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Neon matrix-isolation infrared spectrum of HOOCl measured upon the VUV-light irradiation of an HCl/O₂ mixture

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ABSTRACT

Vacuum ultraviolet (VUV) photolysis of an HCl/O₂ mixture has been carried out to identify HOOCl by the Ne matrix-isolation infrared spectroscopy with the aid of quantum chemical calculations. Newly-observed IR bands at 823, 1363 and 3542 cm⁻¹ are assigned to those of HOOCl on the basis of the isotope shifts with DOOCl and the CCSD(T)/aug-cc-pVDZ calculation. The observed dependence of band intensities on the time of VUV photolysis indicates that HOOCl and HOClO are the photoproducts formed in an early stage. In addition, HOOCl is found to decompose to form HCl in the UV photolysis ($\lambda \ge 365$ nm), which consists with the S₁–S₀ energy separation estimated by the TDDFT method.

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1. Introduction

Photochemistry of molecules including chloride atom is known to be important for atmospheric chemistry, especially in relation to the ozone depletion in the stratosphere. In one of the monumental studies of Molina and Rowland, they found that the chlorine atom produced by the UV irradiation of chlorofluorocarbons (CFCs) catalytically consumed ozone molecules [1]. A multitude of theoretical and experimental studies for ozone depletion have since been reported [2,3] after their model of the photochemical ozone destruction. Short-lived species composed of chlorine and oxygen atoms have been studied extensively to promote better understanding of the chlorine cycles in the atmosphere by IR, UV and fluorescence spectroscopy [4-11]. For example, Johnsson et al. measured the IR spectrum of HOClO and HClO₂ produced by the addition reaction of hydrogen atom with OClO in Ar matrices and determined their geometries with the aid of quantum chemical calculations [6]. The IR spectra of various related species such as ClOO radical [7], HOOClO₂ [8], ClOOCl [9], ClOx [10] have been measured, and continual efforts have since been made to identify the postulated reaction intermediates either theoretically or mechanistically.

Chlorous acid, which is one of the expected intermediates composed of H, Cl and O atoms in the atmosphere, has three isomers shown in Fig. 1 [11]. Two less stable isomers, HOClO and HClO₂, have been detected in matrix experiments [6], but the most stable isomer, HOOCl, has never been identified. This situation seems unusual, because HOOCl is estimated to be more stable than HOClO by as much as 65.3 kJ mol⁻¹ at the CCSD(T)/TZ2P level [12]. Several reaction models have been proposed for stratospheric ozone deple-

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tion, where HOOCl is expected to play an important role as a reaction intermediate. According to Burrows et al. [12], the atmospheric OH + ClO reaction proceeds through the formation of the HOOCl intermediate as

$OH + CIO \rightarrow (HOOCI) \rightarrow HOO + CI$	(1)	

 $OH + ClO \rightarrow (HOOCl) \rightarrow HCl + O_2 \tag{2}$

Since such branching reaction pathways may contribute to understanding of the quantitative material balance in the atmospheric chlorine cycles, several theoretical studies have been made on the potential diagram of the HO + ClO \rightarrow HOOCl reaction [11–17]. However, no experimental information has yet been reported on the chemical properties, photo-reactivity and fundamental spectra of HOOCl, because it has never been identified experimentally.

The chemical species generated by the reaction of H + OCIO have so far been assumed to be HOCIO and $HCIO_2$. The chemical transformation from OCIO to OOCI seems hardly feasible; in fact, no experimental data of HOOCI have yet been available in this reaction system. Hence we have chosen HCI/O_2 reactants in the present study to photochemically generate HOOCI, where the VUV photolysis of HCI/O_2 and DCI/O_2 mixtures in a low-temperature Ne matrix has been carried out to assign the IR spectra of HOOCI and DOOCI.

2. Experimental and calculation methods

Hydrogen chloride (HCl) was synthesized from NaCl (Kanto Chemical) and H_2SO_4 (Wako Pure Chemical Industries), and DCl from D_2SO_4 (Cambridge Isotopes Laboratories) [18]. Oxygen gas (Taiyo Nissan, 99.999%) was used without further purification. The samples were diluted with excess Ne gas (Spectra Gases, 99.9999%), and then mixed gases of HCl/O₂/Ne or DCl/O₂/Ne were



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Fig. 1. Three isomers of chlorous acid. Optimized geometrical parameters of HOOCI and relative energies among the three isomer in kJ mol⁻¹, shown in parentheses, are calculated at the CCSD(T)/aug-cc- pVDZ level.

introduced into a vacuum chamber through a stainless steel pipe and deposited on a CsI plate cooled by a closed-cycle helium refrigerator (Iwatani, Cryomini) at \sim 6 K.

Infrared spectra of the matrix isolated samples were measured with an FTIR spectrophotometer (Jeol, SPX200ST). The spectral resolution was 0.5 or 0.25 cm⁻¹, and the accumulation number was 100. A xenon lamp (Ushio, UER-20-172A) and a super-high-pressure mercury lamp (Ushio, H500) were used as VUV and UV irradiation sources, respectively, and sharp-cut filters (Asahi spectra) were used to select visible and UV wavelengths. Other experimental details have been reported in Ref. [19].

Quantum chemical calculations were performed using the GAUS-SIAN 03 program [20] on TSUBAME, a supercomputer installed in Tokyo Institute of Technology. The CCSD(T)/aug-cc-pVDZ calculation was performed to optimize molecular geometries and estimate their vibrational frequencies, together with their intensities derived by the B3LYP/aug-cc-pVTZ level calculation. The MP2/ aug-cc-pVDZ level calculation with vibrational anharmonicity was performed for vibrational analyses. The method of timedependent density functional theory (TDDFT) at the B3LYP/augcc-pVTZ level was applied to estimation of vertical transition energies.

3. Results and discussion

3.1. Products from the VUV photolysis of HCl/O₂

Fig. 2a shows a difference IR spectrum associated with the 180 min VUV irradiation ($\lambda = 155-195$ nm, $\lambda_{max} = 172$ nm) of HCl/ O₂/Ne = 1/1/2000. Almost all the increasing bands due to the photoproducts, i.e., those caused by the irradiation, are assigned to several species of reported IR spectra. For example, the bands of 969.9, 978.3, 1173.2 and 3556.7 cm⁻¹ are assigned to HOCl0 [6], and those of 1238.9 and 3607.8 cm⁻¹ can be assigned to HOCl0 [21]. Table 1 summarizes these results, together with the other observed bands. No band to be assigned to HClO₂ is detectable in this spectrum. Three intense bands at 823.1 cm⁻¹ (with a side band at 821.1 cm⁻¹), 1362.5 cm⁻¹ (with multiple side bands at 1359.6, 1361.4, 1361.9 and 1363.6 cm⁻¹) and 3542.4 cm⁻¹ (with a side band at 3543.6 cm⁻¹) remain unidentified. The observed band splittings are ascribed to the matrix-site effect, because these side bands were weakened by annealing the matrix sample at 10 K.

Fig. 3a plots the dependence of the intensities of these three bands on the irradiation time. Their time profiles exhibit a uniform trend, which suggests that they are possibly due to an identical photoproduct species. Fig. 3b shows the time profiles of the band intensities of HOCIO and HOCI, which implies that HOCIO is the photoproduct formed in an early stage, while HOCI produced with an induction time is probably formed in a later stage of the photochemical sequence.

A further analysis of the mechanism of these VUV photochemical reactions is complicated, because the photolysis of HCl and O_2 , matrix-cage effects, multi-reaction pathways, etc. must be properly taken into account.

3.2. Assignment of HOOCl as the main photoproduct

As candidates for the main photoproduct, which are composed of H, Cl and O atoms, we have chosen HOOCl, ClO radical/anion, HOOOCl, HOOOOCl, etc. and calculated their vibrational frequencies. Since it has been known that popular B3LYP methods cannot satisfactorily reproduce the vibrational frequencies of molecules composed of several Cl and O atoms, the theory levels including multi-configuration reference functions are required for accurate estimation [22–24]. Therefore, the CCSD(T)/aug-cc-pVDZ level has been used for their vibrational frequencies and the B3LYP/ aug-cc-pVTZ level for their IR intensities. By the following comparison of the three observed wavenumbers with their calculated re-



Fig. 2. IR spectra of VUV photoproducts from HCl/O₂. (a) A difference IR spectrum associated with the 180 min VUV irradiation of HCl/O₂, and (b) a composite spectrum of HOOCl and HOClO simulated at CCSD(T)/aug-cc-pVDZ for vibrational wavenumbers and B3LYP/aug-cc-pVTZ for their intensities. The bands marked with asterisks are assigned to H₂O impurity and daggers to unknown species.

Table 1

IR band assignments of VUV photoproducts from HCl/O2 in Ne matrix.

Obs. $\bar{\nu}/\mathrm{cm}^{-1}$	Calc.	Calc.		Assignment
	$\tilde{\nu}/\mathrm{cm}^{-1\mathrm{a}}$	Int/km mol ^{-1b}	$\tilde{\nu}/\mathrm{cm}^{-1}$	
821.1/823.1	808	47		0–0 stretching of HOOCl
969.9	896	83	965.0 ^d	HO ³⁷ ClO
978.3	904	85	973.9 ^d	HO ³⁵ ClO
1029.0				Unknown
1038.6/1039.8	971	235	1038.7/1039.9 ^e	03
1095.4	940	96	1095.9 ^f	0 ³⁷ ClO
1107.2	951	98	1107.6 ^f	0 ³⁵ ClO
1173.2	1152	48	1176.9 ^d	HOCIO
1238.9	1254	44	1239 ^g	HOCI
1282.0				Unknown
1359.6/1361.4/1361.9/1362.5/1363.6	1389	44		HOO bending of HOOCl
1391.5	1425	49	1388.9 ^h	HOO
1397.6				Unknown
1438.1/1438.5/1439.6/1441.2/1442.3	1495	200	1438.6 ^f	ClOO
1456.3				Unknown
1458.2				Unknown
3542.4/3543.6	3690	44		O–H stretching of HOOCl
3546.3/3548.6/3555.4				H ₂ O impurity
3556.7	3700	80	3527.1 ^d	HOCIO
3607.8	3742	78	3581 ^g	HOCI

^a Calculated at the CCSD(T)/aug-cc-pVDZ level.

^b Calculated at the B3LYP/aug-cc-pVTZ level.

^c Data reported in the literature d-h.

^d In Ar matrix, Ref. [6].

^e In Ne matrix, Ref. [19].

^f In Ne matrix, Ref. [25].

^g In Ar matrix, Ref. [21].

^h In Ar matrix, Ref. [26].

sults, the best agreement between calculation and experiment is found to be a hitherto unidentified species, HOOCI.

The six vibrational wavenumbers of this HOOCl species are calculated to be 356, 410, 623, 808, 1389 and 3690 cm⁻¹ without a scaling factor. Though Francisco et al. reported that HOOCl had three stable conformers with *skew*, *trans* and *cis* geometries [11], our calculation indicates that only the *skew* geometry shown in Fig. 1 is located at the energy minimum, whereas the *trans* and *cis* conformers are on the saddle points. Our optimized geometrical parameters agree well with the reported values estimated by a CASSCF calculation [24]. Three observed bands at 823.1, 1362.5 and 3542.4 cm⁻¹ correspond to the O–O stretching (808 cm⁻¹ from our calculation), the HOO bending (1389 cm⁻¹) and the O–H stretching (3690 cm⁻¹), respectively. Fig. 2b shows a simulated spectrum of an HOOCl/HOClO mixture, where the relative IR intensities of HOOCl and HOClO are adjusted so that the simulated spectrum reproduces the observed one (Fig. 2a) satisfactorily.

Table 1 summarizes the observed and calculated wavenumbers, together with those for the other photoproducts. The experimental bands assigned to OCIO consist with the other experimental values reported in Ref. [25]. Note that the three vibrational bands of HOO-CI measured in the present study agree with the reported values of 818, 1361 and 3559 cm⁻¹, which were predicted from the experimental data of HOOH and CIOOCI by Lee and Rendell [13]. Thus, we conclude that the bands observed at 823.1, 1362.5 and 3542.4 cm⁻¹ can be assigned to the O–O stretching, HOO bending and O–H stretching modes of HOOCI, respectively. The photochemical reactions to form HOOCI and HOCIO are likely to proceed through the OH and CIO intermediates as follows:

$$HCl + O_2 + h\nu_{VUV} (\sim 172 \text{ nm}) \rightarrow [OH + ClO] \rightarrow HOOCl \text{ (and HOClO)}$$
(3)

Fig. 2 shows a comparison of the observed spectrum with the theoretical calculation. One finds that the 1362.5 cm^{-1} band is three times as strong as the 823.1 cm⁻¹ band, whereas they are

theoretically predicted to have comparable IR intensities. The 823.1 cm^{-1} band is accompanied by a satellite band at 821.1 cm^{-1} with comparable intensity, but the observed HOO bending band is still twice as intense as the O–O stretching band. A similar disagreement in the intensities is also recognized for HO-CIO in Fig. 2. Despite the limit of accuracy in the theoretical prediction of the IR intensity, the group of 823.1, 1362.5 and 3542.2 cm⁻¹ bands can thus be assigned to those of HOOCI.

Fig. 3 shows that the concentrations of HOClO and HOOCl reach plateaus at irradiation times of 100 and 200 min, respectively, which are controlled by the rates of creation and annihilation of the HO_2Cl isomers.

3.3. Assignment of deuterated photoproducts

In order to confirm the identification and band assignments described above, we performed a VUV photolysis experiment using DCl/O₂/Ne instead of HCl/O₂/Ne; see Supplementary material. The isotope red-shifts of HOOCI toward DOOCI were calculated to be 1 cm^{-1} for the O–O stretching, 364 cm⁻¹ for the HOO bending and 1002 cm⁻¹ for the OH stretching. In the VUV photolysis of DCl/O₂/ Ne we observed new bands at 823.1, 1021.6 and 2614.8 cm^{-1} , which correspond to the isotope red-shifts of 0, 341 and 928 cm⁻¹, respectively. The agreement between the observed and calculated isotope shifts seems reasonable. The vibrational calculation considering anharmonicity at the MP2/aug-cc-pVDZ level leads to a better agreement regarding the isotope shifts (5, 342 and 911 cm^{-1} , respectively) and the IR intensity patterns. Thus, the photoproducts responsible for the 823.1, 1021.6 and 2614.8 cm⁻¹ bands observed in the VUV photolysis of DCl/O₂ are assigned to DOOCl. In turn, this observation has confirmed the assignment of the HOOCl bands.

The formation rates of HOOCl and HOClO are found to be essentially equal to those of DOOCl and DOClO, respectively, in the VUV photolysis. This observation indicates that the diffusion process of the H/D atom is not the rate-determining step of reaction (3).



Fig. 3. Plots of IR band intensities against VUV irradiation time. (a) The 823.1, 1362.5 and 3542.4 cm⁻¹ bands are assigned to HOOCI. (b) The 978.3, 1173.2 and 3556.7 cm⁻¹ bands are assigned to HOCIO, and the 1238.9 and 3607.8 cm⁻¹ bands to HOCI. The intensity of each band is normalized to its maximum intensity.

3.4. UV photolysis of HOOCl intermediate

After the VUV irradiation for 300 min to generate HOOCl and HOClO, we irradiated visible and UV light to the matrix sample containing the HOOCl and HOClO products. Only the HOClO product was photolyzed upon the visible light irradiation ($\lambda \ge 405$ nm), while the HOOCl and HOClO products were both photolyzed by the UV irradiation ($\lambda \ge 365$ nm). According to Johnsson et al., HOClO was photolyzed at 400 nm [6]; this agrees with our present obser-

vation. Upon the UV light ($\lambda \ge 365 \text{ nm}$) irradiation after the photobleaching of HOClO by the visible light ($\lambda \ge 405 \text{ nm}$), we recorded the IR difference spectrum of Fig. 4. This difference spectrum clearly shows that the UV light ($\lambda \ge 365 \text{ nm}$) photolyzes HOOCl to form HCl and O₂.

$$HOOCl + h\nu_{UV} (\sim 365 \text{ nm}) \rightarrow HCl + O_2$$
(4)

The wavelength thresholds for the photolysis of the isomers correspond with the TDDFT calculation, which estimates the first electronic transition wavelengths of HOOCl and HOClO to be 357 and 413 nm, respectively.

The branching reaction pathways to HOO + Cl and HCl + O₂ in reactions (1) and (2) are known to be important for atmospheric chemistry. As mentioned in Introduction, HOOCl was once postulated as an intermediate of the OH+OCl reaction. However, HOOCl has never been detected experimentally, although it is expected to be the most stable isomer. HOClO is a better-known isomer that exists as a chemically stable molecule, although the latter isomer is less stable by 76 kJ mol⁻¹; in fact, the substance called 'chlorous acid' usually denotes HOClO. This unusual feature is consistent with our present study, where the photochemical isomerization between HOOCl and HOClO was not observed upon the UV light ($\lambda \ge 365$ nm) or visible light ($\lambda \ge 405$ nm) irradiation.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.cplett.2009.06.064.

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Fig. 4. A difference IR spectrum associated with the 30 min UV irradiation ($\lambda \ge 365$ nm) of HOOCI. This difference spectrum was obtained by subtracting the IR spectrum recorded after the photo-bleaching of HOCIO by the visible light ($\lambda \ge 405$ nm). The bands marked with asterisks are assigned to H₂O impurity.

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