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An Experimental Study on the Photochemistry and Vibrational Spectroscopy of Three Isomers of Cl_2O_2 Isolated in Cryogenic Matrices

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Abstract: Chloryl chloride, $ClClO_2$, isolated in cryogenic matrices is subjected to photolysis, producing chlorine chlorite, ClOClO, which in turn is converted into dichlorine peroxide, ClOOCl. ClOClO is also formed by the reactions Cl + OClO and ClOCl + O. The products are identified by means of FTIR spectroscopy using $^{35/37}Cl$ and $^{16/18}O$ isotopic shifts, with the aid of vibrational spectra of related molecules and results of *ab initio* calculations. The thresholds for photodecomposition of ClOClO, $ClClO_2$, and ClOOCl isolated in an argon matrix are above wavelengths of 665, 610, and 360 nm, respectively. Two dissociation channels are observed for both ClOClO and ClOOCl. For ClOClO they are (i) Cl + OClO, leading to $ClClO_2$ and (ii) 2ClO, yielding ClOOCl. For ClOOCl they are (i) ClOO + Cl, resulting in $Cl_2 + O_2$, and (ii) 2ClO, giving rise to ClOClO. The observation of two photolysis paths for ClOOCl is of importance for the catalytic ozone depletion in the polar stratosphere. Irradiation of $ClClO_2$ isolated in a neon matrix resulted in $Cl_2 + O_2$ as the only products. The UV spectra of $ClClO_2$ in the gas phase and in a neon matrix are reinvestigated. Lower limits for the integral band strengths of ClOClO and ClOOCl are derived relative to those of $ClClO_2$. The vibrational data of this study, in conjunction with results of submillimeter spectroscopic investigations, are used to calculate a general valence force field for ClOOCl.

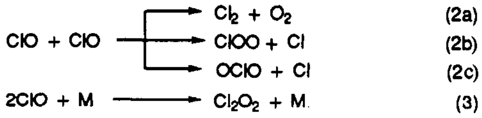
Introduction

During the past few years, chlorine oxides have drawn attention not only in the field of basic chemistry[1] but also as important intermediates for rationalizing the process of ozone depletion in the polar regions.[2] It has been suggested that a catalytic cycle involving the dimerization of ClO and the subsequent photolysis of the products plays an important role.[3]

To our knowledge, the first experimental evidence for Cl_2O_2 isomers arose from a mechanistic study of the formation of OClO in aqueous solutions. From experiments with ^{38}Cl-labeled compounds, chloryl chloride, $ClClO_2$, or chlorine chlorite, ClOClO, was suggested as an intermediate in the following reaction:[4]

$$Cl_2 + 2ClO_2^- \rightarrow 2ClO_2 + 2Cl^- \qquad (1)$$

As a result of early kinetic investigations of the decomposition of ClO into Cl_2 and O_2, a dimer was postulated as an intermediate.[5] Three bimolecular and one termolecular reaction channels have been considered in the kinetics of the ClO self-reaction:



$$ClO + ClO \rightarrow Cl_2 + O_2 \qquad (2a)$$
$$ClO + ClO \rightarrow ClOO + Cl \qquad (2b)$$
$$ClO + ClO \rightarrow OClO + Cl \qquad (2c)$$
$$2ClO + M \rightarrow Cl_2O_2 + M \qquad (3)$$

Kinetic investigations indicate the termolecular channel (3) to be the predominant one at lower temperatures,[6,7] whereas the chemical processes proceeding at room temperature have been interpreted in terms of the bimolecular channels (2).[7]

The first systematic *ab initio* calculations into Cl_2O_2 isomers were reported by McGrath et al.[8] They found three isomers that may be formed under stratospheric conditions: dichlorine peroxide, ClOOCl, chloryl chloride, $ClClO_2$, and chlorine chlorite, ClOClO. The former two have been predicted to be of comparable thermodynamic stability, while the latter one should be more endothermic. Structural parameters and vibrational spectra have also been calculated.[8] Recently Lee et al. presented results of high-level *ab initio* calculations of the heats of formation, structural parameters, vibrational data, and general valence force fields for the three most stable Cl_2O_2 isomers.[9] Novel calculations on the UV/vis spectra of ClOOCl and $ClClO_2$ were reported in ref 10.

The first spectroscopic evidence for a Cl_2O_2 species arose from matrix-isolation studies around 1970. These studies involved, for example, the photolysis of matrix-isolated ClOCl, but the assignment of bands to a specific isomer has remained uncertain.[11] Additional experiments were described in refs 12 and 13, and the observed bands, first assigned to the ClO radical,[12] were later tentatively assigned to chlorine chlorite, ClOClO.[13] As a result of kinetic investigations of the reactions Cl + OClO[14] and O + ClOCl,[15] this Cl_2O_2 isomer was also suggested recently as an intermediate of significant lifetime.

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Spectroscopic investigations of the ClO dimerization have been undertaken several times.[16] However, the identities of the products remained speculative until recently, when Birk et al. showed ClOOCl to be a main product by means of submillimeter spectroscopy.[17] However, the formation of other Cl_2O_2 isomers could not be ruled out. In the IR region, weak bands near 750 and 650 cm^{-1} have been observed in the gas phase[18] as well as in an argon matrix[19] and have been attributed to ClOOCl, whereas the assignment of a band near 560 cm^{-1}, observed in the gas phase, has remained uncertain.

Attempts to prepare chloryl chloride, $ClClO_2$, were reported in the 1950s.[20] The compound remained elusive until very recently, when we were able to synthesize $ClClO_2$ by various routes and to characterize it in noble gas matrices[21,22] and in the gas phase[23] by means of IR and UV/vis spectroscopy.

In the present study, products of the reactions Cl + OClO and O + ClOCl have been trapped in argon matrices to allow us to observe the formation of Cl_2O_2 isomers. The photolysis of matrix-isolated $ClClO_2$ and ClOClO is investigated to obtain a more detailed description of the photochemistry and vibrational spectra of matrix-isolated Cl_2O_2 isomers. A general valence force field of ClOOCl is calculated from experimental data.

Experimental Section

Chemicals. Caution! *Although no explosion occurred during the course of our studies, chlorine oxides are potentially explosive, especially in the presence of organic or oxidizable materials. The chlorine oxides should be handled only with proper safety precautions and only in millimolar quantities.*

OClO (both in natural isotopic composition[24] and enriched in ^{18}O [22]), ClOCl,[24] $Cl^{18}OCl$,[12] $FClO_2$, and $FCl^{18}O_2$ [22] were prepared according to literature methods. Chlorine (99%, Merck), BCl_3 (98%, Merck), and ClF_3 (98%, Baker) were purified by trap-to-trap condensation prior to use. Argon (99.9999%, Messer-Griesheim), neon (99.999%, Linde), and oxygen (99.999%, Linde) were used without further purification.

The reactor for the synthesis of matrix-isolated $ClClO_2$ (cf. ref 22) was prepared in the following manner: about 2 mmol of $AlCl_3$ was synthesized from its elements in a small U-trap and distributed over the inner surface by sublimation.

$ClClO_2$ in the gas phase was prepared by mixing stoichiometric amounts of gaseous $FClO_2$ ($\sim 10^{-2}$ mmol s^{-1}) and BCl_3 ($\sim 3 \times 10^{-3}$ mmol s^{-1}) before the mixture was allowed to enter the absorption cell, which was operated in a flow mode or by stopped flow.

Preparation of the Matrices. During this study, about 15 argon and 6 neon matrices containing $ClClO_2$ were prepared for photoisomerization experiments. In addition, about 30 argon matrices were prepared for investigation of the reactions Cl + OClO and O + ClOCl.

Prior to use, the vacuum lines and transfer capillaries were treated with ClF_3 to remove traces of water. Mixtures of $FClO_2$, Cl_2, or O_2 with Ar or Ne were prepared in a passivated stainless steel high-vacuum line and transferred to the reactors *via* a stainless steel capillary. Gaseous OClO or ClOCl were mixed with Ar in a Duran glass high-vacuum line and transferred *via* a quartz glass capillary into the reaction chamber Y of the codeposition nozzle according to Figure 1. Cl_2/Ar or O_2/Ar, in a typical mixing ratio of 1:50, was passed through a microwave discharge, which ends at point X at the entrance of the mixing device. The discharge products were mixed with OClO/Ar or ClOCl/Ar (1:200 in most experiments) in the small volume Y, about 25 mm in front of the matrix support, where the products of the reactions were quenched at 11 K. Equal amounts of the respective gas mixtures were codeposited for 0.5–1 h, with a usual deposition rate of about 0.8 mmol h^{-1}.

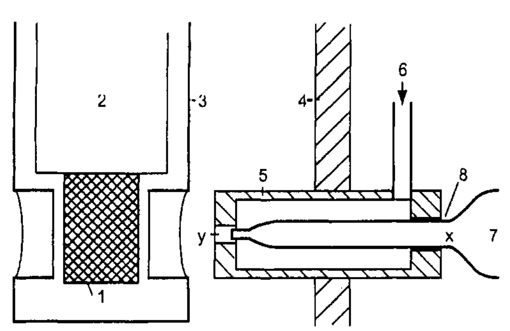

Figure 1. Schematic representation of the matrix assembly for investigations of the reactions Cl + OClO and O + ClOCl. (1) Matrix support, copper block with two mirror surfaces. (2) Liquid helium heat exchanger (4–300 K). (3) Radiation shield (77 K). (4) Vacuum shroud (<10^{-7} mbar). (5) Codeposition nozzle. (6) Entrance for OClO/Ar or ClOCl/Ar. (7) Glass tube with microwave-induced plasma of Cl_2/Ar or O_2/Ar. (8) Indium seal. (X) End of discharge zone;.(Y) Reaction chamber.

Isolation of $ClClO_2$ in a matrix was achieved by passing a mixture of $FClO_2$/Ar (Ne) (1:500) over $AlCl_3$ at 0 °C and quenching the products after a few milliseconds at 11(4) K onto the matrix support (see also ref 22). In a typical experiment, about 2 mmol of matrix gas was deposited within 30 min.

Instrumentation. Matrix IR spectra were recorded on a IFS 66v FT spectrometer (Bruker) equipped with special transfer optics for measurements in the reflectance mode. A DTGS detector, together with a Ge/KBr beam splitter, operated in the region 5000–400 cm^{-1}. A liquid helium-cooled Si bolometer (Infrared Laboratories), together with a 6-μm Mylar beam splitter, were used in the region 550–80 cm^{-1}. 64 and 256 scans, respectively, were coadded for each spectrum, using an apodized resolution of ~ 0.3 cm^{-1}.

UV spectra were recorded with a 1024 Diode Array spectrometer system (Spectroscopy International) using a CLD 30-W deuterium lamp (Zeiss) as light source. Hg emission lines were used for wavelength calibration. Matrix spectra were recorded in the reflection mode using quartz glass fiber optics (Spectroscopy International). Gas-phase spectra were recorded in the transmission mode using a Duran glass cell (optical pass length 10 cm) equipped with quartz glass lenses (Suprasil; Heraeus). Poly(tetrafluoroethylene) valves (Young) allowed measurements in a static or dynamic mode. Pressure control was achieved by a capacitance manometer (MKS Baratron 122A, 10 mbar absolute). The monochromator and the housing of the absorption cell were flushed with N_2 to eliminate absorption of atmospheric O_2.

Photolysis experiments were undertaken in the visible and UV regions using a 250-W tungsten halogen lamp (Osram) and Hg high-pressure lamp TQ 150 (Heraeus), respectively, in combination with various cutoff filters (Schott). The light of the tungsten filament or of the Hg plasma was projected onto the matrix samples *via* water-cooled quartz glass lenses (diameter 50 mm, focal length 50 mm).

Results

UV Spectra of Gaseous and Matrix-Isolated Chloryl Chloride, $ClClO_2$. Perturbations of the energy levels of matrix-isolated molecules in comparison to the gas phase are smallest for neon matrices. In addition, neon matrices are very transparent (they will not scatter) and are thus especially suitable for recording UV spectra.

An initial aim for the study of the photochemistry of $ClClO_2$ isolated in a neon matrix was to measure the UV spectrum of pure ClOOCl after complete photoisomerization of $ClClO_2$. This experiment, however, failed, because no photoisomerization of $ClClO_2$ occurred in a neon matrix. But as a result of our efforts, improved UV spectra of $ClClO_2$ isolated in a neon matrix and in the gas phase have been obtained, in comparison to previous studies.[21, 23] These spectra are shown in Figure 2. The neon matrix spectrum is limited to 230 nm because of the absorption

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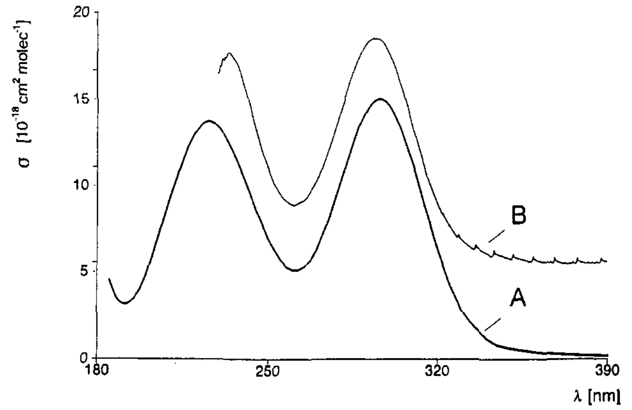

Figure 2. UV spectra of $ClClO_2$ in the gas phase (A) and isolated in a neon matrix (B). The absorption scale for the matrix spectrum is arbitrary.

by the quartz glass fiber optics. Absorption cross sections of gaseous $ClClO_2$ are determined by comparing its absorbance with that of its thermal decomposition product OClO as described previously.[23] These measurements are carried out in transmission mode with a low wavelength limit of ca. 185 nm. Decreasing energy may affect the absorption cross sections up to 195 nm.

The maxima observed at 234 and 293 nm, as well as the band profile of the matrix spectrum, agree well with the gas-phase data (maxima at 226 and 296 nm with $10^{18}\sigma = 13.8$ and 15.1 cm^2 molecule^{-1}). Photolysis of $ClClO_2$ with red light (see below) suggests that it absorbs significantly even in the visible region.

Comparison of the UV spectrum of $ClClO_2$ with those of other covalent chloryl compounds, such as $FClO_2$,[25] $ClOClO_2$,[18,26] $O_3ClOClO_2$,[27] and O_2NOClO_2[28] indicates that the main features of these spectra arise from the ClO_2 chromophore.

Recent *ab initio* calculations on the UV spectrum of $ClClO_2$ by Stanton and Bartlett agree well with the experimental data for the main features.[10] According to these calculations, the maxima at 226 and 296 nm correspond to F and C singlet states of A' symmetry, respectively. An E $^1A''$ state has been predicted to be close to the F state, but it should cause weaker absorptions by a factor of ca. 5. Lowest-lying states are calculated to be in the 300–350-nm region. An estimated error of ±0.2 eV seems to be too small for these states to account for absorption of $ClClO_2$ above 600 nm.

Lower level calculations have predicted absorptions at longer wavelengths.[29,30] However, because *all* of their electronic states have been shifted to energies lower than those of ref 10, it seems unlikely that the lower level calculations provide a better description of the UV spectrum of $ClClO_2$.

Photolysis of Chloryl Chloride, $ClClO_2$. $ClClO_2$, produced and matrix-isolated as described in the Experimental Section, is identified by UV (see above) and IR spectroscopy (ν_5, $\nu_1/2\nu_2$, $\nu_2/2\nu_4$, and ν_3 near 1210, 1040, 520, and 440 cm^{-1}, respectively).[22] In all instances, OClO ($\nu_1 + \nu_3$, ν_3, ν_1, and ν_2 near 2030, 1100, 940, and 440 cm^{-1}, respectively)[31] is present as a byproduct. It is observed in this study that the proportion of OClO depends on the activity and the amount of the $AlCl_3$. At the beginning of deposition, the formation of OClO is favored, while after some treatment with $FClO_2$ the reaction results mainly in $ClClO_2$. Larger amounts of $AlCl_3$ reduce the yield of $ClClO_2$.

A decrease of the amount of $ClClO_2$ isolated in an argon matrix is first observed after its irradiation with red light of wavelengths > 610 nm. Simultaneously, a weak band appears near 995 cm^{-1}. The assignment of this band to chlorine chlorite, ClOClO, is discussed below. Using yellow light of wavelengths > 495 nm enhances the photolysis rate of $ClClO_2$, while bands of OClO remain unchanged. Using the latter cutoff filter, the new band at 995 cm^{-1} shows its maximal intensity after 3 min, remains approximately constant for about 30 min, and decreases slowly afterwards. This absorption is accompanied by a ^{37}Cl isotopic band near 986 cm^{-1}, along with further matrix splittings. After 15 min, three further new bands appear near 754, 648, and 543 cm^{-1}, which increase on prolonged photolysis with a constant intensity ratio of 0.28:1:0.31 (cf. Figure 3). At higher resolution, the bands at 754 and 648 cm^{-1} split into three components with an intensity pattern of 9:6:1 (cf. Figure 4). In the far infrared region (450–80 cm^{-1}), only one weak band at 418.5 cm^{-1} is detected. This band is associated in intensity with the latter species, which is shown below to be dichlorine peroxide, ClOOCl. The vibrational data observed for this molecule, including data obtained from photolysis of ^{18}O enriched $ClClO_2$, are summarized in Table 1. When a cutoff filter at 395 nm is used from the outset, photolysis of $ClClO_2$ is even faster, but neither ClOClO nor ClOOCl is formed. Because no new infrared band appears, it is suggested that $Cl_2 + O_2$ are the only products from $ClClO_2$ under these conditions. ClOO (1442.8 cm^{-1}) is due to photolysis of OClO present as an impurity, as is evident from the ratio of the integrated band intensities.[31]

After almost all of the $ClClO_2$ is converted to ClOOCl, the matrix is irradiated with near UV light. Decomposition of ClOOCl is observed first with a cutoff filter at 360 nm. Simultaneously, an increase in ClOClO is observed. The final photolysis products of ClOOCl are infrared inactive, and it is suggested that thay are $Cl_2 + O_2$.

Using cutoff filters at 530, 495, and 395 nm, the photolysis of $ClClO_2$ isolated in a neon matrix proceeds approximately 5 times slower than that of $ClClO_2$ isolated in an argon matrix, and no infrared-active products are obtained. This demonstrates that $ClClO_2$ will photodissociate in a neon matrix exclusively to Cl_2 and O_2.

The Reaction Cl + OClO. The deposition device used for investigation of the Cl + OClO reaction products is described in the Experimental Section and is shown in Figure 1. Through the inner glass tube an Ar/Cl_2 mixture passes a microwave discharge (see Experimental Section), and the Cl atoms effusing from the orifice are mixed with a concentric stream of Ar/OClO in the chamber Y (volume ~0.02 mL). The resulting products are quenched into the matrix. When the inner and outer orifices of the nozzle are adjusted in the same plane, mixing can occur only in the volume in front of the matrix support (~8 mL). In this case, the only chlorine oxide observed is OClO. When the orifice of the glass tube is located ca. 3 mm inside the outer orifice (cf. Figure 1), mixing of both gas streams is efficient in this small volume Y (~0.02 mL). In this case, $ClClO_2$ (bands near 1210, 1040, and 440 cm^{-1})[22] is formed, together with a species showing absorptions near 995 and 986 cm^{-1}, in an 3:1 intensity ratio. The latter absorptions agree with those observed during photolysis of $ClClO_2$ isolated in an argon matrix. As will be shown below, they are due to ClOClO. The bands of ClOClO weaken in intensity at higher deposition rates and are approximately proportional to the amount of Cl_2 and OClO. The integrated intensity of the 990-cm^{-1} band is slightly less than 4 times those of $\nu_5(ClClO_2)$ near 1210 cm^{-1}. Detail of a typical spectrum obtained after optimized experimental conditions is shown in Figure 5. Spectra containing large amounts of ClOClO allow the detection of further weak bands related in intensity to this species. When the matrix is irradiated with red light, a decrease in these weak bands as well as those near 990 cm^{-1} is first observed

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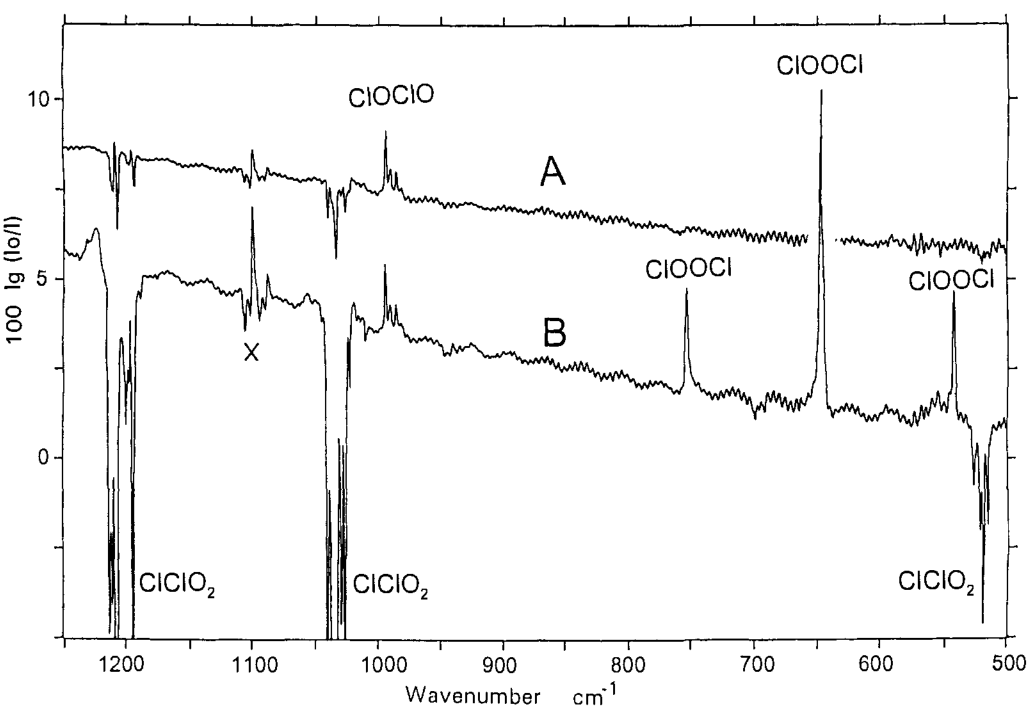

Figure 3. IR difference spectra of $ClClO_2$ isolated in an argon matrix. Spectrum taken after photolysis (λ > 495 nm) minus spectrum taken before photolysis. (A) after 3 min; (B) after 30 min; X marks bands of OClO not completely compensated.

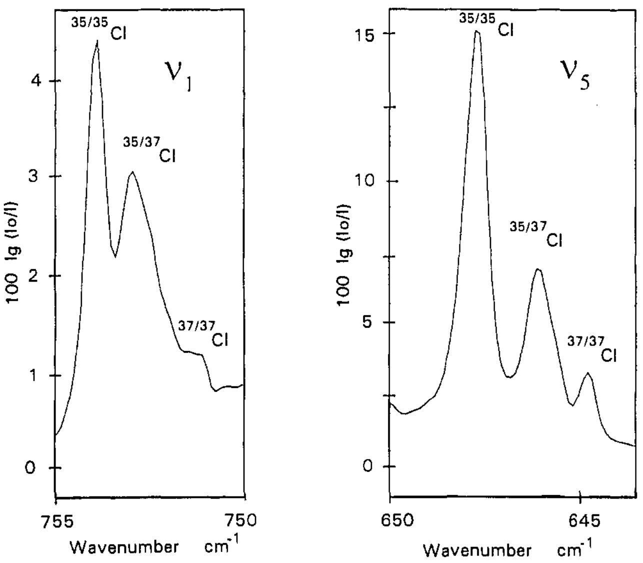

Figure 4. IR spectrum of ClOOCl isolated in an argon matrix (resolution, 0.3 cm^{-1}) in the regions of ν_1 and ν_5.

with a cutoff filter at 665 nm, suggesting that all these bands are due to ClOClO. All observed vibrational bands, together with *ab initio* data, are presented in Table 2. Simultaneously with the decrease in ClOClO, an increase in $ClClO_2$ occurs. Bands of ClOOCl appear when a cutoff filter at 530 nm is used.

In a few experiments, very weak bands due to ClClO (961.5 and 953.2 cm^{-1})[11,13] and Cl_2O_3 (1232.4, 1229.8, 1226.2, 1062.2, and 1058.3 cm^{-1})[19] are also detected.

Further weak or very weak absorptions of monomeric HCl (2888.3, 2870.3, 2851.9 cm^{-1}),[32] CO_2 (2344.9, 2339.2, 633.5, 662.0 cm^{-1}), CO (2138.3 cm^{-1}),[33] ClCO (1877.2, 570.1 cm^{-1}),[34] Cl_2CO (1815.2, 837.2 cm^{-1}),[35] HOCl (1240.0 cm^{-1}),[36] and HCl_2^- (696.0 cm^{-1})[37] are caused by HCl and CO_2 impurities remaining in the Cl_2, as shown by passing Ar/Cl_2 (M/R = 50) through a microwave discharge and subsequently quenching the products in a matrix.

Table 1. Vibrational Wavenumbers (cm^{-1}) and Intensities (km mol^{-1}) of Dichlorine Peroxide, ClOOCl, Isolated in an Argon Matrix in Comparison to Calculated Data[a]

experimental			*ab initio*		
A	I^b	B	C	D	assignment[c]
753.97/		716.03/	810 (16.5)	767 (9.3)	ν_1, ν(OO)
752.9 /	28	735.83			
751.3					
543.0 /		518.8 /	548 (20.2)	570 (13.3)	ν_2, ν_s(ClO)
541.8 /	31	530.0			
d			310 (1.2)	321 (0.1)	ν_3, δ_s(ClOO)
127 ± 20[e]			121 (0.4)	117 (0.3)	ν_4, τ
647.67 /		618.88 /	612 (32.9)	629 (24.1)	ν_5, ν_{as}(ClO)
645.99 /	100	633.84			
644.67					
418.5	10		417 (10.4)	426 (4.5)	ν_6, δ_{as}(ClOO)

[a] A: $^{35}Cl^{16}O^{16}O^{35}Cl/^{37}Cl^{16}O^{16}O^{35}Cl/^{37}Cl^{16}O^{16}O^{37}Cl$. B: $^{35}Cl^{18}O^{18}O^{35}Cl/^{35}Cl^{18}O^{16}O^{35}Cl$. C: $^{35}Cl^{16}O^{16}O^{35}Cl$, CCSD(T)/DZP; ref 9. D: $^{35}Cl^{16}O^{16}O^{35}Cl$, CCSD(T)/TZ2P; ref 9. [b] Relative band strength of natural ClOOCl, $I(\nu_5)$ = 100. [c] Approximate description of modes according to C_2 symmetry. [d] 310 cm^{-1} from force field calculations, see text. [e] From mm-wave measurements, ref 15. 114 cm^{-1} from force field calculations, see text.

The Reaction O + ClOCl. Bands at 994.5 and 985.8 cm^{-1} are also observed in these experiments. Their intensity is approximately proportional to the amount of O_2 and ClOCl. Weak absorptions of ClClO (961.5, 953.2 cm^{-1})[11,13] increase with increasing ClOCl/Ar ratio. They are independent of the O_2/Ar ratio and are formed predominantly at higher microwave power. Unreacted ClOCl is observed at 677.1, 675.0, 638.6, 635.7, and 633.1 cm^{-1}.[38]

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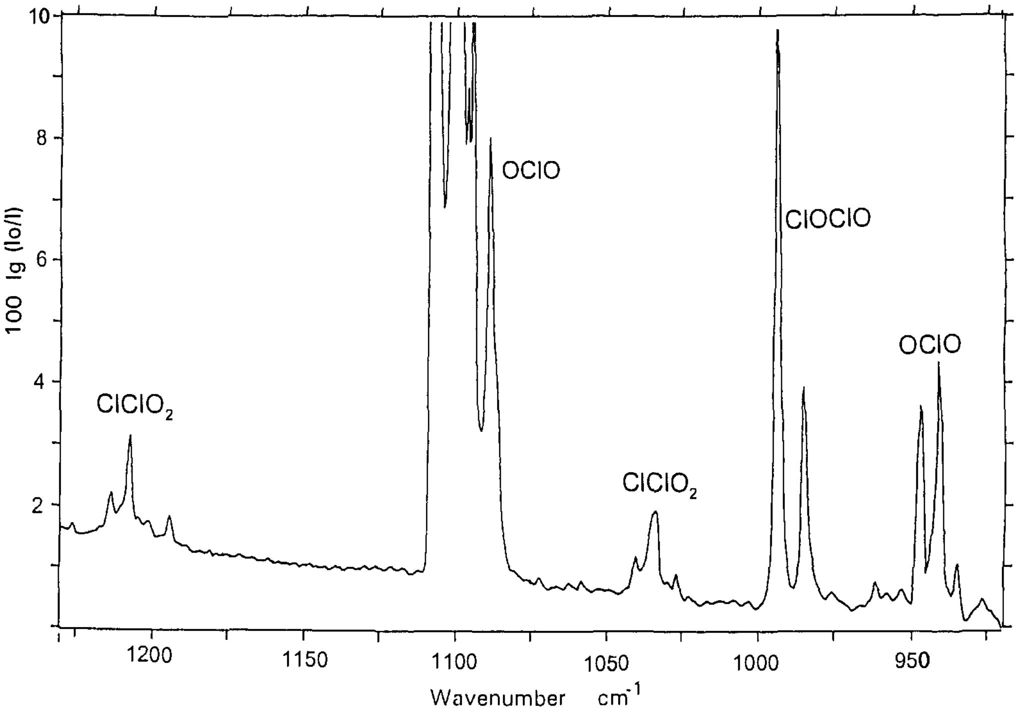

Figure 5. IR spectrum of the matrix-isolated products of the reaction OClO/Ar + Cl/Ar.

Table 2. Vibrational Wavenumbers (cm^{-1}) and Intensities (km mol^{-1}) of Chlorine Chlorite, ClOClO, Isolated in an Argon Matrix in Comparison to Calculated Data[a]

experimental			*ab initio*		
ClOClO′	I[b]	ClOCl^{18}O′	A	B	assignment[c]
994.52[d] 985.80[e]	100	957.6[d] 948.4[e]	912 (31.6)	952 (62.5)	ν_1, ν(ClO′)
695.9	5		661 (8.2)	648 (2.2)	ν_2, ν(ClO)
440.3	5		306 (7.3)	403 (28.3)	ν_3, ν(OCl)
338.7	2		282 (5.2)	341 (5.1)	ν_4, δ(ClOCl)
			144 (6.9)	236 (7.8)	ν_5, δ(OClO′)
			55 (4.3)	90 (4.2)	ν_6, τ

[a] A: ^{35}Cl^{16}O^{35}Cl^{16}O′, CCSD(T)/DZP; ref 9. B: ^{35}Cl^{16}O^{35}Cl^{16}O′, CCSD(T)/TZ2P; ref 9. [b] Relative band strength of natural ClOClO, $I(\nu_1)$ = 100. [c] Approximate description of modes according to C_1 symmetry. [d] ^{35}ClO^{35}ClO′/^{37}ClO^{35}ClO′. [e] ^{35}ClO^{37}ClO′/^{37}ClO^{37}ClO′.

Bands of O_3 (near 2110, 1100, 1040, and 700 cm^{-1}) are also present in experiments without ClOCl. They are due to the recombination of O atoms with O_2.

Use of ClOCl with ca. 75% ^{18}O shifts the bands at 994.5 and 985.8 cm^{-1} by 0.25 cm^{-1} to lower wavenumbers, while absorptions of ClClO at 961.5 and 953.2 cm^{-1} are accompanied by ^{18}O counterparts at 925.2 and 916.5 cm^{-1} (cf. refs 11 and 13) of 3-fold intensity.

Discussion

Identification of the Products and Vibrational Assignment. It is obvious that during photolysis of ClClO$_2$ isolated in an argon matrix two different species are formed. One is observed instantaneously after the first decomposition of ClClO$_2$, whereas the formation of the other one is retarded. In this section we will show the two molecules to be ClOClO and ClOOCl, respectively.

(A) Chlorine Chlorite, ClOClO. The band near 990 cm^{-1} has been observed in previous matrix-isolation studies and has been attributed to a Cl_2O_2 species[11,13] or ClO.[12] In ref 13, it was tentatively assigned to ClOClO on the basis of the observed $^{35/37}$Cl and $^{16/18}$O isotopic shifts, which both are comparable to those of the ClO free radical.

In the present study, this species is observed as both a photoproduct and a precursor of ClClO$_2$ and ClOOCl (see Results section and discussion of the photochemistry), which establishes the assignment as a Cl_2O_2 molecule. The formation of this species in both reactions, Cl + OClO and O + ClOCl, supports the attribution to ClOClO. Our assignment to ν_1, the ClO′ stretching vibration of ClOClO′ (prime indicates terminal oxygen), arises from the comparison of this vibration with ClClO′ (962 cm^{-1})[11,13] and FClO′ (1038 cm^{-1}).[39] Similarly, ν_s(ClO$_2$) and ν_{as}(ClO$_2$) of ClOClO$_2$ (1057 and 1225 cm^{-1})[19,41] are located between those vibrations of ClClO$_2$ (1042 and 1218 cm^{-1})[22,23] and FClO$_2$ (1106 and 1271 cm^{-1}).[42] Comparison of the $^{35/37}$Cl and the $^{16/18}$O′ isotopic shifts with those of ClO,[40] ClClO,[11,13] and FClO[39] indicates that these two atoms are mainly involved in the vibration. This is also confirmed by the very small $^{16/18}$O isotopic shift of the bridging O atom (~0.25 cm^{-1}). In addition, the observation of this isotopic shift establishes the presence of two nonequivalent O atoms.

The bands at 695.9 and 440.3 cm^{-1} are in the region of stretching vibrations of ClO single bonds. By comparison with ClOCl′O$_3$,[41,43] they are assigned to ν_2 = ν(ClO) and ν_3 = ν(OCl′) of ClOCl′O′. The *ab initio* force field of ref 9 indicates ν_1, ν_2, and ν_3 to be essentially unmixed, in agreement with the findings for ClOCl′O$_3$.[41,43] The remaining band observed at 338.7 cm^{-1} is in the region of deformation modes. According to *ab initio* calculations, it is assigned to ν_4, which exhibits strong ClOCl and OClO deformation character, the former being more dominant.

Experimental band positions and relative band strengths agree quite well with CCSD(T) *ab initio* values. With the larger TZ2P basis set, better agreement is obtained for band positions, while relative intensities are better predicted with the DZP basis set.[9]

According to CCSD(T)/TZ2P calculations, the OCl′ bond is longer and weaker than the ClO bond (181.4 versus 172.6 pm), compatible with their much lower OCl′ stretching vibration. Since all predicted stretching modes are lower than the experimental ones (cf. Table 2), the bond lengths in ClOClO are expected to be 2–6% shorter than the predicted ones (cf. ref 1b). Although

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Table 3. Force Constants[a] (10^2 N m^{-1}) and Experimental Potential Energy Distribution (PED)[b] of Dichlorine Peroxide, ClOOCl

		ab initio[c]		PED					
	exptl	CCSD(T)/TZ2P	MP2/TZ2Pf	ν_1	ν_2	ν_3	ν_4	ν_5	ν_6
f_R	3.290	3.147	3.278	0.93	0.52	0.15			
f_r	2.412	2.216	2.920	0.03	1.12	0.27		0.81	0.20
f_α	1.220	1.346	1.413	0.14	0.13	0.90	0.04	0.30	0.73
f_τ	0.1373	0.162	0.151			0.17	0.87		
f_{Rr}	1.076	0.880	0.863	0.19	−0.83	−0.22			
$f_{R\alpha}$	0.532	0.392	0.453	−0.27	0.19	−0.28			
$f_{R\tau}$	0.018	0.036	0.053						
f_{rr}	−0.015	0.030	−0.009						
$f_{r\alpha}$	0.231	0.152	0.215		−0.10	0.13		−0.13	0.10
$f_{r\alpha}$	0.052	−0.029	−0.026						
$f_{r\tau}$	0.0037	0.003	0.004						
$f_{\alpha\alpha}$	0.027	−0.001	0.003						
$f_{\alpha\tau}$	0.0644	0.064	0.074			−0.17	0.08		

[a] R, r(OO); r, r(ClO); α, ∠(ClOO); τ, torsion. Deformation force constants normalized to 100 pm bond length. [b] $^{35}Cl^{16}O^{16}O^{35}Cl$; only contributions ≥ 0.03 are given. [c] Reference 9.

in poorer agreement with the experimental results, the other CC calculations of ref 9 support this view. Further, indirect support comes from a different method: at the CISD/6-31 G* level, OCl′ and ClO bonds are almost equal (171.1 versus 169.8 pm), compatible with much closer stretching vibrations (623 versus 772 cm^{-1}),[44] but in poorer agreement with experimental results.

(B) Dichlorine Peroxide, ClOOCl. The bands near 754, 648, 543, and 419 cm^{-1} are due to a species which is both a photoproduct and a precursor of ClOClO (see Results section and discussion of the photochemistry). This observation suggests an assignment to a Cl_2O_2 isomer as well. The 9:6:1 intensity patterns of the bands near 754 and 648 cm^{-1} obviously show the presence of two equivalent chlorine atoms. When samples enriched in ^{18}O are used, the intensity pattern and the number of isotopic splittings establish the presence of two equivalent oxygen atoms. Considering the structures of H_2O_2, O_2F_2, and CF_3OOX (X = H, F, Cl, CF_3)[45] as well as *ab initio* calculations on ClOOCl,[8,29] the observed bands are assigned to a chain ClOOCl molecule with C_2 symmetry (Table 1), ruling out isomers like *cis*-ClOOCl, cyclic ClOOCl (with a ClCl bond), or OClClO. The molecule must exhibit two ClO stretching modes. The ratios $\nu(^{35}Cl^{16}O^{16}O^{35}Cl)/\nu(^{35}Cl^{18}O^{18}O^{35}Cl)$ are 1.0465 and 1.0466 for the bands near 648 and 543 cm^{-1}, respectively, comparable to those of ClO (1.0402)[40] and ClOCl (1.0414 and 1.432 for ν_1 and ν_3 respectively)[38]. As expected for an asymmetric ClO stretching vibration, the band at 648 cm^{-1} is observed at higher wavenumbers, shows larger $^{35/37}Cl$ isotopic shifts, and has a greater band strength than the one at 543 cm^{-1}, which therefore can be assigned to the symmetric mode. The respective ratio for the absorptions near 754 cm^{-1} is 1.0530, close to the harmonic value of 1.0607 for O_2. Accordingly, this vibration is most likely due to an OO stretching mode.

As one would expect, the ClO stretching modes ν_2 and ν_5 of ClOOCl have been observed at lower wavenumbers than the corresponding modes in ClOCl (677 and 639 cm^{-1}),[38] indicative of weaker ClO bonds. The position of the OO stretching vibration ν_1 can be rationalized by comparison with the related molecules CF_3OOCF_3 (886 cm^{-1}) and CF_3OOCl (823 cm^{-1}).[45]

Bands near 750 and 650 cm^{-1} have also been observed during IR spectroscopic investigations of the ClO dimerization in an argon matrix[19] as well as in the gas phase.[18] Based on an *ab initio* calculation,[8] the former band has been attributed to ν(OO) of ClOOCl, while splittings of the latter have been interpreted as ν_{as}(ClO) and ν_s(ClO) rather than matrix or isotopic splittings.[19] A band near 560 cm^{-1} has been observed in the gas-phase study, but no assignment is given.[18] According to its relative band strength and position, it is obviously assigned to ν_s(ClO) of ClOOCl. No such band has been observed in the previous matrix study, supposedly due to the low signal-to-noise ratio (cf. (Figs.) 2–4 of ref 19). The relatively large gas-phase matrix shift of this band (17 cm^{-1} or 3%) indicates a pronounced perturbation of ClOOCl in an argon matrix compared to the gas phase (see, for example, ref 31, where these effects have been studied for OClO).

Normal Coordinate Analysis of Dichlorine Peroxide, ClOOCl. The general valence force field is calculated to confirm the assignments and to obtain a better description of the bonding in ClOOCl. The computation is carried out using the program NCA[46] with the ground-state effective structural parameters,[17] vibrational wavenumbers (cf. Table 1), and centrifugal distortion constants[17] as input data. The data are weighted according to their experimental uncertainties. Since ν_3 and ν_4 are not observed directly, the CCSD(T)/TZ2P value of 321 cm^{-1} [9] and a value of 127 cm^{-1}, respectively, derived from relative intensities of rotational lines in the ground and first excited torsional states,[17] are used for $^{35}Cl^{16}O^{16}O^{35}Cl$ with an uncertainty of 20 cm^{-1}. Because anharmonic contributions to the vibrational wavenumbers and vibrational contributions to obtain the equilibrium centrifugal distortion constants are difficult to evaluate for ClOOCl, no correction of the experimental data is therefore undertaken. Furthermore, it is suggested that effects of these corrections are of the same order of magnitude as the uncertainties of the force constants which arise from the limitation of the experimental data. Average values of CCSD(T)/TZ2P and MP2/TZ2Pf *ab initio* force constants are used for an initial force field.[9]

In the first step, the four diagonal force constants, f_{Rr}, $f_{R\alpha}$, and f_{rr}, are fitted to the vibrational wavenumbers. In the following step, f_τ is fitted to the centrifugal distortion constants, because they depend most strongly on this force constant. In the last step, all of the force constants are fitted to both the vibrational wavenumbers and centrifugal distortion constants. The resulting experimental force field, together with *ab initio* data and the potential energy distribution, is given in Table 3. The diagonal force constants, as well as f_{Rr}, f_{rr}, and $f_{\alpha\tau}$, are precisely determined, with the remaining interaction constants incorporating larger uncertainties. The observed vibrational wavenumbers are reproduced moderately well, with an average deviation of 0.5 cm^{-1}. These deviations are due to a combined fitting of vibrational and centrifugal distortion data and the fact that anharmonic contributions are not taken into account (cf. ref 31, where these effects have been studied for OClO). The centrifugal distortion constants determine precisely f_τ, giving τ = 114 cm^{-1}, in accordance with the experimental value τ = 127 ± 20 cm^{-1} of ref 17 and the *ab initio* values of ref 9 (cf. Table 1). A value of 310 cm^{-1} is obtained for ν_3, in agreement with *ab initio* values.[9] For the distortion constant d_2 of $^{37}Cl^{16}O^{16}O^{35}Cl$, a value of −0.0227 kHz is obtained, in comparison to the experimental value of

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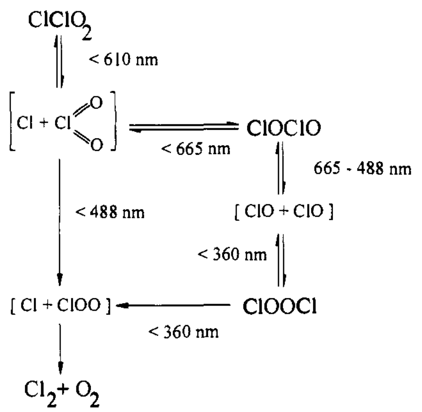

Figure 6. Photochemistry of Cl_2O_2 isomers isolated in argon matrix and wavelengths for dissociation.

−0.0115(57) kHz.[17] All other calculated distortion constants showed an average deviation of 2.3%.

The force constants obtained from experimental data agree well with *ab initio* data (cf. Table 3). As expected from the vibrational spectrum, the OO stretching force constant of 329.0 N m^{-1} is much smaller than that of H_2O_2 (values of ~400–450 N m^{-1} are reported),[47] and the ClO force constant, 241.2 N m^{-1}, is significantly smaller than those in ClOCl (295 N m^{-1})[48] and HOCl (367 N m^{-1}),[49] but much larger than that in ClOO (50.9 N m^{-1}).[31] As is suggested in ref 9, the separation of ν_1 and ν_5 is strongly dependent on f_{Rr}.

Although the potential energy distribution indicates the vibrations of ClOOCl to be mixed, the approximate descriptions of modes in Table 1 are adequate.

The Photochemistry of Matrix-Isolated Cl_2O_2 Isomers. The instant formation of ClOClO during irradiation of $ClClO_2$ isolated in an argon matrix with visible light ($\lambda > 610$, 535, 495 nm) indicates that this molecule is formed without any long-lived intermediate. The following mechanism is suggested: the terminal Cl atom dissociates from $ClClO_2$ and can attack the remaining OClO either at the Cl atom, to re-form $ClClO_2$, or at an O atom, to produce ClOClO (cf. Figure 6).

The isomerization of $ClClO_2$ to ClOClO may also proceed via an intramolecular rearangement. However, the absence of ClOClO and ClOOCl when $ClClO_2$ is photolyzed with light > 395 nm supports the initial dissociation into Cl + OClO: at these wavelengths, isomerization of the intermediate OClO takes place (threshold 488 nm), which obviously proceeds much more readily than migration of the large Cl atom to form ClOClO. The subsequent reaction

$$Cl + ClOO \rightarrow Cl_2 + O_2 \qquad (4)$$

is consistent with the absence of infrared-active photolysis products.

The absence of both ClOClO and ClOOCl during photolysis of $ClClO_2$ isolated in a neon matrix with light > 535 and 495 nm suggests that, at least in this matrix, a second dissociation channel may exist. Initial dissociation into Cl + OClO thus can only lead to the recombination of $ClClO_2$ on account of the reduced size of the cavities in neon, because isomerization of OClO to ClOO does not take place at these wavelengths (cf. Results section and ref 31). Since no infrared-active photoproducts of $ClClO_2$ have been observed, these products are suggested to be Cl_2 and O_2.

A on- step dissociation could proceed *via* simultaneous elongation of both ClO bonds with a decrease of the OClO bond angle. A two-step dissociation may require only one ClO bond to elongate with decreasing OClO angle. A chain intermediate ClClOO could then lead to the final $Cl_2 + O_2$ products.

Under the conditions of photolysis of $ClClO_2$ isolated in argon matrix, ClOClO ($\lambda > 495$ nm) is unstable as well. The retarded formation of ClOOCl suggests that it is rather the photoproduct of ClOClO than of $ClClO_2$. The reaction may proceed *via* dissociation of ClOClO into two ClO radicals, with subsequent recombination to ClOOCl or ClOClO. The isomerization can also involve an intramolecular rearrangement as a single step.

Photolysis of ClOClO, obtained from quenching products of the reaction Cl + OClO in an argon matrix, with light of wavelengths > 665 nm establishes Cl + OClO as another dissociation channel through the formation of $ClClO_2$.

Finally, photodecomposition of ClOOCl is also observed and should proceed *via* Cl + ClOO, leading to the final products $Cl_2 + O_2$, or *via* 2ClO as initial products. The formation of ClOClO during the photolysis of ClOOCl establishes the latter channel to be significant and suggests that under our conditions dimerization of ClO will yield ClOClO as well as ClOOCl. It should be pointed out that these findings do not necessarily contradict previous results that dimerization of ClO leads predominantly to ClOOCl[17] and photolysis of ClOOCl yields mainly Cl + ClOO,[50] but instead our results show further reaction channels to be significant.

Use of cutoff filters at wavelengths 665, 610, and 360 nm has been sufficient to photodissociate ClOClO, $ClClO_2$, and ClOOCl, respectively. These values are obviously lower wavelength limits for the threshold of photolysis, and the corresponding energies, 180, 198, and 332 kJ mol^{-1}, are upper limits for the respective dissociation energies.

From the combination of the *ab initio* values for the heat of formation of the three Cl_2O_2 isomers[9] and the experimental ones for the respective dissociation products,[51] the following dissociation energies are estimated: for ClOClO, 25 (2ClO) and 40 kJ mol^{-1} (Cl + OClO); for $ClClO_2$, 80 kJ mol^{-1} (Cl + OClO); and for ClOOCl, 70 (2ClO) and >80 kJ mol^{-1} (Cl + ClOO). These values are much lower than the upper limits obtained from photolysis experiments. They indicate that in each photolysis a large excess energy is available.

Although the OO bond energy in ClOOCl is lower than the ClO bond energy, ClO bond cleavage has been observed previously as the main photochemical path.[50] This study is the first one to present evidence for the photodissociation into two ClO radicals. A recent *ab initio* study rationalized the preference for the ClO bond cleavage during photolysis: the three lowest pairs of electronic states (each consisting of two almost degenerate states) are well described as n, π_{ClO}, and $\sigma_{ClO} \rightarrow \sigma^*_{ClO}$, respectively.[10] According to these calculations, the lowest states should cause absorptions around 335 nm, in good agreement with our estimated threshold of photodissociation.

Photolysis of $ClClO_2$ isolated in an argon matrix provides further information. When the channel leading to $Cl_2 + O_2$ is insignificant at wavelengths > 495 nm, concentrations and integrated band strengths of ClOClO and ClOOCl can be estimated relative to those of $ClClO_2$. After a very short photolysis time (up to 3 min, when no ClOOCl is observed), a ratio of 1:1.07 ± 0.2 is obtained for the integrated band strength of $\nu_5(ClClO_2)$ near 1200 cm^{-1} and ν_1(ClOClO) near 995 cm^{-1}. After a very long photolysis time (ca. 30 min, when most of $ClClO_2$ is converted into ClOOCl), a ratio of 1:0.23 ± 0.04 is calculated for $\nu_5(ClClO_2)$ near 1200 cm^{-1} and ν_5(ClOOCl) near 648 cm^{-1}. Using these values, integrated band intensities of Cl_2O_2 isomers in IR spectra recorded in between could be reproduced within the error limits. The photolysis channel $Cl_2 + O_2$ is not neccessarily insignificant

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for $ClClO_2$ in an argon matrix as assumed above, and relative band strengths of ClOClO and ClOOCl have to be considered as lower limits. These ratios agree reasonably with those derived from *ab initio* calculations.[9]

The Reactions Cl + OClO and O + ClOCl. A Cl atom may be attached to OClO at an O or at the Cl atom:

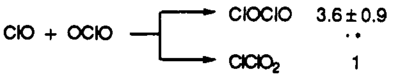
$$Cl + OClO \rightarrow ClOClO \qquad (5a)$$

$$ClOClO \rightarrow 2ClO \qquad (5b)$$

$$Cl + OClO \rightarrow ClClO_2 \qquad (6)$$

The formation of ClO in reaction 5 is well established, while the participation of an intermediate with a significant lifetime is claimed from an observed negative temperature dependence of the rate constant.[14] Reaction 6 has not been previously considered in kinetic investigations, but the formation of $ClClO_2$ during photolysis of Cl_2/OClO mixtures with visible light ($\lambda > 495$ nm) was reported recently.[23]

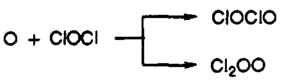
When the products of the reaction Cl + OClO are quenched in an argon matrix, both ClOClO and $ClClO_2$ are observed with an integrated intensity ratio of 3.8:1 between ν_1(ClOClO) near 990 cm^{-1} and ν_5($ClClO_2$) near 1200 cm^{-1}. Taking the ratio of 1.07:1 of the respective integrated band strengths, obtained in the previous section, the following branching ratio is obtained:



(7)

This branching ratio may be surprising at first sight, because according to *ab initio* calculations, ClOClO should be about 40 kJ mol^{-1} higher in energy than $ClClO_2$.[9] Interestingly, a similar ratio of 4:1 has been observed in the reaction Cl + NO_2 leading to ClONO and $ClNO_2$.[52] Golden et al.[53] have applied methods developed by Troe[54] to estimate third-order rate constants for reactions of atmospheric importance from the heats of formation, entropies, association rate constants, etc. Using experimental data where available and plausible data elsewhere, they have been able to reproduce experimental rate constants and the branching ratio for the reaction Cl + NO_2. Based on experimental results, they have used a value of 45 kJ mol^{-1} for the difference in the heats of formation of ClONO and $ClNO_2$. This value is in good agreement with very recent *ab initio* calculations (44 ± 6 kJ mol^{-1})[55] and very close to that found for ClOClO and $ClClO_2$.[9] Golden et al. attributed the preference of ClONO over $ClNO_2$ in the system Cl + NO_2 to the higher entropy of the former, which overcompensates the higher enthalpy in this case.[53]

Analogously to the reaction described above, an O atom may attack ClOCl at a Cl or at the O atom:



(8)

(9)

According to calculations at the HF/3–21 G* level, dichlorine oxide *O*-oxide, Cl_2OO, is much higher in energy than ClOClO,[29] so reaction 9 may not proceed exothermally. This is in agreement with our observations of only a single product, ClOClO. This observation confirms a recent claim that an intermediate with a significant lifetime is involved in reaction 8.[15]

Formation of the (excited) products in the reactions Cl + OClO and O + ClOCl is expected to proceed with only a small, or perhaps even zero, barrier of activation. It is therefore suggested that this formation occurs in the small mixing volume of the nozzle in front of the matrix support (cf. Figure 1). Because of the very small residence time (ca. 0.1–1 ms) and the low partial (ca. 1 μbar) and total pressures (ca. 1 mbar) and because the total pressure outside the nozzle decreases to ca. 10^{-2} mbar, comparison with similar reaction systems[56] suggests that collisional deactivation takes place during condensation of the matrix.

The microwave discharge is capable of forming not only highly excited atoms but also ions, of which the more stable ones (like HCl_2^-) may be isolated in a matrix. However, it is observed that yields of ClOClO and $ClClO_2$ decrease at higher microwave power and flow rates. The resulting larger plasma zone is closer to the mixing chamber, so that highly excited atoms (and ions) reduce the formation of ClOClO and $ClClO_2$ and enhance not only the decomposition of these products but also that of OClO or ClOCl to ClO and an O or Cl atom. In addition, the increased total pressure at higher flow rates may enhance recombination of Cl or O atoms and favor secondary reactions.

ClO, which may result from the decomposition of OClO, ClOCl, and ClOClO, is not observed because of its weak absorptions in the IR region.[57] Absorptions of tertiary products, like ClClO and Cl_2O_3, which may be formed from ClO according to reactions 10 and 12, are at best very weak. This suggests only small amounts of ClO to be present.

Traces of ClClO and Cl_2O_3 can be formed *via* the following reactions:

$$Cl + ClO \rightarrow ClClO \qquad (10)$$

$$O + Cl_2 \rightarrow ClClO \qquad (11)$$

$$ClO + OClO \rightarrow Cl_2O_3 \qquad (12)$$

Conclusion

ClOClO, which was identified tentatively in a previous study, has been observed as a primary product of the reactions Cl + OClO and O + ClOCl. Decomposition of ClOClO can lead to two ClO radicals.[14,15] ClOClO has also been observed as a photoproduct of $ClClO_2$ and ClOOCl. The latter observation is of stratospheric impact, because it establishes firstly that, besides Cl + ClOO, there is another photodissociation channel (2ClO) for ClOOCl and secondly that dimerization of ClO can lead to ClOClO besides ClOOCl. The observation of the strongest band of ClOClO in a study to isolate ClO in an argon matrix (but assigned there to ClO) together with the reported experimental conditions[12] gives evidence that dimerization of ClO to ClOClO can occur not only in the matrix but also in the gas phase. Thus, interpretation of the bimolecular channels of the ClO self-reaction (cf. Introduction) in terms of decomposing (not neccessarily collisionally deactivated) Cl_2O_2 isomers may lead to a simplified global model of the ClO dimerization (cf. ref 7). This view is supported by evidence for intermediates in a variety of reactions involving chlorine oxides and related compounds, such as ClO + OH (HOOCl),[58,59] BrO + ClO (BrOClO, BrOOCl;[60] but also $BrClO_2$ may be possible), OClO + O (ClO_3),[61,62] and BrO + BrO (BrOOBr).[63]

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Photolysis of $ClClO_2$ isolated in an argon matrix and the condensation experiments have allowed a detailed study of the photochemistry and vibrational spectroscopy of matrix-isolated Cl_2O_2 isomers. The force field of ClOOCl obtained from experimental data confirmed the assignments and has yielded information about the bonding in this molecule and the positions of ν_3 and ν_4, which have not been observed directly.

It is known that the matrix cage effect allows reactions to take place which are of minor importance in the gas phase, such as the isomerization of OClO to ClOO.[31] This study has also shown that even two different matrices (argon and neon) can cause a different photochemical reaction due to the difference in size of the matrix cages. Nevertheless, it is suggested that the estimated thresholds for photolysis of the Cl_2O_2 isomers and the two observed photodissociation channels are transferable to gas-phase chemistry.

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