or CO absorbance with  $\text{CHCl}_2\text{COCl}$  absorbance in **Figure 1**, the CO and  $\text{CHCl}_3$  formation was depressed. Formation of  $\text{CHCl}_2$  and ketenes was negligible. Instead major product was found to be  $\text{CO}_2$  which would be produced via reactions of  $\text{COCl}$  and  $\text{CHCl}_2$  with  $\text{O}_2$ . These indicate the reaction predominantly proceed by radical mechanism in the photolysis of  $\text{CHCl}_2\text{COCl}$  similar to that of  $\text{CCl}_3\text{COCl}$ .

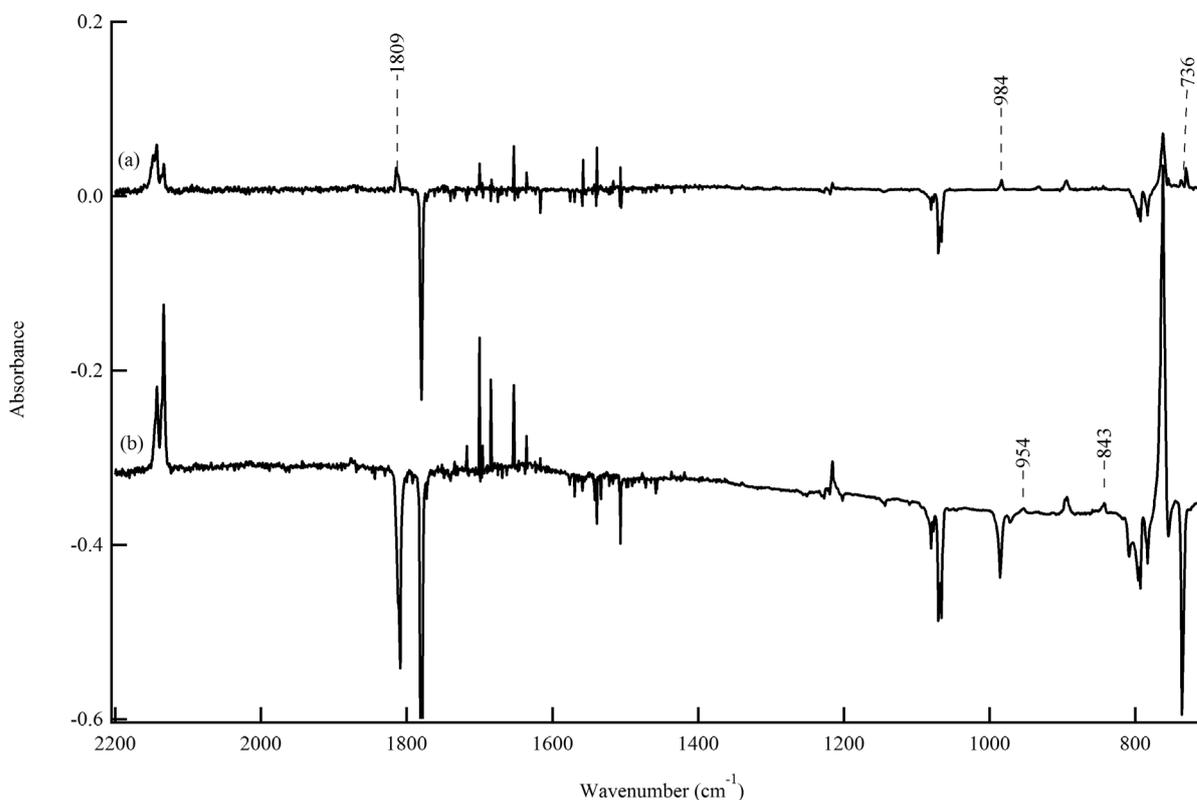
### 3.4. Reaction Mechanism

**Figure 4** shows the integrated absorbance changes of *syn*- $\text{CHCl}_2\text{COCl}$  ( $1784\text{ cm}^{-1}$ ), *gauche*- $\text{CHCl}_2\text{COCl}$  ( $1816\text{ cm}^{-1}$ ),  $\text{CHCl}_3$  ( $766\text{ cm}^{-1}$ ),  $\text{CHCl}=\text{C}=\text{O}$  ( $2150\text{ cm}^{-1}$ ), CO ( $2138\text{ cm}^{-1}$ ),  $\text{CCl}_2=\text{C}=\text{O}$  ( $2155\text{ cm}^{-1}$ ), and  $\text{CHCl}_2$  ( $898\text{ cm}^{-1}$ ) observed in Ar, where the IR intensities of these absorption bands were calculated to be 283, 242, 320, 618, 80, 621, and  $163\text{ km mol}^{-1}$ , respectively, at the B3LYP/aug-cc-pV(T+d)Z level. The *syn*- and *gauche*-

**Table 1.** FTIR spectra of the CHCl<sub>2</sub>COCl photolysis products in the Ar, Kr, Xe, and O<sub>2</sub> matrices.

Wavenumber (cm <sup>-1</sup> )				Assignment
Ar	Kr	Xe	O <sub>2</sub>	
3112				CHCl=C=O
3060				CHCl <sub>3</sub>
3054				CHCl <sub>3</sub>
2844/2836	2836/2827		2838	HCl...CCl <sub>2</sub> =C=O
2809	2809		2807	HCl
2789	2788			HCl
			2342	CO <sub>2</sub>
			2276	<sup>13</sup> CO <sub>2</sub>
2176				
2155	2154/2151	2148	2157	CCl <sub>2</sub> =C=O
2150	2146	2143	2148	CHCl=C=O
2138	2136	2134	2137	CO
			2107	O <sub>3</sub> v <sub>1</sub> + v <sub>3</sub> <sup>a</sup>
2094		2090		<sup>13</sup> CO
			2037	CO <sub>3</sub>
1969				CCO <sup>b</sup>
1878	1877	1877		COCl <sup>c</sup>
	1814	1809		<i>gauche</i> -CHCl <sub>2</sub> COCl
			1436	ClOO <sup>d</sup>
1297	1296	1293		CHCl=C=O
1293	1292	1291		CCl <sub>2</sub> =C=O
	1262	1259		<i>gauche</i> -CHCl <sub>2</sub> COCl
1223	1220	1216		CHCl <sub>3</sub>
1219	1214			CHCl <sub>2</sub> <sup>e</sup>
1113				CHCl=C=O
1107				CHCl=C=O
			1101	O <sub>3</sub> v <sub>1</sub> <sup>f</sup>
		1055		
			1037	O <sub>3</sub> v <sub>3</sub> <sup>f</sup>
	987	984		<i>gauche</i> -CHCl <sub>2</sub> COCl
	965			
		954		Xe <sub>2</sub> H <sup>+g</sup>
934	932	932		CCl <sub>2</sub> =C=O
898	896	894		CHCl <sub>2</sub> <sup>e</sup>
864	861	859		<sup>13</sup> CHCl <sub>2</sub>
	852			Kr <sub>2</sub> H <sup>+g</sup>
		843		Xe <sub>2</sub> H <sup>+g</sup>
			839	COCl <sub>2</sub>
766	764	762		CHCl <sub>3</sub>
	740	736		<i>gauche</i> -CHCl <sub>2</sub> COCl

<sup>a</sup>Ref. [27]. <sup>b</sup>Ref. [24]. <sup>c</sup>Ref. [22]. <sup>d</sup>Ref. [28]. <sup>e</sup>Ref. [23]. <sup>f</sup>Ref. [26]. <sup>g</sup>Ref. [25].



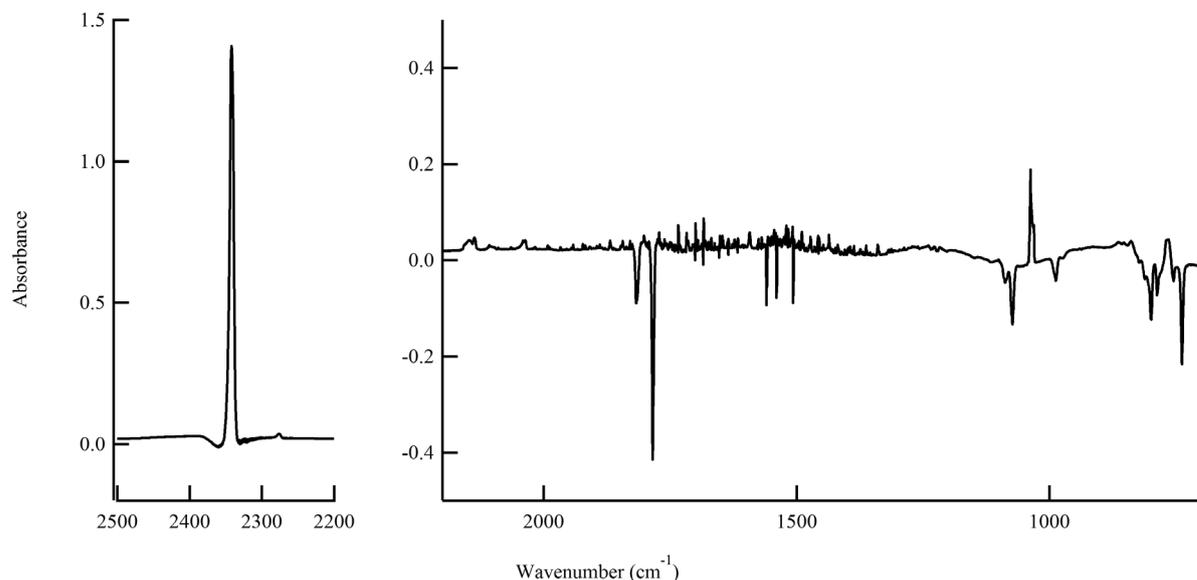
**Figure 2.** Infrared difference spectra upon  $\lambda > 253.7$  nm irradiation of the matrix  $\text{CHCl}_2\text{COCl}/\text{Xe} = 1/1000$ . (a) 30 - 0 min and (b) 420 - 30 min.

**Table 2.** Calculated relative electronic energies in  $\text{cm}^{-1}$  including zero-point vibrational energy corrections.

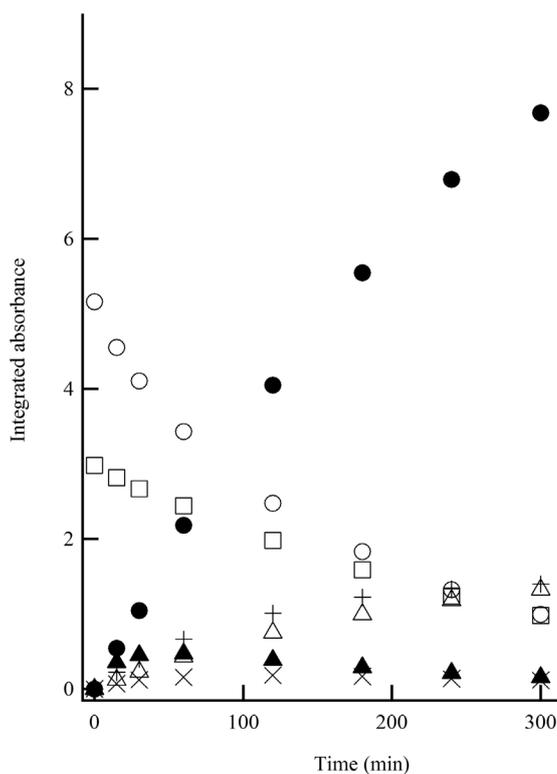
Method	Difference ( <i>gauche</i> to <i>syn</i> )	Barrier ( <i>syn</i> to <i>gauche</i> )
B3LYP/6-311++G(3df,3pd)	157	1208
B3LYP/aug-cc-pV(T+d)Z	117	1161
CAM-B3LYP/6-311++G(3df,3pd)	180	1167
CAM-B3LYP/aug-cc-pV(T+d)Z	149	1123
M06-2X/6-311++G(3df,3pd)	211	1186
M06-2X/aug-cc-pV(T+d)Z	186	1164
MP2/6-311++G(3df,3pd)	225	1316
MP2/aug-cc-pV(T+d)Z	191	1234
CCSD/aug-cc-pVDZ	132	1239

$\text{CHCl}_2\text{COCl}$  possess the different decay rates. The  $\text{CCl}_2=\text{C}=\text{O}$  and  $\text{CHCl}_2$  showed the growth and decay profiles. The relative yield of  $\text{CHCl}_3:\text{CHCl}=\text{C}=\text{O}:\text{CCl}_2=\text{C}=\text{O}$  at the irradiation time of 360 min was found to be 1:0.09:0.008. There is an obvious contrast as compared with the relative yield obtained in the photolysis of the matrix  $\text{CH}_2\text{COCl}/\text{Ar}$  where the ratio of  $\text{CH}_2\text{Cl}_2:\text{CHCl}=\text{C}=\text{O}$  was found to be 1:7.5 [12].

Even in  $\text{O}_2$ , the ketene species were found to be produced, though the yields decreased greatly. It indicates the majority of the ketene species were formed in the triplet state by the radical mechanism. It seems plausible to explain the dominant radical mechanism in the triplet state by the enhanced intersystem crossing from  $S_1$  caused by substitution of the chlorine atoms with methyl hydrogen atoms of acetyl chloride. Therefore, we focus on the triplet surface reaction after intersystem crossing and the ground state reaction after internal conversion. **Figure 5** shows the energy diagram for the  $\text{CHCl}_2\text{COCl}$  photolysis initiated by 253.7 nm irradiation. The photon energy at a wavelength of 253.7 nm corresponded to  $113 \text{ kcal}\cdot\text{mol}^{-1}$ . The reaction enthalpies of three elementary reac-

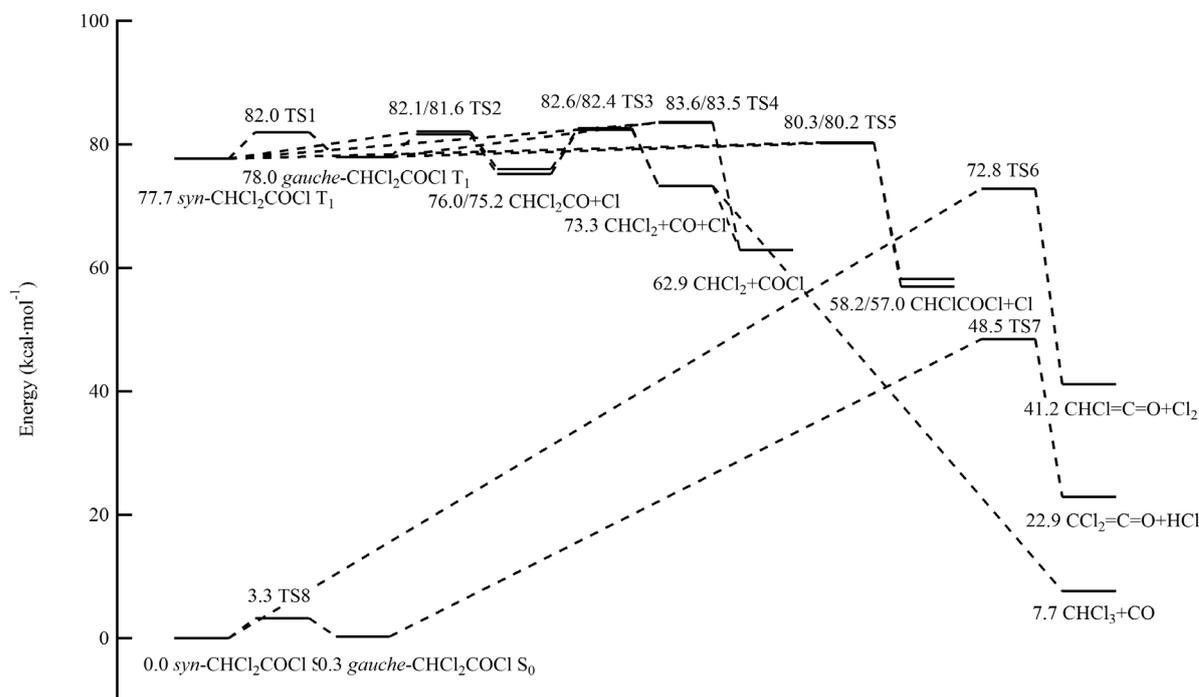


**Figure 3.** Infrared difference spectrum upon  $\lambda > 253.7$  nm irradiation of the matrix  $\text{CHCl}_2\text{COCl}/\text{O}_2 = 1/1000$  for 480 min.



**Figure 4.** Integrated absorbance changes of (○) *syn*- $\text{CHCl}_2\text{COCl}$ , (□) *gauche*- $\text{CHCl}_2\text{COCl}$ , (●)  $\text{CHCl}_3$ , (+)  $\text{CHCl}=\text{C}=\text{O}$ , (Δ)  $\text{CO}$ , (▲)  $\text{CCl}_2=\text{C}=\text{O}$ , and (×)  $\text{CHCl}_2$  upon  $\lambda > 253.7$  nm irradiation of the matrix  $\text{CHCl}_2\text{COCl}/\text{Ar} = 1/1000$ .

tions, C(O)-Cl, C-C, and  $\text{CHCl}-\text{Cl}$  bond cleavages from the  $T_1$  equilibrium states are calculated to be  $-1.7$ ,  $-14.8$ , and  $-19.5$   $\text{kcal}\cdot\text{mol}^{-1}$  for *syn*- $\text{CHCl}_2\text{COCl}$  and  $-2.8$ ,  $-15.1$ , and  $-20.9$   $\text{kcal}\cdot\text{mol}^{-1}$  for *gauche*- $\text{CHCl}_2\text{COCl}$ , respectively, where the reaction barriers are calculated to be 4.4, 5.8, and 2.6  $\text{kcal}\cdot\text{mol}^{-1}$  for *syn*- $\text{CHCl}_2\text{COCl}$  and 3.7, 5.6, and 2.2  $\text{kcal}\cdot\text{mol}^{-1}$  for *gauche*- $\text{CHCl}_2\text{COCl}$ , respectively. The C-C dissociation on the  $T_1$  surface possesses the highest barrier, while  $\text{CHCl}-\text{Cl}$  dissociation the lowest barrier. Radical species  $\text{CHCl}_2$  and  $\text{COCl}$



**Figure 5.** Energy diagram for the  $\text{CHCl}_2\text{COCl}$  photolysis.

can be also produced from the dissociation of  $\text{CHCl}_2\text{CO}$  into  $\text{CHCl}_2$  and  $\text{CO}$ , followed by the recombination of  $\text{CO}$  with  $\text{Cl}$ . The  $\text{CHClCOCl}$  would be further photodissociated. The reaction barrier for the formation of  $\text{CHCl=C=O} + \text{Cl}_2$  in the  $S_0$  state was calculated to be higher compared with that for the formation of  $\text{CCl}_2=\text{C=O} + \text{HCl}$ . The SAC-CI calculation showed the  $S_1$  and  $T_1$  states of  $\text{CCl}_2=\text{C=O}$  possess the mixing characters of  $\pi\sigma_{\text{C-Cl}}^*$  and  $\pi\text{Rydberg}$ ,  $-0.87$  (HOMO  $\rightarrow$  LUMO) +  $0.30$  (HOMO  $\rightarrow$  LUMO+3). Upon UV irradiation the C-Cl bond dissociation would occur to form  $\text{CCO}$ .

For the  $\text{CHCl}_2\text{COCl}$  photolysis in the rare gas matrices, the C-C bond cleaved  $\text{CHCl}_3$ ,  $\text{CO}$ ,  $\text{CHCl}_2$ , and  $\text{COCl}$  were dominantly produced similar to the  $\text{CCl}_3\text{COCl}$  photolysis and contrary to the  $\text{CH}_2\text{ClCOCl}$  photolysis, where ketene formation was a major process. For the  $\text{CHCl}_2\text{COCl}$  photolysis in  $\text{O}_2$ , both ketene and  $\text{CHCl}_3$  formations were greatly depressed, while for  $\text{CH}_2\text{ClCOCl}$ , the formation of ketene was slightly depressed. On the basis of these results it will be reasonable to consider that the reaction mechanism drastically changed between  $\text{CH}_2\text{ClCOCl}$  and  $\text{CHCl}_2\text{COCl}$  from the concerted mechanism in the  $S_0$  state to the radical mechanism in the  $T_1$  state.

## 4. Conclusion

UV light photolysis of  $\text{CHCl}_2\text{COCl}$  was investigated in cryogenic Ar, Kr, Xe, and  $\text{O}_2$  matrices. In Ar, Kr, and Xe, the formation of  $\text{CHCl}_3$  and  $\text{CO}$  became the dominant process over the ketene formation. The C-C bond cleaved products  $\text{CHCl}_2$  and  $\text{COCl}$  were also observed. In Kr and Xe, photoisomerization from *syn*- to *gauche*- $\text{CHCl}_2\text{COCl}$  was observed at the early stage of the irradiation. As the number of the chlorine atom substitution to methyl group of acetyl chloride increased, the C-C bond cleaved product yield in the triplet state increased, which can be attributed to an internal heavy-atom effect where the intersystem crossing rate was enhanced.

## Acknowledgements

The author thanks Prof. Tsuneo Fujii and Prof. Hiromasa Nishikiori (Shinshu University) for their helpful discussions.

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