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Infrared Spectroscopic and ab Initio Study of $HOOClO_2$

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$HOOClO_2$ was produced by addition of hydrogen atoms to a mixture of O_2 and OClO on the surface of growing argon matrixes at 17 K. The compound was identified by infrared spectroscopy utilizing the H to D and $^{18}O_2$ and $^{16,18}O_2$ spectral shifts. The matrices were irradiated with the full radiation from a 300-W Xe lamp. $HOOClO_2$ was eliminated by the irradiation, but we were unable to identify the photodecomposition product. Ab initio calculations show that HOO binds to OClO with a bond strength intermediate between a van der Waals interaction and a covalent bond.

Introduction

Anthropogenic chlorine has been shown to play a significant role in the depletion of stratospheric ozone. However the stratospheric chlorine budget is still under discussion. It has been suggested that perchloric acid may represent an important sink for chlorine between 15 and 20 km.[1] No observations of stratospheric perchloric acid have been made, and no formation mechanism has been established. Jaeglé et al.[1] suggested that sulfate aerosol particles may oxidize ClO and form $HClO_4$. HCl and $HClO_4$ have been observed in reactions of ClO on sulfuric acid:[2]

$$ClO \rightarrow HClO_4 + \text{products} \qquad (1)$$

$$ClO \rightarrow HCl + \text{products} \qquad (2)$$

Simonaitis et al.[3] proposed the three-body reaction:

$$ClO_3 + OH + M \rightarrow HClO_4 + M \qquad (3)$$

Prasad and Lee[4] suggested a two-step reaction where $ClO{\cdot}O_3$ radicals formed would react with peroxy radicals and form perchloric acid:

$$ClO{\cdot}O_2 + O_3 \rightarrow ClO{\cdot}O_3 + O_2 \qquad (4)$$

$$ClO{\cdot}O_3 + HO_2 \rightarrow HClO_4 + O_2 \qquad (5)$$

Another possibility for the formation of $HClO_4$ in the stratosphere would be to form a compound (precursor) which after photolytical rearrangement could form $HClO_4$. The precursor would preferably be an isomer of $HClO_4$. This paper shows that HO_2 radicals can add to OClO to form the $HClO_4$ isomer $HOOClO_2$:

$$HO_2 + OClO \rightarrow HOOClO_2 \qquad (6)$$

$HOOClO_2$ decomposed slowly when irradiated with the water-filtered radiation from a Xe lamp. We have not been able to identify the photodecomposition product.

Experimental Section

Chlorine dioxide was prepared by dripping sulfuric acid (Merck p.a.) on potassium perchlorate (Fluka purum p.a., >99.0% pure) under vacuum. The chloride dioxide was collected at −78 °C and was kept at −196 °C. Before an experiment was performed, the trap containing OClO was pumped on for 5 min at −78 °C.

Gas mixtures of hydrogen (AGA), deuterium (L'Air Liquide, 99.7% D), normal oxygen (AGA, 99.999%) or $^{18}O_2$ (Isotec, 97.3% ^{18}O), and argon (L'Air Liquide, 99.9995%) were prepared by standard manometric techniques. $^{16,18}O_2$ was prepared by running a discharge through a 1/1 mixture of $^{16}O_2$ and $^{18}O_2$ for about 2 h. The initial concentration ratio of hydrogen/argon was varied between 1/25 and 1/75. Not all hydrogen is trapped in the matrix, and the efficiency of the microwave discharge is likely to vary between experiments. The concentration ratio oxygen/argon was varied between 1/38 and 1/75. The deuterium/argon and $^{18}O_2$/argon ratios were kept at 1/38. A regulated flow of argon mixed with oxygen (or $^{18}O_2$) was passed over solid chlorine dioxide, kept at ca −110 °C. A second regulated flow of argon mixed with hydrogen (or deuterium) was passed through a microwave discharge in a quartz tube, excited by a microwave generator (Opthos MPG 4). To minimize the irradiation of the matrix, the quartz tube had a 90° bend immediately before entering the cryostat. Nupro needle valves were used for the regulation of the two gas flows. The total deposition rate was 10 mmol/h and the deposition time 3 h. The deposition temperature was 17 K. The matrixes were formed on a CsI-sapphire window cooled by a Leybold RDK 10-320 closed cycle cryocooler.

Infrared spectra were recorded between 500 and 4000 cm^{-1} at 0.5 cm^{-1} resolution with a Bruker 113v FTIR spectrometer.

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TABLE 1: Absolute Energies

ANO-S: Cl, 13s,10p,4d > 6s,5p,2d; O, 10s,6p,3d > 4s,3p,1d; H, 7s,3p > 3s,1p

ANO-L: Cl, 17s,12p,5d,4f > 6s,5p,2d,1f; O, 14s,9p,4d > 4s,3p,1d; H, 8s,4p > 3s,1p

ANO-L+: Cl, 17s,12p,5d,4f > 7s,6p,3d,2f; O, 14s,9p,4d > 5s,4p,2d; H, 8s,4p > 4s,1p

basis set	symmetry	geometry	SCF	MP2	MP2-S	MP2-g1	MP2-g2
			Results Obtained for the HOOClO$_2$ System				
ANO-S	C_s	opt(SCF)	−759.2074285	−60.2238799			
ANO−S	no	opt(SCF)	−759.2185103	−760.2367767			
ANO-L	no	opt(SCF)	−759.2879052				
ANO-L +	no	ANO-L	−759.2966172	−760.4120881			
cc-pVTZ	no	cc-pVTZ	−759.2615809	−760.4568956			
			Results Obtained for the HOO System				
ANO-S	C_s	opt(SCF)	150.2004355		−150.5805091	−150.580792	−150.5804279
ANO-L	C_s	opt(SCF)	−150.2141963				
ANO-L+	C_s	ANO-L	−150.2177135		−150.6275754	−150.6277498	−150.6274067
cc-pVTZ	C_s	cc-pVTZ	−150.2371476		−150.679770		
			Results Obtained for the ClO$_2$ System				
ANO-S	C_{2v}	opt(SCF)	−609.0321544		−609.6479932	−609.6571584	−609.6560015
ANO-L	C_{2v}	opt(SCF)	−609.0773563				
ANO-L+	C_{2v}	ANO-L	−609.0809077		−609.7615342	−609.7695549	−609.7685077
cc-pVTZ	C_{2v}	cc-pVTZ	−609.0620714		−609.7459632		

After a first spectrum had been recorded, the matrix was irradiated with the full radiation from a 300-W Xe lamp for approximately 0.5 h, using a water filter to remove the near-infrared radiation from the lamp. In one experiment the matrix was irridiated by using a Continuum NY 81-20 YAG (266 nm, 0.35 W). The spectrum after photolysis was then ratioed against the spectrum before photolysis.

The OClO concentration in the matrix varied between different experiments, even when the thermostat temperatures were identical, probably since the surface area of OClO in the trap varied. In some experiments significant amounts of OClO aggregates were present, in other experiments the OClO aggregate band was absent. The amount of product formed increased with the OClO concentration, but the ratios between the product band intensities were constant. The photolysis rate of the products was significantly smaller in the presence of OClO aggregates.

TABLE 2: Calculated Geometries for the Three Species

	SCF/ANO[a]	MP2/6-31G**	MP2/cc-PVTZ	exptl
		ClO$_2$		
R(Cl,O)	1.427 Å	1.516 Å	1.489 Å	1.470 Å[b]
φ(O,Cl,O)	116°	120°	118°	117°[b]
		HOO		
R(O,O)	1.360 Å	1.326 Å	1.312 Å	1.330 Å[c]
R(H,O)	0.948 Å	0.976 Å	0.972 Å	0.97 Å[c]
φ(O,O,H)	104°	104°	104°	104.3°[c]
		HOOClO$_2$[d]		
R(ClO)	1.411 Å	1.491 Å	1.499 Å	
R(ClO)	1.402 Å	1.535 Å	1.471 Å	
R(ClO*)	1.635 Å	2.516 Å	2.415 Å	
R(O*O*)	1.376 Å	1.404 Å	1.374 Å	
R(O*H*)	0.949 Å	0.981 Å	0.977 Å	
φ(OClO)	113°	118°	116°	
φ(O*O*H*)	104°	102°	103°	
φ(O*O*Cl)	110°	86°	88°	
φ(O*Cl O)	103°	80°	82°	
φ(O*ClO)	105°	111°	107°	

[a] ANO-L 7s6p3d2f/5s4p2d/4s1p.[6] [b] Jones, H.; Brown, J. M. *J. Mol. Spectrosc.* **1981**, *90*, 222. [c] Lubic, K. G.; Amano, T.; Uehara, H.; Kawaguchi, K.; Hirota, E. *J. Chem. Phys.* **1984**, *81*, 4826. [d] Atoms marked with an asterisk to the right belong to the HOOCl part in HOOClO$_2$.

Computational Methods and Results

To investigate the thermodynamic stability, structure, and vibration frequencies of the HOOClO$_2$ species, we have performed a series of quantum chemical ab initio calculations with the program systems MOLCAS[5] and GAUSSIAN.[6] Three different basis sets of ANO-type[7,8] were used, and with the two smaller basis sets full geometry optimizations were performed at the SCF level. The total energies obtained are given in Table 1 together with a specification of the basis sets used. The effect of correlation was then estimated using the MP2 method.

Previous calculations have indicated that HOOClO$_2$ is not stable with respect to dissociation to HOO and ClO$_2$.[9] To investigate the thermodynamics of this process, we have performed similar calculations on the ClO$_2$ and HOO radicals. The Cl−O bond is very weak and sensitive both to the basis set used and to the level of correlation. To get a balanced description of the reaction path one would also need to perform a calculation that is able to describe the multiconfigurational nature of the bond. This makes the description of the system rather complicated. For these open shell systems, the CASSCF code of the MOLCAS program system was used as an open shell SCF program, with the singly occupied orbital as an active orbital. The CASPT2 code was used as an MP2 program, and three different choices of zeroth-order Hamiltonians were investigated. With the standard Fock matrix formulation of the CASPT2 equations, the bond energies are usually underestimated. For nonisogyric reactions one will therefore get a considerable systematic error that is proportional to the number of bonds formed. The g1 and g2 formulations of the zeroth-order Hamiltonian are designed to remove this error.[10] In Table 2 we present the geometries obtained with the two smaller basis sets, and in Table 3 we show the energetics obtained for the formation of HOOClO$_2$ from HOO and ClO$_2$. From this table it is clear that *f*-basis functions are crucial for a balanced description of the energetics of the process studied. For the two larger basis sets used in this study we obtain results that indicate that HOOClO$_2$ is around 10 kcal/mol more stable than the reactants. To obtain an accurate description of the vibrational frequencies, the reactants and product were optimized at the MP2 level and the harmonic frequencies were calculated on both SCF and MP2 levels. The vibrational frequencies were

TABLE 3: Calculated Heat of Reaction for HOO + ClO_2 → $HOOClO_2$

basis set[a]	geometry	method	heat of reaction (kcal/mol, 0 K)
ANO-S	opt (C_s)	SCF	15.8
ANO-S	opt(SCF) (C_s)	PT2	2.9
ANO-S	opt(SCF) (C_s)	PT2-G1	8.8
ANO-S	opt(SCF) (C_s)	PT2-G2	7.9
ANO-S	opt	SCF	8.8
ANO-S	opt(SCF)	PT2	−5.2
ANO-S	opt(SCF)	PT2-G1	0.7
ANO-S	opt(SCF)	PT2-G2	−0.2
ANO-L	opt	SCF	2.3
ANO-L+	ANO-L	SCF	1.3
ANO-L+	opt(SCF)	PT2	−14.4
ANO-L+	opt(SCF)	PT2-G1	−9.3
ANO-L+	opt(SCF)	PT2-G2	−10.1
cc-pVTZ	opt(MP2)	MP2	−19.6

[a] Basis set, see Table 1

TABLE 4: Harmonic Frequencies Calculated on SCF and MP2 Levels of Theory, Compared to Experimentally Observed Fundamentals

SCF/ANO	MP2/6-31G**	MP2/cc-pVTZ	exptl
	Results Obtained for the ClO_2 System		
553	422	443	450.2[a]
1152	982	1007	947.1[a]
1334	1109	1181	1106.5[a]
	Results Obtained for the HOO System		
1169	1235	1234	1100.8[b]
1431	1458	1458	1388.9[b]
4076	3712	3691	3413.0[b]
	Results Obtained for the $HOOClO_2$ System		
137	136	138	
395	162	166	
383	230	250	
514	407	295	
575	427	432	
703	454	487	
743	618	610	
1127	922	1006	
1192	1116	1139	
1339	1254	1244	
1608	1318	1340	
4051	3656	3636	

[a] Müller, H. S. P.; Willner, H. **1993**, *97*, 10589. [b] See ref 13.

TABLE 5: Frequencies and Shifts for Reactant and Products at MP2 Level of Theory, with the cc-pVTZ Basis Set

dominating deformation	HO_2ClO_2	exptl	HOO	exptl[11]	OClO	exptl[17]	shift	exptl
OH stretch	3636	3527	3691	3413			−55	114
OOH bend	1340	1283	1458	1389			−118	−106
OO stretch	1006	893	1234	1101			−228	−204
ClO a	1244	1207			1181	1108	63	99
ClO s	1139	1046			1007	947	132	99
ClO s	487				443	450	34	
	610							
	432							
	295							
	250							
	166							
	138							

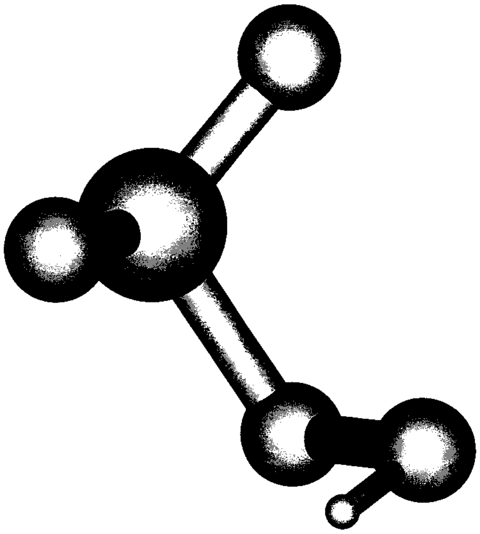

Figure 1. $HOOClO_2$ optimized on the MP2 level of theory and with a cc-pVTZ one-particle basis set.

TABLE 6: Equilibrium Constant and Expected Concentration of $HOOClO_2$ from ab Initio Calculations

T (K)	reaction energy (0 K, kcal/mol)	equilibrium constant	[$HOOClO_2$] (cm^{-3})
180	10	1.05×10^{-18}	1.13×10^{-2}
180	20	1.45×10^{-6}	1.64×10^{7}
200	10	1.12×10^{-19}	1.22×10^{-3}
200	20	9.52×10^{-9}	1.41×10^{7}
220	10	1.83×10^{-20}	1.98×10^{-4}
220	20	1.57×10^{-10}	1.53×10^{6}

calculated using the recently developed algorithms for large one-particle basis sets[11] and the Gaussian package.[6] At the SCF level of theory the bond strengths are usually overestimated due to the fact that the bond-breaking process is not well described in the Hartree−Fock approximation. This is particularly important when the energy surface is very shallow; thus the MP2 method can give very unreliable results, due to the fact that the wave function is not described well as a single configuration in the outer region of a bond breaking, and this will affect the frequencies. This is exactly what happens for the $HOOClO_2$ system (Table 2), at the SCF level where rather short Cl−O bond distances are obtained, and on the MP2 level of theory, the very weak HOO−ClO_2 bond is elongated to around 2.5 Å. The MP2 result must therefore be looked at with some scepticism, at least for the description of the HOO−ClO_2 bond. The geometry of the system may therefore change substantially if a multiconfigurational description that includes dynamic correlation is used throughout the calculation.

However qualitative conclusions concerning the shifts for the internal vibrational frequencies could be drawn from the MP2 result. Comparing the experimental and ab initio frequencies obtained on the MP2 level, we obtain a very good agreement between the calculated and experimental shifts of the reactants, when $HOOClO_2$ is formed. The only exception is the OH stretch (Table 5). This could be explained by the formation of an artificial hydrogen bond (2.3 Å) in the calculated structure of $HOOClO_2$ (Figure 1). For a more balanced description of the bond-forming process, a CASSCF/CASPT2 optimization of the HOO−ClO_2 distance was performed. The active space was chosen to be the sum of the single occupied orbitals in the open shell systems. As one may expect the bond distance increases compared to the SCF result to 2.0 Å; however, this is not as long as obtained with the MP2 method. The energy of reaction only changes marginally, 10.8 kcal/mol, using the g1 zeroth-order Hamiltonian and a cc-pVTZ basis set.

Table 6 shows the calculated equilibrium constant for energies of formation of $HOOClO_2$ of −10 and −20 kcal/mol (excluding zero point vibration energy) at different temperatures. Our calculations indicate that the energy of reaction is somewhere between these limits. The last column of the table gives the

TABLE 7: Bands Assigned to $HOOClO_2$[a]

wavenumber (cm^{-1})	assignment	experiment
839.5	$^{18}O-^{18}O$ stretch	H, $^{18}O_2$
840.9	$^{18}O-^{18}O$ stretch	D, $^{18}O_2$
864.4	$^{16}O-^{18}O$ stretch	H, $^{16,18}O_2$
865.9	$^{16}O-^{18}O$ stretch	D, $^{16,18}O_2$
864.8	$^{16}O-^{18}O$ stretch	D, $^{16,18}O_2$
889.7	$^{16}O-^{16}O$ stretch	D, $^{16}O_2$
893.2	$^{16}O-^{16}O$ stretch	H, $^{16}O_2$
956.7	$D^{16}O^{16}O$ bend	H, $^{16}O_2$
1038.6	^{37}ClO s	H, $^{18}O_2$
1039.3	^{37}ClO s	H, $^{16}O_2$
1045.6	^{35}ClO s	H, $^{18}O_2$
1046.4	^{35}ClO s	H, $^{16}O_2$
1047.1[b]	^{35}ClO s	D, $^{18}O_2$
1048.3[b]	^{35}ClO s	D, $^{16}O_2$
1194.4	^{37}ClO as	H/D, $^{16}O_2/^{18}O_2$
1207.4	^{35}ClO as	H/D, $^{16}O_2/^{18}O_2$
1278.1	$H^{18}O^{18}O$ bend	H, ^{18}O
1279.8	$H^{16}O^{18}O$ bend	H, $^{16,18}O_2$
1282.6	$H^{16}O^{16}O$ bend	H, $^{16}O_2$
2588.5	^{18}OD stretch	D, $^{18}O_2$
2604.7	^{16}OD stretch	D, $^{16}O_2$
3493.4	^{18}OH stretch	H, $^{18}O_2$
3505.6	^{16}OH stretch	H, $^{16}O_2$
3514.4	^{18}OH stretch	H, $^{18}O_2$
3526.7	^{16}OH stretch	H, $^{16}O_2$

[a] H, hydrogen; D, deuterium; H/D, hydrogen or deuterium. Wavenumbers in italics are bands partially overlapped by bands of other compounds. [b] Bands due to ^{37}Cl not observed.

calculated concentration of $HOOClO_2$ using the peroxy radical concentration 5 pptv[12] and the OClO concentration 200 pptv,[13] which have been observed in the stratosphere. As is seen from the table, a significant concentration of $HOOClO_2$ could form if the energy of reaction is close to the upper limit.

Experimental Results and Discussion

It was found in earlier work from this laboratory[14] that hydrogen atoms add to OClO to form HOClO and $HClO_2$. We have also found that peroxy radicals can be formed in argon matrixes in a sufficient concentration to make it possible to study their complexes with stable molecules[15] by co-depositing atomic hydrogen, molecular oxygen, and the desired complex partner. In this paper we extend the previous work to a study of the interaction of peroxy radicals and chlorine dioxide. Hydrogen atoms, molecular oxygen, and chlorine dioxide were co-deposited in argon matrixes. The IR spectra were recorded after the matrix depositions had numerous absorption bands. Most of these had been observed in the earlier experiments.[14,15] However one set of bands required the simultaneous presence of H atoms, molecular oxygen, and chlorine dioxide in the matrix. The ratios between these bands were the same in different experiments, with significantly different concentrations of reactants. All these bands except two, at 610 and 978 cm^{-1}, decreased at the same rate when the matrix was irradiated with a Xe lamp. It seems reasonable to assign the new, photosensitive bands to a single reaction product, P. The bands of P in experiments with different isotopic composition are collected in Table 7. As indicated in the table, a few of the bands of P were partially overlapped by bands of other compounds and were most clearly seen in the ratio between the spectra before and after photolysis. Only a few of the compounds in the matrix were affected by the irradiation: OClO[16] isomerized to ClOO; HOClO[14] and P were decomposed. When the matrix contained OClO aggregates, they were converted to Cl_2O_4, Cl_2O_3, and ClOClO as has been observed earlier.[17] Neither HOO nor HOOH was decomposed. When the matrix was irradiated with 266-nm radiation from a YAG laser, peroxy radicals were decomposed.

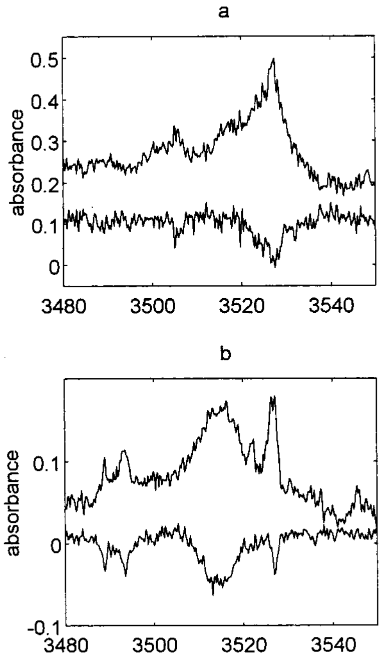

Figure 2. $HOOClO_2$: *x*-axis, cm^{-1}; upper curves, before photolysis; lower curves, after 30 min of photolysis; the curves have been shifted vertically for clarity. (a) $H-^{16}O$ stretch at 3527.5 (overlapped by HOClO, ν(HO), at 3527.1 cm^{-1}) and 3505.6 cm^{-1}. (b) $H-^{18}O$ stretch at 3514.4 and 3493.4 cm^{-1}. Note the difference in the photolysis rate of the broad band near 3527 cm^{-1} in panel a ($HOOClO_2$ + HOClO) and the band at 3527.5 cm^{-1} in panel b (HOClO).

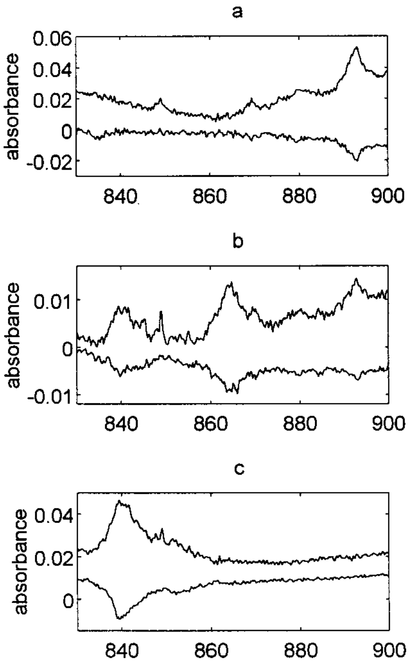

Figure 3. $HOOClO_2$: *x*-axis, cm^{-1}; upper curves, before photolysis; lower curves, after 30 min of phototlysis; the curves have been shifted for clarity. (a) (H)O−O stretch at 893.2 cm^{-1} in $H/^{16}O_2$ experiments. (b) (H)O−O stretch at 841, 865, and 893.2 cm^{-1} in $H/^{16}O^{18}O$ experiments. (c) (H)O−O stretch at 841 cm^{-1} in $^{18}O_2$ experiments.

In experiments with H and D atoms, P bands were observed in the OH region at 3527 cm^{-1} and in the OD region at 2605 cm^{-1}, respectively. In $^{18}O_2$ experiments the bands shifted to 3515 and 2586 cm^{-1}. The ratio between the OH and OD stretches (1.3539) is close to the corresponding ratio for HOCl

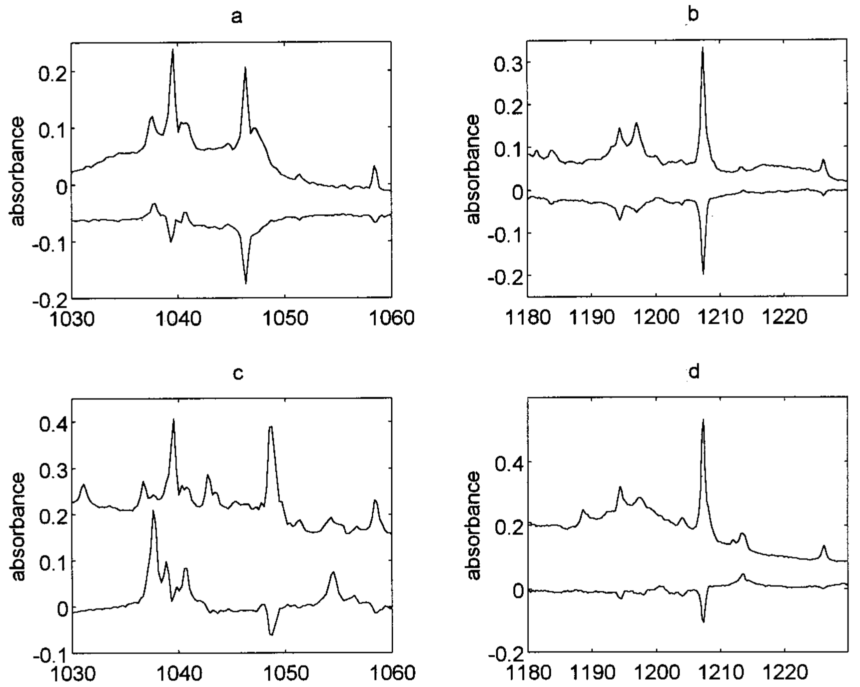

Figure 4. $HOOClO_2$: *x*-axis, cm^{-1}; upper curves, before photolysis; lower curves, after 30 min of photolysis; the curves have been shifted for clarity. (a) Symmetric ClO stretch at 1046.4 cm^{-1} (with a ^{37}Cl isotope satellite at 1039.7 cm^{-1}, overlapped by O_3,ν_{as} at 1039.6 cm^{-1}) in $H/^{16}O$ experiments. (b) Antisymmetric ClO stretch at 1207.4 cm^{-1} (with a ^{37}Cl isotope component at 1194.4 cm^{-1}) in $H/^{16}O_2$ experiments. (c) Symmetric ClO stretch at 1048.3 cm^{-1} (^{37}Cl isotope shift not observed) in $D/^{16}O_2$ experiments. (d) Antisymmetric ClO stretch at 1207.4 cm^{-1} (with a ^{37}Cl satellite at 1194.4 cm^{-1}) in $D/^{16}O_2$ experiments. Note the agreement in panels a and b (taken from the same experiment) and in panels c and d (taken from the same experiment) of the photolysis rates of the ClO stretches.

(1.3542), HOClO (1.3538), and $HOClO_3$ (1.3545). The ^{16}OH to ^{18}OH and ^{16}OD to ^{18}OD shifts are exactly as expected for an isolated OH(OD) stretch. The band coincides with the corresponding band of HOClO. However it was always more than twice as intense as expected from the intensities of the other HOClO bands present. It was significantly broader than the HOClO band from H + OClO experiments. Note also that no $H^{18}OClO$ or $D^{18}OClO$ was formed in $^{18}O_2$ experiments, so the ^{18}OH and ^{18}OD bands were observed free from overlap with other bands. IR spectra of the $^{16}O{-}H$ and $^{18}O{-}H$ stretches are shown in Figure 2.

P has a relatively weak band at 893 cm^{-1}, which shifts to 890 cm^{-1} with DOO and to 841 and 842 cm^{-1} with $H^{18}O^{18}O$ and $D^{18}O^{18}O$. In experiments with $H^{16}O^{18}O$ and $D^{16}O^{18}O$ the corresponding bands were observed at 865 and 866 cm^{-1}, respectively (Figure 3). The isotope shifts show that the band is due to an O−O stretch. In fact its position is relatively close to the O−O stretch in hydrogen peroxide, 865.6 cm^{-1}.[18]

In the H atom experiments with $^{16}O_2$, $^{16,18}O_2$, and $^{18}O_2$ we observed a P band at 1282.6, 1279.8, and 1278.1 cm^{-1}, respectively. With D atoms the 1282.6-cm^{-1} band was shifted to 956.7 cm^{-1}. The ratio 1.341 between the H and D bands is close to the corresponding ratio for the OH and OD bending absorptions of hydrogen peroxide (1.335).[18] Overlap with $D^{18}O^{18}OD$ (bands at 943.2, 949.0, 954.7, 957.4 cm^{-1}) made it impossible to observe the $D^{16}O^{18}O$ and $D^{18}O^{18}O$ bending absorptions.

In addition P has two bands at 1046.4 and 1207.4 cm^{-1} (^{35}Cl). Both bands have clear ^{37}Cl satellites at 1039.3 and 1194.4 cm^{-1} (Figure 4). The position of the 1207.4-cm^{-1} band does not change in $^{18}O_2$ or D experiments. The 1046.4-cm^{-1} band shifts to 1045.6 cm^{-1} with $H^{18}O^{18}O$, to 1048.3 cm^{-1} with $D^{16}O^{16}O$, and to 1047.1 cm^{-1} with $D^{18}O^{18}O$. The insensitivity to isotope exchange shows that these bands are associated with the OClO part of P. The ^{35}Cl to ^{37}Cl shifts suggest that the 1045.6-cm^{-1} band is due to a symmetric ClO shift and the 1207.4-cm^{-1} band to an antisymmetric ClO stretch. In an antisymmetric ClO stretch the Cl atom moves orthogonal to a bond from chlorine to the rest of the molecule; therefore no or only very small isotope shifts are expected for this vibration. In a symmetric ClO stretch the chlorine atom will try to compress and expand a bond to the rest of the molecule; therefore observable isotope shifts are expected.

The absorption bands assigned to P show that it contains a peroxy part, for which we observe the OH and OO stretches and the HOO bend. It also contains an OClO group as shown by the presence of the symmetric and antisymmetric OClO stretching vibrations in its spectrum. The ^{35}Cl to ^{37}Cl shift of the antisymmetric stretch gives an estimate of the OClO angle of 115°. The ^{16}O to ^{18}O and H to D shifts of the symmetric ClO stretch show that the two groups are bound to each other. Large concentrations of peroxy radicals and of OClO are present in the matrixes studied, and it therefore seems reasonable to assume that P is formed by the addition of a peroxy radical to OClO, with the free oxygen of the peroxy radical bound to the chlorine atom of OClO. We did not observe the $(HO)OCl(O_2)$ stretch, possibly since it is below 500 cm^{-1}.

Separate experiments were carried out with perchloric acid and with [D]perchloric acid in order to find the precise band positions of these compounds. A comparison between the spectra shows that perchloric acid is not a photodecomposition product of P under the experimental conditions of this work. A photolytical rearrangement of $HOOClO_2$ to $HOClO_3$ may be possible in the presence of sulfate aerosols. We have not been able to identify any band that could be referred to as a product band from the photolysis of P. When we tried to increase the amount of product bands by increasing the amount of P on the matrix, OClO aggregates were formed. A possible result of the

TABLE 8: Photosensitive, Not Identified Bands that Required the Simultanous Presence of Hydrogen, Oxygen, and OClO in the Matrix

group[a]	wavenumber (cm^{-1})	experiment[b]	intensity
A	787.3	D	vw
A	971.6	D	vw
C	972.8	H	w
A	979.7[c]	D	vw
A	1002.6[d]	D	vw
B	1372.8[e]	H, $^{18}O_2$	w
B	1375.8[e]	H, $^{18}O_2$	w
B	1849.2		1.0[g]
B	1850.6		1.0[g]
B	1852.7		0.8[g]
B	2767.8	D, $^{18}O_2$	w
C	3586[f]	H, $^{16}O_2$	w

[a] A, bands that decreased at approximately the same rate as the P bands; B, bands that were totally eliminated from the matrix after 30 min after irradiation by the Xe lamp; C, bands that were only weakly photolyzed. [b] Experimental conditions required for the band to be present. H, hydrogen; D, deuterium; H/D, hydrogen or deuterium. [c] Partly overlapped by band at 978.1 cm^{-1}. [d] Partly overlapped by $D^{18}O^{18}O$ (band at 999.1 cm^{-1}). [e] Partly overlapped by HOO (band at 1388.9 cm^{-1}). [f] Partly overlapped by HOCl(band at 3586.7 cm^{-1}). [g] Relative intensities, the bands varied randomly in the series of experiments.

irradiation of $HOOClO_2$ is dissociation to HOO and ClO_2. Subsequent irradiation of ClO_2 then leads to the formation of ClOO.

In addition to the P bands we observed a number of weak, photosensitive bands which were not identified. They were collected into three groups, A, B, and C, and are given in Table 8. The bands at 971.6 and 979.7 cm^{-1} in Table 8 are probably identical with two bands close to 971.6 and 979.7 cm^{-1}, respectively, in the reaction D + OClO.[14] The addition of O_2 to the matrix suppresses the production of $HClO_2$ from the reaction H(or D) + OClO → HOClO and $HClO_2$. Traces of ClO_3 (bands at 1072.4, 1060.5, 562.7 cm^{-1}) were probably due to the addition to OClO of oxygen atoms from small amounts of water that passed through the microwave discharge.

Conclusion

Peroxy radicals can add to OClO to form $HOOClO_2$ with a stability intermediate between a van der Waals complex and a covalently bound molecule. Gaseous $HOOClO_2$ may be stable at stratospheric temperatures. Hydrogen bonding in sulfate aerosol particles may help to increase its stability.

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