

Original Research Article

Matrix Isolation and Theoretical Study on the Photolysis of CH₂ClCOCl

ABSTRACT

UV light photolysis of chloroacetyl chloride (CH₂ClCOCl) has been investigated by infrared spectroscopy in cryogenic Ar, Kr, Xe and O₂ matrices. In all matrices, the main photolysis products were CHCl=C=O and HCl, while the minor products were CH₂Cl₂ and CO. In CH₂ClCOCl/Ar, photoisomerization from *anti*- to *gauche*-CH₂ClCOCl was observed at the early stage of the irradiation. The results show the reactions predominantly proceed by the concerted mechanisms.

Keywords: Chloroacetyl chloride, Photolysis, Cryogenic matrix, Ketene

1. INTRODUCTION

Chlorinated acetyl chlorides are known to be produced in the oxidation of chlorinated ethenes [1, 2]. Photodissociation of chlorinated acetyl chlorides becomes environmentally important process. Potential release of Cl by photochemical reaction in the atmosphere enhances Cl cycle ozone depletion. In the chlorine atom initiated oxidation of chlorinated ethenes, relatively high product yields of chlorinated acetyl chloride were reported by Hasson and Smith [3]. In the Ar matrix, hydroxyl radical reacts with tetrachloroethene to yield trichloroacetyl chloride [4].

Chloroacetyl chloride exists as an *anti* or *gauche* conformer caused by the difference in the relative orientation of two C–Cl bonds [5]. Infrared spectra of chloroacetyl chloride in gas, liquid and solid phases, and matrix isolated were observed by many groups [6-10]. As for the reaction, Allen and Russell studied the pyrolysis of chloroacetyl chloride using infrared laser, where 1,2-HCl elimination occurred to produce chloroketene [11]. In a Xe matrix, Davidovics et al. obtained the photolysis product of chloroketene [12]. Previously, we studied the CCl₃COCl photolysis in the Ar and O₂ matrices, the C–C bond cleavage was found to be the major reaction path [13] in contrast to the acetyl chloride, CH₃COCl, photolysis [14, 15], where the four-center elimination to yield HCl·ketene complex occurred in the S₀ state after internal conversion from the S₁ state. For the CF₃COCl photolysis, the CF₃Cl and CO were produced via the radical mechanism [16]. That substitution of the halogen atom changed the reaction mechanism is of great interest.

In the present study, we investigated the UV light photolysis of CH₂ClCOCl in cryogenic Ar, Kr, Xe and O₂ matrices with the aid of the calculation using the B3LYP and MP2 methods. The computational results were used to interpret the infrared spectra. Reaction mechanism was discussed based on the differences observed in four matrices.

2. EXPERIMENTAL DETAILS

Light irradiation was performed using a low pressure mercury short arc lamp (HAMAMATSU L937-04, $\lambda > 253.7$ nm). IR spectra were measured in the range 4000–700 cm^{-1} with 1.0 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 O_2 (Okaya Sanso) were used without further purification. Chloroacetyl chloride (Wako Pure Chemicals) was used after freeze-pump-thaw cycling at 77 K. Dichloromethane (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) with the 6-311++G(3df,3pd) basis set and using Becke's three-parameter hybrid density functional [17] in combination with the Lee–Yang–Parr correlation functional, (B3LYP) [18] with the aug-cc-pV(T+d)Z basis set. 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 [19].

3. RESULTS AND DISCUSSION

3.1 $\text{CH}_2\text{ClCOCl}/\text{Ar}$

A mixture of $\text{CH}_2\text{ClCOCl}/\text{Ar}$ was deposited on a CsI window with a ratio of $\text{CH}_2\text{ClCOCl}/\text{Ar} = 1/1000$. In the infrared spectrum obtained after deposition, a strong band was observed at 1829 cm^{-1} , which can be assigned to the C=O stretching vibration of *anti*- CH_2ClCOCl [6, 9]. Fig. 1(a) shows the infrared difference spectrum obtained after $\lambda > 253.7$ nm irradiation of a matrix $\text{CH}_2\text{ClCOCl}/\text{Ar}$ for 210 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. The growth bands at 1140, 1060, 1054, 822, 813 and 810 cm^{-1} are in good agreement with those of *gauche*- CH_2ClCOCl [9], although the band at 1790 cm^{-1} previously assigned to the C=O stretching vibration of *gauche*- CH_2ClCOCl decreased with the increased shoulder at 1784 cm^{-1} . Durig et al. determined the enthalpy difference between two conformers to be 587 cm^{-1} [6] from far infrared spectrum measurements where *anti* conformer was more stable. The calculation at the B3LYP/aug-cc-pV(T+d)Z level shows that the *anti* rotamer is more stable than the *gauche* rotamer by 599 cm^{-1} (ΔG° at 298 K), indicating that the *gauche/anti* population ratio before UV irradiation is 0.086/1 at 298 K. Relative integrated intensity of the bands I_{1790}/I_{1829} was obtained to be 0.20 from the spectrum before light irradiation considering with the calculated IR intensity ratio of $I_{\text{gauche}}/I_{\text{anti}} = 1.15$ at the B3LYP/aug-cc-pV(T+d)Z level, which is larger than that expected from the Boltzmann distribution. The frequency calculation with the anharmonic correction at the MP2/6-311++G(3df,3pd) level revealed that the band at 1790 cm^{-1} was assignable to the overtone band of the CH_2 rocking vibration of *anti*- CH_2ClCOCl . The barrier height for the conversion from the *anti* to *gauche* rotamer is calculated to be 1098 cm^{-1} in the S_0 ground state indicating that the conversion between the *anti* 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. Further irradiation made us possible to distinguish the

product bands due to different growth behavior. Fig. 1(b) shows the infrared difference spectrum obtained by subtracting the spectrum measured after 210 min irradiation from that measured after 630 min irradiation. In addition to the *anti*-CH₂ClCOCl depletion, the bands due to *gauche*-CH₂ClCOCl decreased. The band at 1784 cm⁻¹ showing depletion in Fig. 1(b) was much broader than that in Fig. 1(a) which enables us to reconfirm that the band at 1784 cm⁻¹ is the C=O stretching vibration band of *gauche*-CH₂ClCOCl overlapping with the band due to *anti*-CH₂ClCOCl. Prominent doublet bands at 2153 and 2147 cm⁻¹ continued to grow with the different growth rates during the prolonged irradiation period. Three doublet bands at 1302 and 1297 cm⁻¹, 1120 and 1113 cm⁻¹, and 808 and 804 cm⁻¹ showed the same growth behavior as those of the 2153 and 2147 cm⁻¹ bands, respectively, which are assignable to the C=C stretching, C-H in-plane bending, C-Cl stretching and C=O stretching vibrations of CHCl=C=O, respectively. Davidovics et al. measured infrared bands of CHCl=C=O at 2141.4, 1293, 1107 and 842.2 cm⁻¹ in a Xe matrix [12]. The bands at 2857 and 2809 cm⁻¹ were assigned to the stretching vibration of HCl where the growth behaviors of the bands at 2857 and 2809 cm⁻¹ correspond to those of the bands at 2147 and 2153 cm⁻¹ of CHCl=C=O, respectively. Weak bands at 1268 and 749 cm⁻¹ were assigned to the CH₂ wagging and CCl₂ antisymmetric stretching vibrations of CH₂Cl₂, respectively, by comparing with the wavenumbers of authentic CH₂Cl₂ in Ar. Weak bands in the 3000–2700 cm⁻¹ region except HCl were assigned to the combination and overtone bands. In contrast to the CCl₃COCl photolysis, the band due to COCl was not observed.

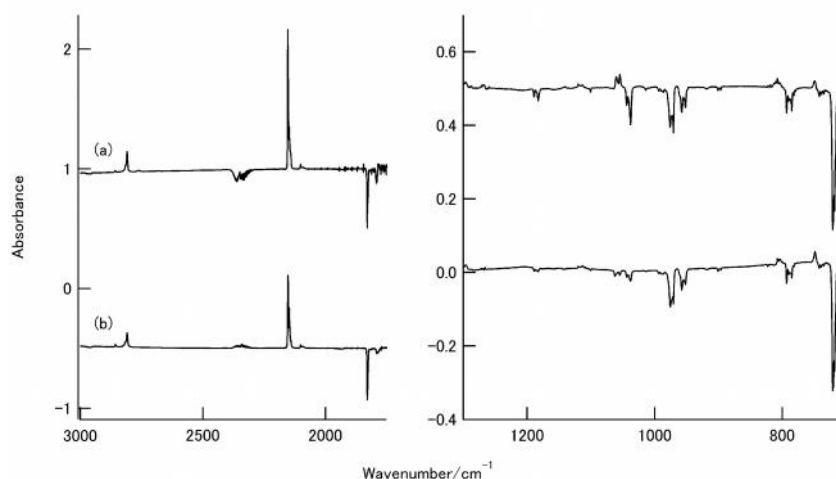


Fig. 1. Infrared difference spectra upon $\lambda > 253.7$ nm irradiation of the matrix CH₂ClCOCl/Ar = 1/1000. (a) 210–0 min and (b) 630–210 min.

Table 1. FTIR spectra of photochemical reaction products of the CH₂ClCOCl in the Ar, Kr, Xe and O₂ matrices.

Wavenumber/cm ⁻¹				species
Ar	Kr	Xe	O ₂	
3134			3132	CHCl=C=O...HCl π complex
3115			3115	CHCl=C=O...HCl n complex
2885				HCl
2857	2843	2826	2850	HCl...CHCl=C=O n complex
2816/2809	2810/2804	2808	2805	HCl...CHCl=C=O π complex
	2762			CHCl ₂ ⁻ [20]

			2343	$^{12}\text{CO}_2$
			2276	$^{13}\text{CO}_2$
2153	2149	2146	2157	$\text{CHCl}=\text{C}=\text{O}\cdots\text{HCl}$ π complex
2147	2145	2142	2152	$\text{CHCl}=\text{C}=\text{O}\cdots\text{HCl}$ n complex
2140	2142	2133	2145	CO
2101			2107	O_3 $\nu_1 + \nu_3$ [21]
2090	2097			^{13}CO
				$\text{CHCl}=\text{C}=\text{O}$
			2037	CO_3
1784				<i>gauche</i> - CH_2ClCOCl overlapped with combination band of <i>anti</i> - CH_2ClCOCl
1302	1303	1293		$\text{CHCl}=\text{C}=\text{O}\cdots\text{HCl}$ π complex
1297				$\text{CHCl}=\text{C}=\text{O}\cdots\text{HCl}$ n complex
1268	1267	1263	1268	CH_2Cl_2
1140			1136	<i>gauche</i> - CH_2ClCOCl
1120				$\text{CHCl}=\text{C}=\text{O}\cdots\text{HCl}$ π complex
1113		1112	1112	$\text{CHCl}=\text{C}=\text{O}\cdots\text{HCl}$ n complex
1109				$\text{CHCl}=\text{C}=\text{O}\cdots\text{HCl}$ n complex
1060			1101	O_3 ν_1 [22]
1054				<i>gauche</i> - CH_2ClCOCl
			1057	<i>gauche</i> - CH_2ClCOCl
			1036	O_3 ν_3 [22]
		954		Xe_2H^+ [23]
			900	CHCl_2 [24]
			892	CHCl_2 [24]
	853			Kr_2H^+ [23]
		844		Xe_2H^+ [23]
822			820	<i>gauche</i> - CH_2ClCOCl
818			816	<i>gauche</i> - CH_2ClCOCl
813				<i>gauche</i> - CH_2ClCOCl
810			810	<i>gauche</i> - CH_2ClCOCl
808			807	$\text{CHCl}=\text{C}=\text{O}\cdots\text{HCl}$ π complex
804			803	$\text{CHCl}=\text{C}=\text{O}\cdots\text{HCl}$ n complex
748	747	746	750	CH_2Cl_2
		731		Xe_2H^+ [23]

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Two sets of bands assignable to $\text{CHCl}=\text{C}=\text{O}$ vibrations were measured. They showed different growth behavior accompanying with HCl different in wavenumbers, indicating the presence of two different structures for the $\text{CHCl}=\text{C}=\text{O}\cdots\text{HCl}$ complex in spite of the matrix site effect. Two stable structures were calculated for the $\text{CHCl}=\text{C}=\text{O}\cdots\text{HCl}$ complexes as shown in Fig. 4, where the hydrogen atom of HCl points to the carbon atom of CHCl (π complex) or O atom (n complex). Similar structures were proposed for the $\text{CH}_2=\text{C}=\text{O}\cdots\text{HCl}$ complexes [25]. On the basis of the MP2/6-311++G(3df,3pd) calculation, two species characterized by the absorption bands at 3134, 2809, 2153, 1302, 1120 and 808 cm^{-1} , and 3115, 2857, 2147, 1297, 1113 and 804 cm^{-1} were identified with the π and n complexes of $\text{CHCl}=\text{C}=\text{O}\cdots\text{HCl}$, respectively.

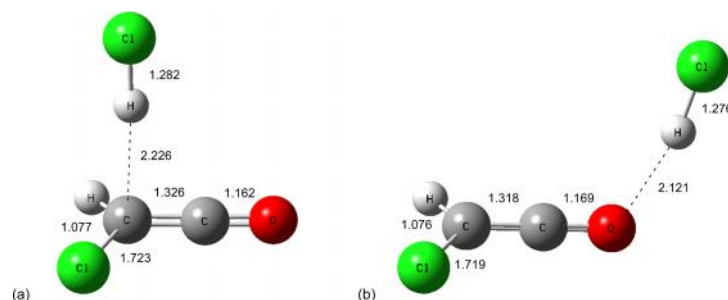


Fig. 2. Optimized equilibrium structures of the $\text{CHCl}=\text{C}=\text{O}\cdots\text{HCl}$ complexes calculated at the MP2/6-311++G(3df,3pd) level. Bond lengths are in Å. (a) π complex and (b) n complex.

3.2 $\text{CH}_2\text{ClCOCl/Kr}$ and $\text{CH}_2\text{ClCOCl/Xe}$

Figs. 3(a) and 4(a) show the infrared difference spectra obtained upon $\lambda > 253.7$ nm irradiation of the matrices $\text{CH}_2\text{ClCOCl/Kr}$ and $\text{CH}_2\text{ClCOCl/Xe}$, respectively. The strong absorption bands were observed at approximately 2145 cm^{-1} which were assigned to the CO stretching vibrations of $\text{CHCl}=\text{C}=\text{O}$ and CO. Due to the weak intensities of the bands of $\text{CHCl}=\text{C}=\text{O}$ except for the C=O stretching band, the presence of the two complexes was not evident, though the splitting were observed in the 2145 cm^{-1} region. As can be seen in Figs. 2(b) and 3(b), the higher wavenumber side of these bands decreased in intensities. The products $\text{CHCl}=\text{C}=\text{O}$ were further photodissociated in the Kr and Xe matrices. The SAC-Cl calculation showed the S_1 state of $\text{CHCl}=\text{C}=\text{O}$ possesses the mixing characters of $\pi\sigma_{\text{C-Cl}}^*$ and $\pi\text{Rydberg}$, $-0.59(\text{HOMO} \rightarrow \text{LUMO}) - 0.53(\text{HOMO} \rightarrow \text{LUMO}+1) + 0.48(\text{HOMO} \rightarrow \text{LUMO}+3)$. The C-Cl bond dissociation would occur. Absorption bands due to CH_2Cl_2 were observed at 1267 and 747 cm^{-1} , and 1263 and 746 cm^{-1} , in the Kr and Xe matrices, respectively. The band at 853 cm^{-1} in the Kr matrix was assigned to the ν_3 of Kr_2H^+ [23]. The bands at 954 , 844 and 731 cm^{-1} in the Xe matrix were assigned to the $\nu_3 + 2\nu_1$, $\nu_3 + \nu_1$ and ν_3 of Xe_2H^+ , respectively [23]. For comparison, the infrared difference spectrum of the photolysis products of the matrix $\text{CH}_2\text{Cl}_2/\text{Xe}$ is shown in Fig. 4(c). The similar product bands were observed at 954 , 844 and 731 cm^{-1} . It indicates that the photolysis product CH_2Cl_2 of CH_2ClCOCl was also further decomposed to yield Kr_2H^+ or Xe_2H^+ . It will be plausible that the band at 844 cm^{-1} previously assigned to the ν_5 of $\text{CHCl}=\text{C}=\text{O}$ is reassigned to the $\nu_3 + \nu_1$ of Xe_2H^+ .

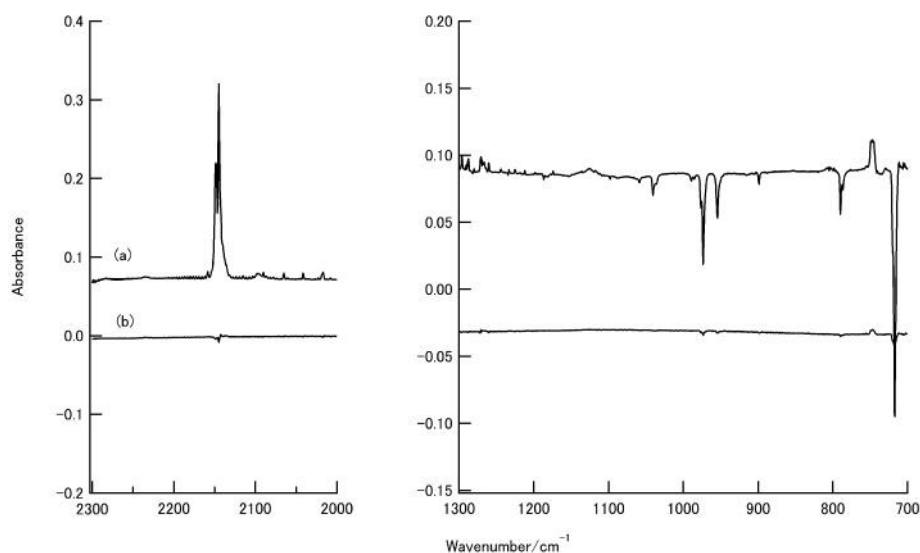


Fig. 3. Infrared difference spectra upon $\lambda > 253.7$ nm irradiation of the matrix $\text{CH}_2\text{ClCOCl/Kr} = 1/1000$ for 360 min. (a) 330–0 min and (b) 360–330 min.

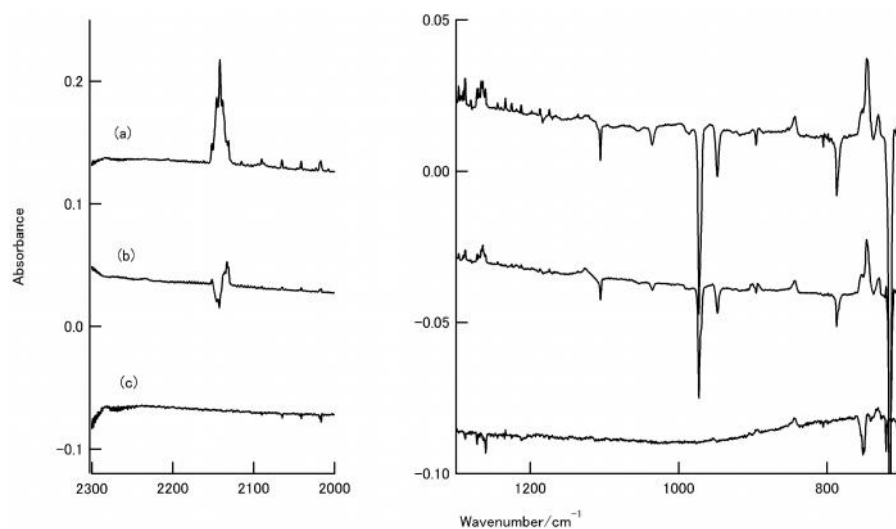


Fig. 4. Infrared difference spectra upon $\lambda > 253.7$ nm irradiation of the matrix $\text{CH}_2\text{ClCOCl/Xe} = 1/1000$. (a) 180–0 min and (b) 420–180 min. (c) Infrared difference spectra upon $\lambda > 253.7$ nm irradiation for 180 min of the matrix $\text{CH}_2\text{Cl}_2/\text{Xe} = 1/1000$.

3.3 $\text{CH}_2\text{ClCOCl/O}_2$

In order to clarify the route of the CHCl=C=O and CH_2Cl_2 formation i.e. the radical or concerted mechanism, the reactive O_2 matrix was used. Fig. 5 shows the infrared difference spectrum obtained after 300 min irradiation of the matrix $\text{CH}_2\text{ClCOCl/O}_2$. Product bands

were assigned by comparison with the spectrum observed in the photolysis of the $\text{CCl}_3\text{COCl}/\text{O}_2$ matrix [13]. Due to the photolysis in O_2 at 253.7 nm, ozone formation is prominent at 1038 cm^{-1} (ν_3) [22]. Other O_3 absorption bands were observed at 2107 ($\nu_1 + \nu_3$) and 1101 cm^{-1} (ν_1) [21, 22]. The 2342 and 2276 cm^{-1} bands are assigned to ν_3 vibrations of $^{12}\text{CO}_2$ and $^{13}\text{CO}_2$, respectively. The 2037 cm^{-1} band is attributed to CO_3 complexed with Cl [13]. In $\text{CH}_2\text{ClCOCl}/\text{O}_2$, the bands at 2157 , 2152 and 835 cm^{-1} due to $\text{CHCl}=\text{C}=\text{O}$ were observed. Absorption bands due to CH_2Cl_2 were observed at 1268 and 750 cm^{-1} . These strongly suggest the concerted mechanism is dominant for the photolysis of CH_2ClCOCl .

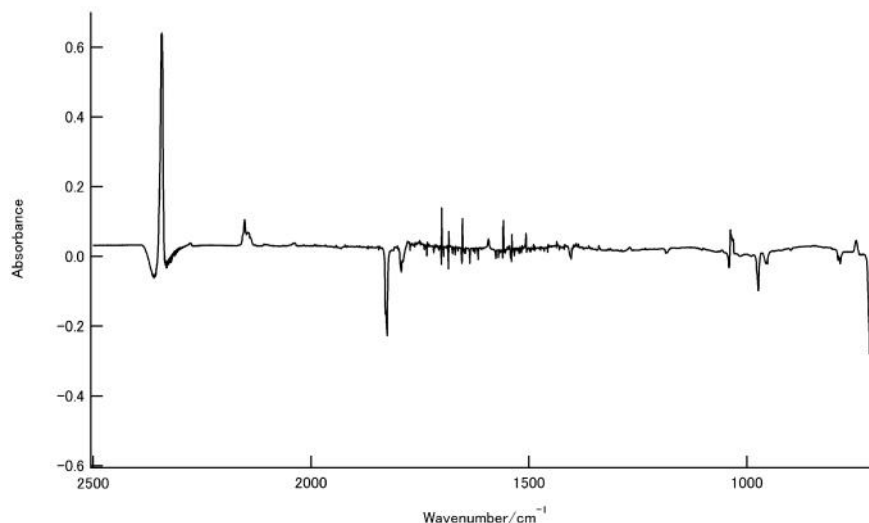


Fig. 5. Infrared difference spectrum upon $\lambda > 253.7\text{ nm}$ irradiation of the matrix $\text{CH}_2\text{ClCOCl}/\text{O}_2 = 1/1000$ for 420 min.

4. CONCLUSIONS

UV light photolysis of CH_2ClCOCl was investigated in cryogenic Ar, Kr, Xe and O_2 matrices. In $\text{CH}_2\text{ClCOCl}/\text{Ar}$, photoisomerization from *anti*- to *gauche*- CH_2ClCOCl was observed at the early stage of the irradiation. The $\text{CHCl}=\text{C}=\text{O}$ and HCl were measured as dominant products, while CH_2Cl_2 and CO as minor products. The results show the reactions predominantly proceed by the concerted mechanisms.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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