Matrix reaction of the oxygen atom with the $CBrCl_3$ molecule Identification of phosgene complexes with Cl_2 and Br_2

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Abstract

FT-IR spectroscopy has been coupled with the matrix isolation technique to investigate the mechanism of the $CBrCl_3$ photooxidation by ozone at 12 K by UV light. $COCl_2$ is observed as the only primary product and CO as a secondary photolysis product. A 35 K warm up after photolysis generated phosgene complexes with Cl_2 and Br_2 . Identification of these molecular complexes was performed with mixtures of laboratory synthesized phosgene with X (X=Cl_2, Br_2) trapped in argon matrices.

INTRODUCTION

Halogenated methanes emitted into the troposphere are oxidized in the stratosphere via a sequence of radical reactions initiated by photolysis of the ozone molecule (O_3) with atomic oxygen [1]. Catalytic reactions of the resulting ClO_x and BrO_x species are responsible for the depletion of stratospheric ozone. Despite the relatively low BrO_x mixing ratio [2], bromine reaction chemistry is particularly important because the BrO/BrO and BrO/ClO reactions are faster than the corresponding ClO/ClO process [3]. However, the understanding of the potential environmental effects of bromine compounds requires determination of their tropospheric sinks and their resultant oxidation products. With this aim, and as a continuation of our previous studies in the same field [4,5], we have investigated for the first time the reaction of CBrCl₃ with atomic oxygen in argon matrices. Oxygen atoms in triplet or singlet states were produced in situ by a dissociation process following the UV photolysis of ozone molecules.

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EXPERIMENTAL

All the experiments were conducted in a closed cycle Air Product displex refrigerator, model 202A. The gas mixtures were prepared by standard manometric techniques and sprayed at 20 K through a dual jet system onto a cold golden mirror. Infrared spectra were recorded at 12 K by a 113 FT-IR Bruker spectrophotometer at a resolution of 0.5 cm^{-1} (100 scans). The optical beam path was modified by a reflecting unit.

Ozone photolysis was carried out with a 90 W high-pressure mercury lamp (envelope removed) or a xenon lamp (150 W) used together with cut-off filters such as Schott WG 345 (cut-off 320 nm) and Schott WG 280 (cut-off 270 nm). If one takes into account the values of the quantum yield for the formation of $O(^{3}P)$ and $O(^{1}D)$ atoms as a function of the irradiation wavelength [6], by using the latter filter, the primary process is the production of $O(^{3}P)$ from ozone. CBrCl₃ from Merck was distilled at low temperature on a vacuum line. Oxygen and argon of stated purity 99.999% were purchased from Air Liquide. Phosgene was prepared by the gas-phase reaction between CBrCl₃ and ozone. Excess ozone was removed by pumping at 93 K and COCl₂ was distilled three times at 200 K on a vacuum line.

RESULTS AND DISCUSSION

CBrCl₃/Ar

Spectra of $CBrCl_3$ in argon matrices have been previously investigated by King [7]. The chlorine and bromine isotopic patterns of the bands were recorded and isotopic frequencies were assigned. Our spectra were in good agreement with these reported values.

Full irradiation of a CBrCl₃/Ar (1/800) sample for 17 h with the mercury lamp produced new weak bands in the 910 and 850 cm⁻¹ regions as illustrated in Fig. 1. From literature data, bands at 898.1 and 895.5 cm⁻¹ can be assigned to the v_3 mode of the CCl₃ radical [8] and bands at 888.5–886.5 and 835.3– 833.4 cm⁻¹ to the CBrCl₂ radical [9]. After annealing the matrix at 40 K, a narrowing of the bands was observed with a better resolved individual chlorine isotopic contribution. At the same time the unassigned 862.4 cm⁻¹ band disappeared and a new band at 870.1 cm⁻¹ was observed.

Under the same irradiation conditions, the photodissociation of $CHCl_3$ and $CFCl_3$ was not observed. The dissociation energy of the C–Br bond is weaker than that of C–Cl and C–F [10]. Formation of the $CBrCl_2$ radical is probably due to a secondary reaction in the matrix cage. The weak photodissociation of $CBrCl_3$ after prolonged irradiation can be considered as negligible and has not been taken into account in its reaction with atomic oxygen.



Fig. 1. FT-IR spectra of $CBrCl_3/Ar$ (1/600) in the 910-850 cm⁻¹ spectral region: (a) after deposition, before photolysis at 12 K; (b) after 17 h photolysis at 12 K using the high-pressure mercury lamp; (c) after 17 h photolysis at 12 K using the high-pressure mercury lamp, followed by a 35 K warm up.

CBrCl₃/O₃/Ar

After co-deposition of CBrCl_3/Ar (1/500) and O_3/Ar (1/200) mixtures, the spectrum showed bands due only to the parent molecules, leading to the conclusion that there is no significant interaction between CBrCl_3 and O_3 .

Sample photolysis with the light of the high-pressure mercury lamp for a period totalling 12 h reduced $CBrCl_3$ by 10% without observable $CBrCl_3$ photodissociation products, destroyed ozone and produced a number of new features as shown in Fig. 2. Figure 3 shows expanded scale scans of the new bands of interest at different times. Table 1 summarizes frequencies and relative intensities of the product absorptions arising from irradiation.

The strongest band in the spectrum at 1815.7 cm^{-1} and other doublets at 837.4-836.3, 578.7 and $568.6-565.0 \text{ cm}^{-1}$ can be assigned to the COCl₂ molecule by comparison to the directly deposited sample of Schnöckel [11]. The only other observed product was CO, characterized by absorptions at 2142.1, 2138.5 and 2136.6 cm⁻¹ [12]. The relatively complicated pattern of absorption



Fig. 2. FT-IR spectra of $CBrCl_3/O_3/Ar$ (1/5/1000): (a) after deposition, before photolysis; (b) after 12 h photolysis at 12 K using the high-pressure mercury lamp.



Fig. 3. Evolution of the spectrum of $CBrCl_3/O_3/Ar (1/5/1000)$ with the time of irradiation (highpressure mercury lamp) in the 1850-1790 cm⁻¹, 860-820 cm⁻¹ and 600-550 cm⁻¹ spectral regions. Irradiation time: (a) 0; (b) 15 min; (c) 25 min; (d) 45 min; (e) 60 min.

TABLE 1

Frequencies (cm^{-1}) and absorbance (A) of product bands after 12 h irradiation with a highpressure mercury lamp of an argon matrix containing CBrCl₃ and O₃; frequencies shifted by ¹⁸O in brackets.

$\nu (\mathrm{cm}^{-1})$	A ^c	Assignment
2142.6 (2091.0)	0.07	
2140.6 (2089.6)	0.01	CO:COCl ₂
2138.5-2136.8 (2087.3-2085.8)	0.16	CO
1840.8-1839.0°	0.02	COCl ₂
1834.8ª	0.04	>
1829.8ª	0.02 J	$(\nu_2 + \nu_4 + \nu_5)$
1820.3ª	sh .	$\text{COCl}_2(\nu_1)$ second site?
1818.6-1817.1 ^a (1781.5)	sh	COCl_2 : CO (ν_1)
1815.7-1814.5ª (1777.9-1777.1)	0.48	$\operatorname{COCl}_2(\nu_1)$
1810.1 ^b (1773.4)	vvw	$\operatorname{COCl}_2: \operatorname{Cl}_2(\nu_1)$
1803.2-1801.5 ^b (1770.5-1769.5)	0.08	Not identified
1653.1-1652.3	0.03	$\operatorname{COCl}_2(2\nu_4)$
863.2 ^b	sh	
859.5 ^b (857.0)	0.04	Not identified
853.1 ^b	0.04	COCl_2 : $(\operatorname{Cl}_2)_n(\nu_4)$
847.7 ^b	0.07	$\operatorname{COCl}_2:\operatorname{Cl}_2(\nu_4)$
842.1 ^b	sh	
840.9-839.6	sh	$\text{COCl}_2:\text{CO}(\nu_4)$
837.5-836.3ª (834.9-833.8)	0.65-0.35	$\operatorname{COCl}_2(\nu_4)$
831	0.05	
583.8 ^b	sh	Not identified
578.7ª	0.03	$\operatorname{COCl}_2(\nu_6)$
572.2ª	0.01	
568.4-564.9°	0.04-0.02	$\operatorname{COCl}_2(\nu_2)$

*Decreased on annealing.

^bIncreased strongly after annealing.

^cvvw, very very weak; sh, shoulder.

which is observed in our spectra for the $\nu_{\rm CO}$ mode of phosgene even at lower CBrCl₃/O₃/Ar concentration (1/4/4000) can be explained either by stabilization of COCl₂ in two or more distinct sites in the matrix or by weak interaction with neighbouring species such as O₂ or CO. Splitting observed for ν_2 and ν_4 modes is due to the ³⁵Cl-³⁷Cl shift [11].

Experiments performed with an isotopic ozone sample of natural 50% oxygen 18 enrichment provided further confirmation for the assignment of the features. The $\nu_{\rm CO}$ pattern observed for the mixed isotopic species indicates that only one oxygen atom in the molecule gives rise to these features. When the sample was subjected to prolonged photolysis, other weak bands at 1810, 1803.2– 1801.5, 863.2, 859.5, 847.7 and 583.8 cm⁻¹ appeared. After destruction of ozone, the peak assigned to the CO molecule continued to grow in intensity. This observation suggests that CO arises from the secondary photolysis of $COCl_2$ according to the scheme: $COCl_2 \rightarrow CO + Cl_2$.

The time dependence of $COCl_2$ and O_3 evolution revealed that the O_3 decay and the $COCl_2$ formation followed first order kinetics with the same rate of reaction.

We also studied the wavelength dependence on the reaction between $CBrCl_3$ and the oxygen atom. Experiments were performed using a xenon lamp and filters 280 WG and 345 WG. Again the formation of $COCl_2$ is observed with a lower yield, showing that oxygen in the triplet state is sufficiently reactive.

In summary, the analysis carried out indicates that the reaction between $CBrCl_3$ and atomic oxygen yields $COCl_2$ as the only observable primary product. No reaction intermediate was identified. The addition of the oxygen atom is concomitant with elimination of Br and Cl atoms. However, the BrCl species characterized by absorption at 440 cm⁻¹ [13] was not observed. Bromine [14,15] or chlorine [16–18] oxides were also not detected.

ANNEALING OF THE PHOTOLYZED MATRIX

After the annealing at 35 K of the photolyzed matrix, the absorptions assigned to the $COCl_2$ molecule produced by irradiation diminished strongly. In parallel, weak bands observed after prolonged photolysis at 1810, 1803.2–1801.5, 863.5, 859.5, 847.7 and 583.8 cm⁻¹ grew strongly, denoting formation of complexes between phosgene and other molecular species which diffuse during annealing. Figure 4 illustrates this behaviour both for experiments with natural and isotopic ozone. Furthermore a new absorption band appeared at 1488 cm⁻¹ which was displaced to 1444 and 1403 cm⁻¹ in isotopic ozone experiments.



Fig. 4. Comparison of the photolyzed matrix spectrum (lower trace) and the spectrum of the photolyzed matrix after annealing at 35 K for: (a) $CBrCl_3/{}^{16}O_3/Ar$ (1/5/1000); (b) $CBrCl_3/{}^{18}O_3{}^{16}O_3/Ar$ (1/5/1000). Irradiation time: (a) 12 h; (b) 8 h.

These last bands can be assigned to the O–O stretching vibration of the O_2Br radical on the basis of the matrix infrared spectrum of the O_2Br radical recorded by Tevault and Smardzewski from matrix reactions of bromine atoms with the O_2 molecule [19].

In order to assign other bands owing to molecular complexes of phosgene with the different species in the matrix, we have investigated matrix isolation studies of the interaction between phosgene, prepared as described in the experimental section, and O_2 , CO, Cl_2 and Br_2 molecules. Such complexes between the carbonyl group and halogen molecules are little known. Only one such complex between formaldehyde and chlorine has been identified by IR in a solid nitrogen matrix [20].

COMPLEXES BETWEEN PHOSGENE AND O2, CO, Cl2 AND Br2 SPECIES

$COCl_2/O_2/Ar$

Addition of molecular oxygen to a $COCl_2/Ar$ mixture forming typically $COCl_2/O_2/Ar \Leftrightarrow 1/5/1000$ showed no change from the initial spectra, denoting the absence of any observable interaction between phosgene and oxygen.

$COCl_2/CO/Ar$

When CO was deposited with COCl_2 in an argon matrix $(\text{COCl}_2/\text{CO}/\text{Ar} \Leftrightarrow 1/1/1000)$, new bands at 2143 and 2140 cm⁻¹ appeared in addition to the usual CO transitions [12]. At the same time, peaks at 1818.0, 1817.1 and 840.3-839.1 cm⁻¹ appeared as shoulders on the ν_1 and ν_4 bands of the COCl₂ monomer. These bands were previously observed in our spectra after irradiation of a CBrCl₃/O₃/Ar mixture and thus they were due to an interaction between COCl₂ and CO molecules produced by photodissociation of COCl₂ in neighbouring sites.

COCl₂/Cl₂/Ar

The spectrum of COCl_2 in an argon matrix doped with Cl_2 ($\text{COCl}_2/\text{Cl}_2/\text{Ar} \Leftrightarrow 1/2/1000$) displayed new features at 1810 cm⁻¹ and 848.8–847.8 cm⁻¹ in the domain of ν_1 and ν_4 fundamental modes of COCl_2 as shown in Fig. 5. In the low-frequency region a new weak triplet with relative intensity 9/6/1 was measured at 546, 539, and 531 cm⁻¹, respectively (Fig. 6). After annealing or when the dopant/argon molar ratio increased, new bands at 1807–1804.6 cm⁻¹ grew strongly at the same time as the appearance of a doublet at 853.6–852.5 cm⁻¹.

The 1810.1 cm⁻¹ and 848.8–847.8 cm⁻¹ bands observed at high dilution must be assigned to the COCl₂ submolecule engaged in a 1:1 molecular complex between phosgene and Cl₂. The Cl₂ molecule is not infrared active but the



Fig. 5. FT-IR spectra in the 1850–1750 cm⁻¹ and 870–820 cm⁻¹ spectral regions of: (a) $COCl_2/Ar (1/1000)$; (b) $COCl_2/Cl_2/Ar (1/2/1000)$; (c) $COCl_2/Br_2/Ar (1/2/1000)$.



Fig. 6. FT-IR spectrum in the 560–520 cm⁻¹ spectral region of $COCl_2$ deposited in argon with Cl_2 ($COCl_2/Cl_2/Ar \Leftrightarrow 1/2/1000$).

spectroscopic constants of chlorine isolated in argon have been determined by laser-induced fluorescence and Raman spectroscopy [21]. The ω_e values were found at 554.5 cm⁻¹, 547.2 cm⁻¹ and 539.3 cm⁻¹ for ³⁵Cl₂, ^{35,37}Cl₂ and ³⁷Cl₂, respectively. In a complex the chlorine stretching is allowed by symmetry. The triplet observed at 546, 539 and 531 cm⁻¹ in our spectra is appropriate for the

different isotopic Cl₂ fundamental in the complex (abundance of natural isotopes ³⁵Cl and ³⁷Cl: 75.5% and 24.5%, respectively). The observed red shift in the Cl₂ fundamental suggests charge transfer into the unfilled chlorine σ^* antibonding molecular orbital in the ground state of the complex. At present, ab initio calculations are being performed in order to determine the structure and bonding of this complex. Thus, such species were produced after annealing the CBrCl₃/O₃/Ar photolyzed matrix but they were also present as traces after prolonged photolysis before annealing. This last observation could indicate that the chlorine atom produced with COCl₂ during the photoprocess escapes from the cage under energy in excess of that required for photodissociation [22]. Bands which appeared after annealing or Cl₂ concentration increasing could be assigned to (Cl₂)_mCOCl₂ aggregates.

$COCl_2/Br_2/Ar$

The presence of Br₂ in a COCl₂/Ar mixture (COCl₂/Br₂/Ar \Leftrightarrow 1/2/1000) induces, in the ν_1 and ν_4 COCl₂ regions, a band at 1804.8 cm⁻¹ and a doublet at 857.2–856.1 cm⁻¹ (Fig. 5). They are assigned to the 1:1 molecular complex COCl₂: Br₂. Unfortunately the complexed Br₂ stretching fundamental (\leq 317 cm⁻¹ [21]) was not measured. Table 2 compares the values of ν_1 and ν_4 modes of phosgene for the two different halogen molecules engaged in 1:1 complexes with COCl₂. The observed red shift on ν_1 and the blue shift on ν_4 increases on going from Cl₂ to Br₂.

After annealing of the photolyzed $CBrCl_3/O_3/Ar$ mixture, bands characterizing the $COCl_2:Br_2$ complex were observed but they were overlapped by stronger bands at 1801.3 and 859.5 cm⁻¹, correlated with a lower band at 583 cm⁻¹. Complementary experiments showed that these last bands cannot be assigned to a $COCl_2$ dimer or to oxalylchloride $(COCl)_2$ [23], and they still require identification.

TABLE 2

Mode	$\frac{\text{COCl}_2}{\nu^0(\text{cm}^{-1})}$	$COCl_2:Cl_2$		$COCl_2: Br_2$	
		$\nu(\mathrm{cm}^{-1})$	$\frac{\Delta v}{v^0}$	$\nu(\mathrm{cm}^{-1})$	$\frac{\Delta v}{v^0}$
<i>v</i> ₁	1815.6 1814.2	1810.3	0.2%	1804.8 1803.7	0.6%
V4	837.4 836.3	848.8 847.8	1.3%	857.2 856.1	2.3%

Comparison of ν_1 and ν_2 phosgene modes in the COCl₂:X₂ complex (X=Cl, Br) embedded in argon matrices ($\Delta \nu = \nu_{\text{COCl}_2}^0 - \nu_{\text{COCl}_2:X_2}$)

CONCLUSION

The photolysis of dilute argon matrices containing O_3 and CBrCl₃ molecules at 12 K generated the COCl₂ molecule which produced CO species in a secondary reaction. The cleaving of CBr and CCl bonds, also observed with atomic oxygen in the triplet state, probably arises from a transition state [BrOCCl₃]^{*} or [ClOCCl₂Br]^{*}, which has not been isolated. Vibrational spectra of complexes of COCl₂ with Cl₂ and Br₂ in argon matrices were performed in order to identify new species formed in the photolyzed matrix after a warm up at 35 K. Further experiments on the reaction of O atoms with other bromine compounds of the series (Br)_xC(H)_{4-x} are presently underway by our Norwegian REAM^a partner, C. Nielsen.

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