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Photochemistry of $SO_2/Cl_2/O_2$ Gas Mixtures: Synthesis of the New Peroxide $ClSO_2OOSO_2Cl$

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Photochemically induced gas-phase reactions of $Cl_2/SO_2/O_2$ mixtures at −78 °C have been investigated on a preparative scale. The sulfuryl chlorides $ClSO_2(OSO_2)_nCl$, $n = 0$, 1, or 2, along with SO_3 and the hitherto unknown bis(chlorosulfuryl)peroxide, $ClSO_2OOSO_2Cl$, have been obtained. The new peroxide has been purified by trap-to-trap distillation and conclusively characterized by gas-phase and matrix IR, as well as Raman, spectroscopy. At room temperature, the peroxide decomposes to form quantitatively Cl_2 and SO_3. DFT calculations suggest that $ClSO_2OOSO_2Cl$ occurs at ambient temperatures in at least two different rotamers, whereas in matrix-isolation experiments in Ar at 15 K only the most stable form has been found. The mechanism of the formation of the peroxide via the $ClSO_2OO•$ peroxy radical and the supposed involvement of the $ClSO_3•$ intermediate is discussed.

Introduction

The catalytic or photolytic treatment of SO_2/Cl_2 mixtures affords well-known routes for the industrial synthesis of sulfuryl chloride Cl_2SO_2.[1,2] However, in the presence of oxygen, for example in the atmospheric degradation of SO_2, the Cl_2/SO_2 photolysis reaction sets in train a catalytic oxidation cycle (eqs 1−4) for the conversion of SO_2 to SO_3 (eq 5).[3]

$$Cl_2 + h\nu \rightarrow 2\ Cl• \qquad (1)$$

$$2\ Cl• + 2\ SO_2 \rightarrow 2\ ClSO_2• \qquad (2)$$

$$2\ ClSO_2• + 2\ O_2 \rightarrow 2\ ClSO_2OO• \qquad (3)$$

$$2\ ClSO_2OO• \rightarrow Cl_2 + 2\ SO_3 + O_2 \qquad (4)$$

$$2\ SO_2 + O_2 \rightarrow 2\ SO_3 \qquad (5)$$

The $ClSO_3•$ radical and its dimer are possible intermediates in eq 4. They could play an important role in atmospheric chemistry, particularly in regions of high Cl_2 and SO_2 abundances.[4] Reactions 1−4 can also account for chemical processes in the Venus stratosphere similar to the O_2-destroying reactions reported for $CO/O_2/Cl_2$ mixtures. Both processes have been suggested to explain the unexpectedly low oxygen content of the Venus stratosphere.[3,5]

To the best of our knowledge, the $ClSO_3•$ radical has not been reported. In contrast, the analogous $FSO_3•$ radical, in equilibrium at ambient temperature with FSO_2OOSO_2F, has been the subject of several investigations during the past 50 years.[6] F atoms, generated by photolysis of F_2, were shown to react with SO_3 to give FSO_2OOSO_2F in high yield.[7]

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However, the chloro analogue $ClSO_2OOSO_2Cl$ has not been reported so far.

Experimental Section

Chemicals. The chemicals Cl_2 (99.8%), SO_2 (99.98%), SO_3, Cl_2SO_2 were obtained from commercial sources and purified by trap-to-trap distillation, whereas CCl_4, Ar (6.0), and O_2 (5.1) were used as received. $ClSO_2OSO_2Cl$ was synthesized through the thermal reaction between CCl_4 and SO_3 according to the reported procedure.[8]

Photochemical Reactions. Volatile materials were manipulated in a glass vacuum line equipped with a capacitance pressure gauge (MKS Baratron 221 AHS-1000, Wilmington, MA, USA), three U-traps, and valves with PTFE stems (Young, London, UK). The vacuum line was connected via a flexible stainless steel tube to a 5.5 L glass photoreactor equipped inside with a UV lamp (Heraeus TQ 150 Z2) in a double-walled glass insert cooled by water. The vacuum line was also connected to an IR gas cell (optical path length 200 mm, with 0.5 mm thick Si wafers as windows) in the sample compartment of the FTIR instrument. This arrangement made it possible to follow the course of the reaction during the synthesis and to monitor, at a later stage, the improvement in the purification process. The products were stored in glass ampoules under liquid nitrogen. The ampoules were opened and flame-sealed by means of an ampule key.[9] Different amounts of the gaseous reactants were mixed in the photoreactor held at dry ice temperature, and the pressure was monitored during the reactions. The reaction mixtures were irradiated until no pressure decrease was observed. The photolysis products were separated by trap-to-trap condensation, and the progress was monitored by gas-phase IR spectroscopy.

Spectroscopy. IR spectra of the gaseous samples were recorded with a resolution of 2 cm^{-1} in the range 4000−400 cm^{-1} with a Bruker Vector 25 spectrometer, and the Raman spectra of liquid samples with a Bruker-Equinox 55 FRA 106/S FT-Raman spectrometer equipped with a 1064 nm Nd:YAG laser. IR spectra of Ar matrices were recorded in reflectance mode with the Bruker IFS 66v spectrometer with transfer optics. An MCT (DTGS) detector, together with a KBr/Ge beam splitter, was used in the region 5000−650 (400) cm^{-1}. One-hundred scans were added for the spectra with apodized resolutions of 0.5 (2) cm^{-1}.

Matrix Isolation. A few milligrams of pure $ClSO_2OOSO_2Cl$ were transferred to a small U-trap connected to the inlet nozzle of the matrix apparatus. This nozzle made of quartz consisted of a tube with an internal diameter of 4 mm and an outlet opening of 1 mm diameter. Its temperature could be raised by heating over a length of 20 mm. A stream of Ar (2 mmol h^{-1}) was directed over the sample held at −65 °C, and the resulting gas mixture was condensed on the matrix support (a rhodium-plated copper mirror) held at 15 K. Details of the matrix apparatus are given elsewhere.[10]

Theoretical Calculations. Quantum chemical calculations were performed using the *Gaussian 03* program system.[11] Geometry optimizations were sought using standard gradient techniques by simultaneous relaxation of all of the geometrical parameters. The calculations of vibrational properties were carried out at potential energy minimum geometries for which no imaginary vibrational frequency was found.

Results and Discussion

Photochemical Reactions between Cl_2, SO_2, and O_2. In preliminary experiments, gaseous mixtures of SO_3 and Cl_2 were irradiated with light at wavelengths >320 nm (Heraeus TQ 150, Z2 lamp) at −25 °C, but apparently no reaction took place. In contrast, irradiation of gaseous mixtures of Cl_2, SO_2, and O_2 (λ > 320 nm) at −78 °C yielded, together with the known products Cl_2SO_2, SO_3, $ClSO_2OSO_2Cl$, and $ClSO_2OSO_2OSO_2Cl$, the hitherto unknown peroxide $ClSO_2OOSO_2Cl$. The product distribution was dependent on (i) the proportions of the reactants, and (ii) the conditions during workup because the peroxide was found to be thermally rather unstable. The highest yield of the peroxide was obtained from mixtures of $Cl_2/SO_2/O_2 \approx 1:2:10$ at a total pressure of 550 Torr measured at ambient temperature. At dry ice temperature, the pressure decreased to 380 Torr, and further to 340 Torr during irradiation. Volatile products were distilled into three traps held at −90, −120, and −196 °C. Excess oxygen was pumped off, whereas Cl_2SO_2 was trapped at −120 °C, and the less volatile compounds remained in the reactor at −78 °C. In a further distillation, using traps at −70, −110, and −196 °C, the reactor was allowed to warm up slowly to room temperature. Subsequently, $ClSO_2OOSO_2Cl$ was evaporated and retained in the −70 °C trap, together with some Cl_2SO_2 and $ClSO_2OSO_2Cl$. $ClSO_2OSO_2OSO_2Cl$ was found as a residue in the photoreactor. The raw product was purified by several trap-to-trap distillations from −20 °C using traps at −50, −80, and −196 °C. Pure $ClSO_2OOSO_2Cl$ was finally collected in the −50 °C trap as a colorless solid. When the peroxide was allowed to reach room temperature, it decomposed giving SO_3 and Cl_2 in a molar ratio of 2:1.

All of the volatile products were identified by their IR and Raman spectra. The infrared bands of Cl_2SO_2 were compared with those of a commercial sample.[12] $ClSO_2OSO_2Cl$ was identified by the IR spectrum of the vapor and the Raman spectrum of the liquid. Because we observed small differences between our spectra and those reported previously,[13] the identity of $ClSO_2OSO_2Cl$ was confirmed by the spectrum of an authentic sample.[8] Monomeric SO_3 was detected in

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the gas phase by its IR spectrum, whereas γ-SO_3 was identified by comparison of the Raman spectrum of a solid sample sealed in a glass tube with the reported details.[14]

Proposed Reaction Mechanism. Starting from photochemically produced chlorine atoms according to eq 1, different alternative routes to the observed products can be proposed. The borosilicate glass used for the photo reactor transmits light of wavelengths >320 nm. Thus, photodecomposition of the reactions products (e.g., sulfuryl chlorides) is expected to be negligible.[15,16] Chlorine atoms are known to react with sulfur dioxide to give sulfuryl dichloride, presumably via the short-lived $ClSO_2$ radical, as depicted in eqs 2 and 6.[3,17]

$$ClSO_2\bullet + Cl\bullet \rightarrow Cl_2SO_2 \qquad (6)$$

The initial formation of $ClSO_2\bullet$ has been recently proved by laser irradiation at 355 nm of Ar matrices containing Cl_2 and SO_2.[18] However, in the presence of excess of molecular oxygen, reaction (6) will be efficiently suppressed because O_2 competes with the Cl• atom to give the peroxy radical $ClSO_2OO\bullet$ (eq 3). There is a large number of precedents where similar peroxy radicals are formed in the presence of O_2.[19−23]

It is safe to conclude that the peroxy radicals $ClSO_2OO\bullet$ are involved in the formation of all of the products identified apart from Cl_2SO_2. The low-temperature recombination of $ClSO_2OO\bullet$ radicals (eq 7) is the most feasible route leading to the novel peroxide $ClSO_2OOSO_2Cl$. A similar reaction pathway has been recently reported for several formylperoxy radical derivatives.[24−26]

$$2\ ClSO_2OO\bullet \rightarrow ClSO_2OOSO_2Cl + O_2 \qquad (7)$$

Apart from SO_3, that may be formed via the catalytic cycle (eqs 1−5) outlined above, Cl_2SO_2 and $ClSO_2OOSO_2Cl$ are the main products of the $Cl_2/SO_2/O_2$ system. Note that the low stability of $ClSO_2OOSO_2Cl$ eventually results in a second chemical cycle (eqs 1−3, 7, and 8) that gives rise to the oxidation of SO_2 to form SO_3 via the unstable $ClSO_2OOSO_2Cl$ that decomposes according to eq 8. As in the cycle represented in eqs 1−5, this second cycle also proceeds with complete regeneration of the Cl• atoms initially consumed.

$$ClSO_2OOSO_2Cl \rightarrow 2\ Cl\bullet + 2\ SO_3 \qquad (8)$$

The compounds $ClSO_2(OSO_2)_nCl$, $n = 1$ or 2, are thought to be formed in secondary reactions via the reduction of $ClSO_2OOSO_2Cl$ by SO_2. In a kinetic study of the analogous reaction between FSO_2OOSO_2F and SO_2, $FSO_2(OSO_2)_2F$ was shown to be formed.[27]

The $ClSO_3\bullet$ radical could be formed during the stepwise thermal decomposition of the peroxide according to eq 9 but it decomposes rapidly according to eq 10.

$$ClSO_2OOSO_2Cl \rightarrow 2\ ClSO_3\bullet \qquad (9)$$

$$2\ ClSO_3\bullet \rightarrow 2\ Cl\bullet + 2\ SO_3 \qquad (10)$$

Unsuccessful attempts to produce the $ClSO_3\bullet$ radical by pyrolysis of $ClSO_2OOSO_2Cl$ and subsequent matrix isolation of the products can thus be rationalized.

Dissociation of $ClSO_2OOSO_2Cl$ was found to be irreversible. Thermal decomposition to SO_3 and Cl_2 takes place in the gas phase according to a first-order rate law with a half-lifetime of 15 min at ambient temperature. The decomposition of $ClSO_2OOSO_2Cl$ in the liquid phase follows the same channel, as revealed by the growth of bands of both SO_3 and Cl_2 during the measurements of the Raman spectrum. It is interesting to note that the $ClSO_3\bullet$ radical behaves similarly to the chlorinated alkoxy radicals $ClCO_2$[28] and CF_2ClO,[29] which decompose rapidly by chlorine extrusion.

Vibrational Spectra of Bis(chlorosulfuryl)peroxide. The IR spectrum of bis(chlorosulfuryl)peroxide, $ClSO_2OOSO_2Cl$, was measured for gaseous and Ar matrix-isolated samples, whereas the Raman spectrum was recorded for the neat liquid. Figure 1 shows the IR spectrum of $ClSO_2OOSO_2Cl$ vapor and the Raman spectrum of the liquid. Experimental wavenumbers and calculated IR and Raman spectra of the conformer predicted to be most stable (theoretical calculations below) are listed in Table 1. A tentative assignment of some of the more intense bands is also given in Table 1. However, the DFT calculations predict rather strong coupling between deformations and S−Cl stretching modes that prevent any simple descriptive assignment of these low-lying modes.

The FTIR spectrum of pure $ClSO_2OOSO_2Cl$ isolated in a solid Ar matrix is shown in Figure 2. The expected $^{35/37}Cl$ isotopic splitting of the S−Cl stretching bands appears to be obscured by matrix site splittings of the absorptions. In further experiments using a heated spray-on nozzle, an additional absorption occurred at 1385.1 cm^{-1} that was readily assigned to SO_3.[30,31] At 95 °C, the decomposition

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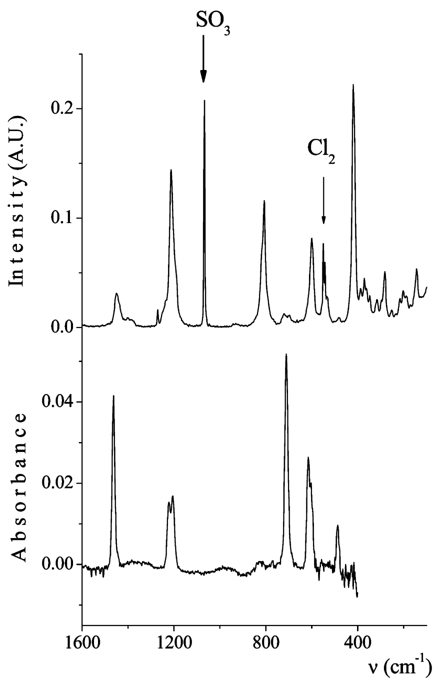

Figure 1. Vapor-phase FTIR spectrum (bottom; resolution: 2 cm^{-1}, pressure: 0.1 mbar, and optical path length of 20 cm) and Raman spectrum (top; liquid at room temperature, excitation at 1064 nm, 150 mW) of $ClSO_2OOSO_2Cl$.

Table 1. Experimental (Vapor-Phase IR, Liquid Raman and Ar Matrix IR) and Calculated (B3P86/6-31+G*) Wavenumbers (in cm^{-1}) and Relative Intensities of $ClSO_2OOSO_2Cl$

IR (gas)[a]	Raman (liquid)[a]	IR (Ar matrix)[a,b]	B3P86/6-31+G*[c]			assignment
				I (IR)[d]	I (Ra)[d]	
	1450(m)	1464.5(m)	1443	14	30	$\nu_{as}SO_2$
1463(vs)	1401(w)	1454.8(s)	1435	48	8	$\nu_{as}SO_2$
		1438.3(w)				
	1234(sh)	1220.3(sh)				
1222(s)	1212(vs)	1216.7(s)	1195	9	100	ν_sSO_2
1205(s)		1199.9(s)	1180	16	<1	ν_sSO_2
	817(sh)	808(vw)	904	<1	52	νO−O
	807(vs)					
	720(w)		755	<1	16	νS−O
711(vs)	698(w)	708.2(vs)	664	100	3	νS−O
613(s)	600(vs)	611.7(vs)	580	25	41	δSO_2
		599.1(vs)	570	37	2	δSO_2
		557.3(w)	543	7	2	ρSO_2
		521.1(w)	515	3	5	ρSO_2
		503.5(w)				
488(m)		485.3(s)	449	9	5	
	419(vs)		391	<1	36	νSCl
			387	<1	25	νSCl
	371(w)		350	<1	8	
	347(vw)		342	<1	13	
	316(vw)		314	1	2	
			273	<1	<1	
	281(w)	281(w)	263	<1	11	
	203(vw)		181	<1	3	
	143(w)	142(w)	124	<1	8	
	84(w)		57	<1	3	
			49	<1	1	
			39	<1	1	

[a] Relative intensities in parentheses: w weak, m medium, s strong, vs very strong, sh shoulder. [b] Most-abundant matrix site. [c] Most-stable rotamer. [d] Predicted relative intensities.

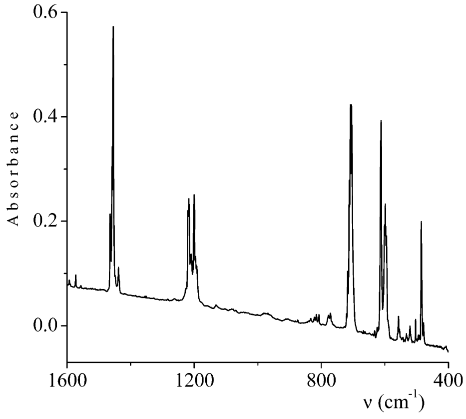

Figure 2. FTIR spectrum in the spectral region 1600−400 cm^{-1} of $ClSO_2OOSO_2Cl$ isolated in an Ar matrix.

Table 2. Relative Energies Δ*E* (in kcal mol^{-1}) of Different Conformers of $ClSO_2OOSO_2Cl$ Calculated at the B3P86/6-31+G* Approximation

structure	τ_1 O−O−S−Cl	τ_2 O−O−S−Cl	τ S−O−O−S	Δ*E* [kcal mol^{-1}]
G^-G^-	73.3	73.3	111.0	0.00
G^+G^-	−75.1	69.5	130.5	1.09
G^+G^+	−73.4	−73.4	153.5	1.70
AG^-	−170.4	72.8	116.5	2.74
AG^+	179.8	−75.3	133.0	3.07
AA	179.1	179.1	120.6	5.05

of $ClSO_2OOSO_2Cl$ was almost complete, with the SO_3 signal being the most intense feature in the IR spectrum. No clear signs attributable to a second conformer of the peroxide were observed in the spectra taken at different nozzle temperatures, indicating that only bands of the most stable rotamer are likely to appear in the IR spectrum of the matrix-isolated sample and that fast relaxation to the most stable form took place during low-temperature deposition.

IR and Raman spectra of $ClSO_2OOSO_2Cl$ were calculated using the B3P86 functional that has been shown in preliminary calculations to reproduce satisfactorily the vibrational spectra of several compounds containing the $-SO_2-$ moiety. The B3P86/6-31+G* approximation was used throughout. Prior to the vibrational calculations, the most-stable conformer and possible conformational equilibria have been studied theoretically.

Assuming a nonplanar (gauche) S−O−O−S structure, several conformers are feasible, depending on the orientations of each of the $-SO_2Cl$ groups. Relaxed potential energy curves, in which the O−O−S−Cl torsional angles were scanned in steps of 10°, yield six minima that are designated as G^-G^-, G^+G^-, G^+G^+, AG^-, AG^+, and AA, where G or A correspond to gauche or anti O−O−S−Cl torsional angles, and the positive and negative signs refer to an anticlockwise and clockwise rotation, respectively. The structures of these six conformers, each of them occurring as enantiomeric pairs, were optimized by simultaneous relaxation of all of the geometrical parameters. All of them correspond to stable structures for which no imaginary frequencies occur.

Table 2 presents the relative energy differences of the six conformers together with their optimized torsional angles. The most stable structure according to the B3P86/6-31+G* approximation corresponds to the G^-G^- form (Figure 3), followed by the G^+G^- conformer that is predicted to lie approximately 1 kcal mol^{-1} to higher energy. This result is

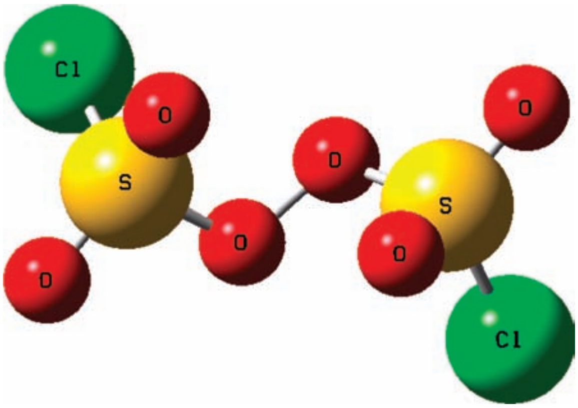

Figure 3. B3P86/6-31+G* molecular model of the most-stable conformer G^-G^- of $ClSO_2OOSO_2Cl$.

in agreement with the structure reported for FSO_2OOSO_2F.[32] The electron diffraction pattern produced by gaseous FSO_2OOSO_2F was found to be consistent with either an equilibrium between G^-G^- and G^+G^+ or a mixture of the G^-G^- and G^+G^- forms.

The vibrational spectra of the different conformers of $ClSO_2OOSO_2Cl$ were simulated with the B3P86/6-31+G* approximation. The results for the three most stable forms in the experimental range (above 400 cm^{-1}) is presented in Table S1 of the Supporting Information. The theoretical spectra of the radicals $ClSO_2OO\cdot$ and $ClSO_3\cdot$ were also calculated with the same approximation (Tables S2 and S3 of the Supporting Information). In light of these theoretical results, we can conclude that there are no clear signs in the experimental spectra of any of these species.

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Supporting Information Available: Theoretical wavenumbers (in cm^{-1}) of the G^-G^- G^+G^- and G^+G^+ forms of $ClSO_2OOSO_2Cl$ and of $ClSO_3$ and $ClSO_2OO$ the radical above 400 cm^{-1} calculated with the B3P86/6-31+G* approximation. This material is available free of charge via the Internet at http://pubs.acs.org.

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[32] Hagen, K.; Hedberg, K.; Gard, G.; Aubke, F. *J. Mol. Struct.* **2001**, *567*−*568*, 1–10.