Reaction between Atomic Oxygen and Bromomethanes Studied by Matrix Isolation Infrared Spectroscopy

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The reactions of CH_3Br, $CHBr_3$, and CBr_4 with atomic oxygen in argon matrices were studied by infrared spectroscopy. Both $O(^1D)$ and $O(^3P)$ was generated *in situ* by the UV photolysis of ozone. $O(^1D)$ reacted with CH_3Br to give $H_2CO + HBr$ or $CO + H_2 + HBr$, with CBr_4 to give $COBr_2 + Br_2$ or $CO + 2Br_2$, and with $CHBr_3$ to give $HCOBr + Br_2$, $COBr_2 + HBr$ or $CO + HBr + Br_2$. Additional experiments were carried out with $CDBr_3 + O$ and $CHBr_3 + {}^{18}O$. The analogue reactions with $O(^3P)$ resulted in only the carbonyl intermediates. All the carbonyl compounds decomposed upon prolonged photolysis resulting in HBr and CO as final products in the matrix. The initial step of the reactions is discussed, and an overall reaction pathway is proposed.

The environmental problems connected with the release of man made halocarbons into the atmosphere was recognised in the early seventies, when the inertness of CFCs (chlorofluorocarbons) to tropospheric breakdown was discovered.[1] The fact that the CFCs could reach the stratosphere, where they photolysed, releasing active chlorine atoms, instigated extensive investigations of the atmospheric chemistry involving chlorine.[2] The acknowledgement of bromine's ozone destruction potential came soon after,[3] but because of the much smaller abundance its atmospheric impact did not initially receive the same amount of attention. Although much less bromine is released into the atmosphere, it is extremely important in the ozone destruction due to (1) the bromine chlorine synergism,[4] (2) the instability of bromine reservoir species, and (3) the weakness of the C–Br bond facilitating photolysis at lower altitudes in the stratosphere where ozone is most abundant and where a fractional destruction implicates a maximum ozone loss.

The destruction of halocarbons in the atmosphere has several pathways. The major breakdown process in the troposphere involves reaction with the OH radical. In the stratosphere direct photolysis is another possibility and reaction with atomic oxygen a third. Only a few spectroscopic studies of products from oxygen atom reactions with halocarbons have so far been presented,[5–9] among these is a comparative study of CH_2Cl_2 and CH_2Br_2 reactions.[9] In the following we present our results from similar product studies of the reactions between $O(^1D)$ and $O(^3P)$ and CH_3Br, $CHBr_3$ and CBr_4 in argon matrices. Preliminary results from this study have been published earlier.[10]

Experimental

The experiments were carried out by co-depositing mixtures of the CH_xBr_y/Ar (1:500) and O_3/Ar (1:200) through a dual-nozzle system onto the cold window of an Air Products 202A Displex unit at 15 K. Infrared spectra were obtained in the 4000–500 cm^{-1} region at 1 cm^{-1} resolution using a Bruker IFS 88 Fourier transform spectrometer. Dual nozzle deposition was employed in order to avoid surface induced reactions between the halocarbons and ozone. The atomic oxygen was generated *in situ* by photolysis of the ozone using filtered UV light from a medium pressure mercury lamp. A 280 nm cut-off filter results in $O(^1D)$ as well as $O(^3P)$ production from the ozone photolysis, a 320 nm cut-off filter results in only $O(^3P)$.[11] The halocarbons did not show any sign of photodecomposition upon exposure to wavelengths longer than 280 nm. Ozone was generated from high-grade oxygen by electrical discharge in a closed system and trapped in liquid nitrogen. The CH_3Br, $CHBr_3$ and CBr_4 were standard p.a. laboratory reagents that were checked for impurities by GC-MS before use. Deuterated bromoform and ${}^{18}O_2$ originated from Eurisotop.

Results

Parent compounds. Our infrared spectra of matrix isolated ozone are in good agreement with literature data,[12,13] but they invariably show traces of both CO and F_2CO originating from the vacuum line discharge synthesis of ozone. The infrared bands of CH_3Br are listed in the Table 1 and compared with previous results of the vapour[14] and of matrix isolation.[15] The similar data for

Table 1. Infrared spectral data (in cm⁻¹) for CH_3Br.

| Vapour Ref. 17 | Argon matrix | | Interpretation |
	Ref. 18	This work	
3056.6	3054.5	3055 (m)	v_4
	2977.9 (m)[a]	2977 (w-m)	$v_3 + v_4 + v_6$
2973	2967.4 (s)	2966 (s)	v_1
2862.0	2850.6 (m)	2850 (w)	$2v_5$
1442.7	1436.0 (s)	1437 (s)	v_5
1305.9	1300.4 (s)	1300 (s)	v_2
954.4	952.8 (s)	952 (s)	v_6
610.5		603 (w)	v_3

[a] Abbreviations: s, strong; m, medium; w, weak.

CHBr₃ and CDBr₃ are given in Tables 2 and 3, respectively, together with those of the gas phase[16] and earlier matrix isolation work.[17] To our knowledge CDBr₃ has not been studied by matrix isolation before. With the exceptions of v_3 and v_6, falling outside the range of our experimental set-up, the remaining fundamental modes have been observed. The infrared bands of CBr₄ are shown in Table 4 and are compared with data from the liquid[18] and with results from an earlier matrix isolation study.[19] Photolysis of the parent matrix isolated bromine compounds did not result in observable decomposition products within the timescales used in our experiments.

Table 2. Infrared spectral data (in cm⁻¹) for CHBr₃.

| Vapour Ref. 19 | Argon matrix | | Interpretation |
	Ref. 20	This work	
3049.8 (m)[a]		3063 (m)	v_1
		1331 (m)	$2v_5$
1148.6 (vs)	1153.5	1153 (s)	v_4
	1147.0	1146 (m)	
		695 (w)	$v_2 + v_6$
668.8 (vs)	667	667 (s)	v_5
	664	644 (m)	
542.6 (w)	543.5	542 (m)	v_2
223.2 (vw)			v_3
155			v_6

[a] Abbreviations: s, strong; m, medium; w, weak.

Table 3. Infrared spectral data (in cm⁻¹) for CDBr₃.

Vapour Ref. 19	Argon matrix	Interpretation
2272.5 (m)[a]	2281 (m)	v_1
	1286 (m)	$2v_5$
	1166 (m)	$v_2 + v_5$
851.5 (vs)	869 (s)	v_4
	851 (s)	
645.2 (vs)	645 (vs)	v_5
	627 (m)	
524.1 (w)	524 (w)	v_2
222.3		v_3
155.1		v_6

[a] Abbreviations: s, strong; m, medium; w, weak.

Table 4. Infrared spectral data (in cm⁻¹) for CBr₄.

| Liquid Ref. 21 | Argon matrix | | Interpretation |
	Ref. 22	This work	
		1345 (w)[a]	$2v_3$
671	675	675 (s)	v_3
267			v_1
182			v_4
122			v_2

[a] Abbreviations: s, strong; m, medium; w, weak.

Photolysis of CH₃Br/O₃. The matrix spectra of co-deposited CH₃Br and O₃ in argon revealed no additional bands. Annealing the matrix to 35 K for 30 min showed no new features in the spectrum, thus indicating that if any complexation is taking place it is too weak to induce an observable pertubation of the parent bands.

After 15–20 min of irradiation ($\lambda > 280$ nm) several new features appeared in the characteristic spectral regions of carbonyls, CO and HBr (Table 5). Prolonged irradiation resulted in an increase of the band intensities in the CO and HBr regions and a corresponding decrease in the other bands. Growth curves showed that there were two reaction channels: one leading to a carbonyl compound and another leading direct to CO and HBr. Further, the carbonyl product was very stable towards photolysis. After 28 h of UV irradiation the 1728 cm⁻¹ band showed a slight decrease, and it was still present after 46 hours of irradiation. Annealing at 35 K for 30 min resulted in small spectral changes. Exerts of the IR spectra are shown in Fig. 1.

When UV light with $\lambda > 320$ nm was used for generating O(³P) very small spectral changes appeared. After several hours of irradiation, weak traces of the 2886, 2819, 1728, 1495, 1247 and 1173 cm⁻¹ bands were observed.

Photolysis of CHBr₃/O₃. The spectrum of co-deposited CHBr₃ and O₃ in argon showed no additional bands that could be attributed to any strong complex formation as for the methylbromide. After irradiation ($\lambda > 280$ nm)

Table 5. Product bands (in cm⁻¹) from the CH₃Br + O(¹D) experiment.

$CH_3Br/^{16}O_3$

Vib. freq.	Assignment
2886 (w)[a]	v(CH) in $H_2CO\cdots HBr$
2819 (w)	v(CH) in $H_2CO\cdots HBr$
2520 (m)	v(HBr) in $OC\cdots HBr$
2340 (w)	v(HBr) in $H_2CO\cdots HBr$
2152 (s)	v(CO) in $OC\cdots HBr$
1728 (s)	v(C=O) in $H_2CO\cdots HBr$
1495 (w)	δ(CH) in $H_2CO\cdots HBr$
1247 (w)	δ(CH) in $H_2CO\cdots HBr$
1173 (w)	δ(CH) in $H_2CO\cdots HBr$

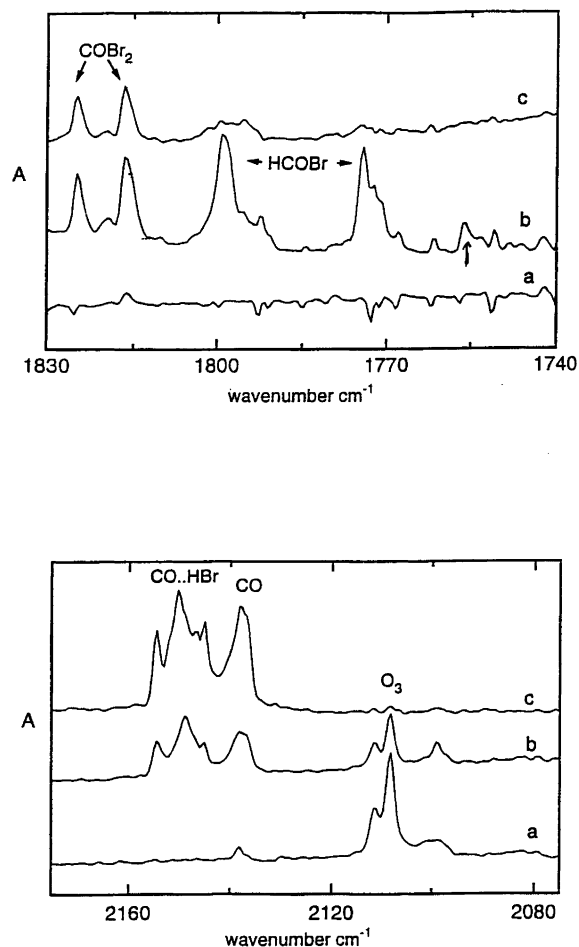[a] Abbreviations: s, strong; m, medium; w, weak.

Fig. 1. Upper: The carbonyl stretching region for $CHBr_3/O_3$ in an argon matrix. (a) After deposition, (b) after 1 h of UV irradiation filtered at 280 nm, (c) after 15 h of UV irradiation filtered at 280 nm. Lower: The CO and O_3 vibrational regions for $CHBr_3/O_3$ in an argon matrix. (a) After deposition, (b) after 1 h of UV irradiation filtered at 280 nm, (c) after 31 h of UV irradiation filtered at 280 nm.

the spectrum revealed several new bands: Tables 6 and 7 summarise the results from experiments with $CHBr_3/O_3$, $CDBr_3/O_3$ and $CHBr_3/^{18}O_3$. Bands which disappeared upon prolonged photolysis are collected in Table 6, while

bands increasing throughout the experiment are listed in Table 7. Exerts of the IR spectra are shown in Fig. 2. Some of the experiments showed traces of the $1816\ cm^{-1}$ band (attributed to $COBr_2$, vide infra) after deposition. Mass spectrometry of the staring sample showed no impurities and $COBr_2$ is probably formed in the reservoir bulb during deposition. Experiments with a 320 nm cut-off filter giving only $O(^3P)$ resulted in negligible reaction: no bands in the HBr or CO region, and only traces of the carbonyl region bands were observed.

Growth curves of the primary product bands are shown in Figs. 3a–3c. As can be seen, the $1825\ cm^{-1}$ band correlate with the $744\ cm^{-1}$ band (Fig. 3a), the 1816 with the $737\ cm^{-1}$ band (Fig. 3b), and the 1799 and 1774 and $1755\ cm^{-1}$ bands have very similar time profiles (Fig. 3c) that differ significantly from those of the 1825/744 and $1816/737\ cm^{-1}$ pairs. Growth curves for the bands in the CO and HBr regions of the spectrum (not given) reveal that there is a direct channel as well as an indirect (photolytic) channel to these compounds.

Photolysis of CBr_4/O_3. The co-deposited CBr_4 and O_3 sample revealed no bands other than those of the parent molecules. Irradiation of the mixture only resulted in a few new features. In the carbonyl region bands appeared at 1822 and at $1816\ cm^{-1}$. In the CO region a new band grew up at $2147\ cm^{-1}$ in addition to the free CO band at $2138\ cm^{-1}$ present from the beginning. Annealing the photolyzed matrix at 30 K increased the intensity of the $1822\ cm^{-1}$ band somewhat and certainly gave a substantial increase in the $2147\ cm^{-1}$ band. Experiments carried out with the 320 nm filtered ligh source giving $O(^3P)$ show the same carbonyl bands, but the $2147\ cm^{-1}$ band does not appear.

Discussion

The lifetime of $O(^1D)$ is ca. 150 s in the gas phase,[20] 32 s in a neon matrix[21] and 0.78 s in a SF_6 matrix.[22] A recent study of the photochemistry of ozone in argon matrices suggests that once an $O(^1D)$ atom escapes the matrix cage where it is generated, it moves easily through the argon lattice because of the short-range attractive inter-

Table 6. Intermediate product bands (in cm^{-1}) from the $CHBr_3 + O(^1D)$ experiments.

$CHBr_3/^{16}O_3$	$CHBr_3/^{18}O_3$	$CDBr_3/^{16}O_3$	
Vib. freq.	Vib. freq.	Vib. freq.	Assignment
1825 (m)[a]	1783 (m)	1826 (m)	$v(C=O)$ in $COBr_2\cdots HBr$
1816 (m)	1775 (m)	1816 (m)	$v(C=O)$ in $COBr_2$
1799 (sm)	1742 (m)	1745 (m)	$v(C=O)$ in HCOBr
1774 (sm)	1737 (m)	1739 (m)	$v(C=O)$ in $HCOBr\cdots Br_2$
1756 (w)	1716 (w)	1724/21 (w)	$v(C=O)$ in $HCOBr\cdots HBr$
	773 (mw)		$v(C-Br)$ in $COBr_2\cdots HBr$
	766 (mw)		$v(C-Br)$ in $COBr_2$
745 (m)	737 (m)	745 (m)	$v(C-Br)$ in $COBr\cdots HBr$
738 (m)	729 (m)	738 (m)	$v(C-Br)$ in $COBr_2$

[a] Abbreviations: s, strong; m, medium; w, weak.

Table 7. Final product bands (in cm^{-1}) from the CHBr$_3$ + O(^{1}D) experiments.

CHBr$_3$/^{16}O$_3$	CHBr$_3$/^{18}O$_3$	CDBr$_3$/^{16}O$_3$	
Vib. freq.	Vib. freq.	Vib. freq.	Assignment
2518 (m)[a]	2518 (m)	1808 (m)	v(HBr) in HBr···CO
2515 (m)	2515 (m)	1806 (m)	
2510 (w)	2510 (w)	1804 (w)	
2507 (w)	2507 (w)	1800 (w)	
2502 (w)	2502 (w)		
2498 (m)	2498 (m)	1797 (m)	v(HBr) in (HBr)$_2$···CO
2488 (w)	2488 (w)	1795 (w)	v(HBr) in (HBr)$_2$···CO
2154 (sm)	2103 (m)	2155 (m)	v(CO) in CO···(HBr)$_2$/CO···HBr
2150 (w)			
		2150 (w)	
2149 (w)			
2147 (m)	2097 (m)	2146 (m)	v(CO) in CO···Br$_2$
2145 (w)			
2138 (sm)	2087 (m)	2138 (sm)	v(CO)CO

[a] Abbreviations: s, strong; m, medium; w, weak.

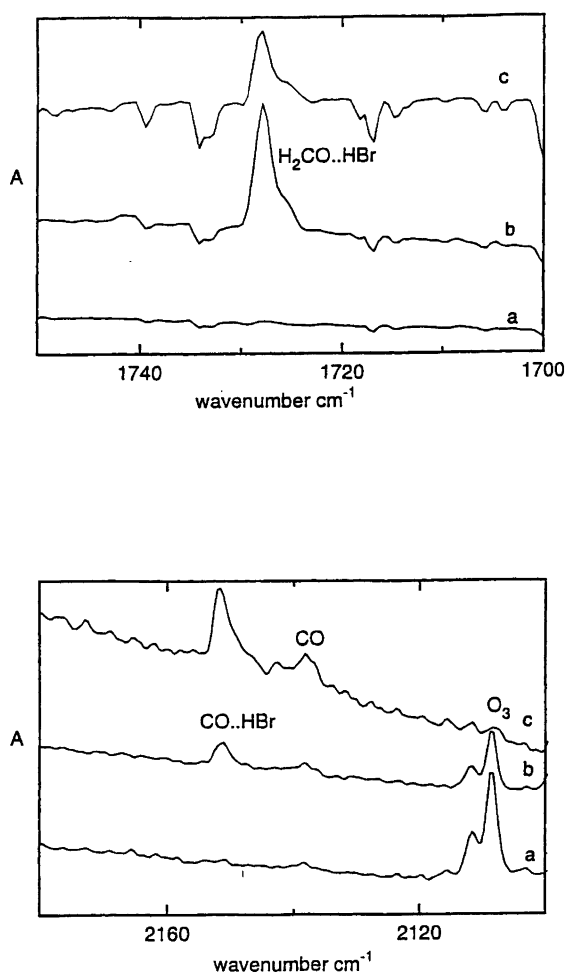*Fig. 2.* Upper: The carbonyl stretching region for CH$_3$Br/O$_3$ in an argon matrix. (a) After deposition, (b) after 1 h of UV irradiation filtered at 280 nm, (c) after 28 h of UV irradiation filtered at 280 nm. Lower: The CO and O$_3$ vibrational regions for CH$_3$Br/O$_3$ in an argon matrix. (a) After deposition, (b) after 1 h of UV irradiation filtered at 280 nm, (c) after 28 h of UV irradiation filtered at 280 nm.

action between argon and O(^{1}D).[23] This is not the case for the O(^{3}P) atom, which experiences a long range repulsive interaction with the argon lattice.[23] Molecules, on the other hand, can in most cases neither rotate nor diffuse outside their original trapping site in an argon matrix at 15 K. In this study we have therefore assumed that the singlet atomic oxygen (and to a lesser degree the triplet atomic oxygen) can move around in the matrix before reacting with the halocarbons (or O$_2$ or O$_3$). The organic reactant can not diffuse, but reaction products may dissipate their surplus energy by elbowing their way through the matrix.

The intermediates formed in the reactions (H$_2$CO, HCOBr and COBr$_2$) absorb in the region between 240 and 310 nm. The UV spectrum of H$_2$CO is well known,[24] with v$_m$ at 310 nm, whereas the spectra of HCOBr and COBr$_2$ have not been reported. However, their v$_m$ should be located somewhere between that of COCl$_2$ and H$_2$CO, and COCl$_2$ is known to have a v$_m$ of 230 nm.[25] We therefore expect photolytic decompostition of the intermediates present in our experiments when using the irradiation wavelengths reported here.

The spectral data from the matrix reaction between atomic oxygen and CHBr$_3$ are much more complex than those from the CH$_3$Br and CBr$_4$ reactions. We will therefore discuss the latter results first.

CH$_3$Br + O. The first set of bands appearing after irradiation (Table 5) can unambiguously be assigned to the H$_2$CO···HBr complex. This complex has previously been studied in an argon matrix, and all its bands were identified. [26] The complex proved very photostable under our conditions, but it eventually decomposed after extremely long irradiation to give the CO···HBr complex characterized by the 2518 and 2154 cm^{-1} bands.[27,28] When the photolysis generated O(^{1}D) the CO···HBr complex was also observed early in the experiment. The results from the O(^{3}P) experiments show that the same H$_2$CO···HBr complex is formed here (although in smaller
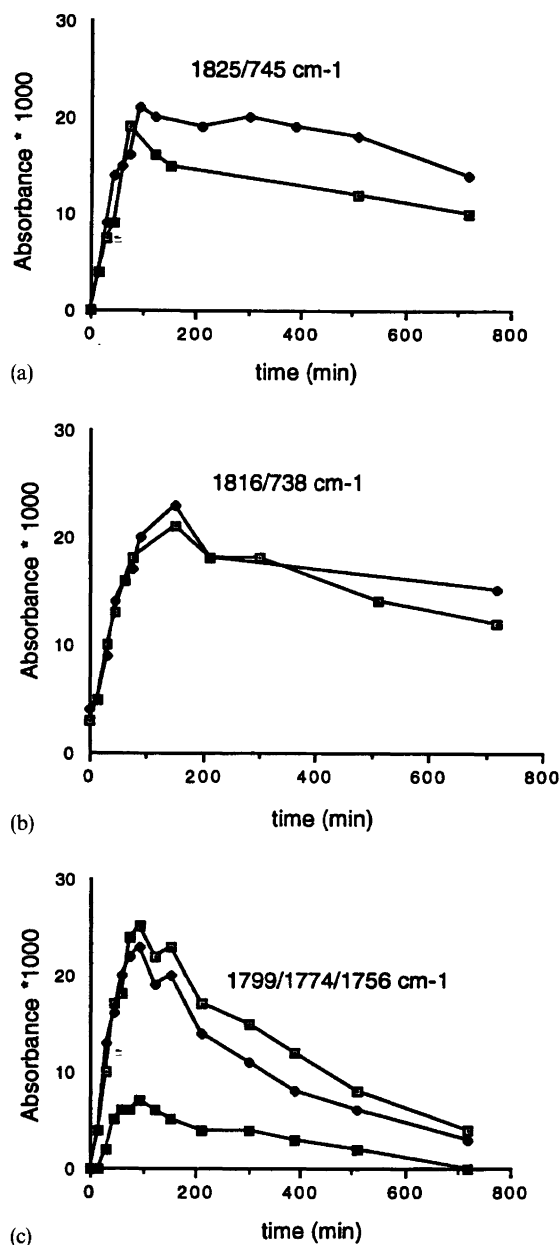
Fig. 3. Curves showing the peak intensity vs. photolysis time for the bands from the CHBr$_3$/O$_3$ experiment. (a) The 1825 and 744 cm^{-1} absorptions. (b) The 1816 and 737 cm^{-1} absorptions. (c) The 1799, 1774 and 1755 cm^{-1} absorptions.

quantity) and that CO is not formed directly in the reaction.

CBr$_4$ + O. The few IR bands appearing when CBr$_4$ reacts with atomic oxygen are easily assigned as the possibilities for complexation are limited. In the carbonyl stretching region the 1816 cm^{-1} feature is assigned to free COBr$_2$ which previously has been studied in an argon matrix.[29] In addition, we also obtained authentic spectra of COBr$_2$ for direct verification. Undoubtedly, the band at 1822 cm^{-1} originates from perturbed COBr$_2$, but a blue shift of 6 cm^{-1} is not in accordance with a standard *n*-

aσ complex with Br$_2$. For comparison, the C=O stretching mode in the H$_2$CO··Cl$_2$ complex is red-shifted by 10 cm^{-1}.[30] The band could *a priori* be due to a dimer, but as dimers were not observed in the matrix spectra of pure COBr$_2$ we dismiss this possibility. We are hence left with a bromine complexed or cage perturbed COBr$_2$ as the only possibility and tentatively ascribe the 1822 cm^{-1} band to Br$_2$···COBr$_2$. The new band in the CO region at 2147 cm^{-1}, blue-shifted by 9 cm^{-1}, is assigned to the Br$_2$···CO complex in accordance with recent results from high-resolution IR vapour studies.[31]

CHBr$_3$ + O. Some of the bands that appeared after irradiation of CHBr$_3$/O$_3$ in argon are easy to assign on the basis of the growth curves (Figs. 3a–3c), the results from the CBr$_4$ + O reaction, the previous study of the CH$_2$Br$_2$ + O reaction,[9] and the additional information provided by using isotopes. Two of the five bands in the carbonyl region (Table 6) show no wavenumber shift when using CDBr$_3$ as reactant but are shifted to 1783 and 1774 cm^{-1}, respectively, when using ^{18}O. Thus both of the 1825 and 1816 cm^{-1} bands and the corresponding bands in the C–Br stretching region at 745 and 737 cm^{-1} are due to COBr$_2$. The 1816/737 cm^{-1} pair arises from free COBr$_2$, in agreement with the results from the CBr$_4$ + O reaction and with the previous matrix-isolation study which also reports the same isotopic shifts as here.[29]

The 1825/745 cm^{-1} band pair is assigned to a perturbed/complexed COBr$_2$ in analogy to the situation described above. This interpretation relies on the reasonable assumption that Br$_2$ can move in the matrix after being formed in a reaction which is exothermic by several hundred kJ mol^{-1}.[9] The alternative interpretation that the band pair originates from a COBr$_2$···HBr complex is dismissed for two reasons. (1) In other carbonyl–HBr complexes the carbonyl band is red-shifted by 10–20 cm^{-1}. (2) Repeated attempts at generating a standard of this complex in the matrix failed. Only free COBr$_2$ and free HBr were observed when the two compounds were co-deposited.

In the experiment with^{18}O, the C–Br stretching region contains two band pairs at 773/766 and 737/729 cm^{-1}, as opposed to only one pair found in the ^{16}O and the CDBr$_3$ experiments. The IR spectrum of COBr$_2$ has two bands in this region: the v_4 band at 737 cm^{-1} and the $v_2 + v_5$ combination band at 778 cm^{-1} enhanced by Fermi resonance.[29] The reason that we only observe the combination band for C^{18}OBr$_2$ is connected with the fact that the Fermi resonance is stronger here than in C^{16}OBr$_2$.[29]

The remaining bands in the carbonyl region all show wavenumber shifts when using CDBr$_3$ and ^{18}O reactants. Hence, the bands are associated with HCOBr in one form or another. We follow the spectral interpretation in the matrix isolation study of the O + CH$_2$Br$_2$ reaction,[9] where the band at 1799 cm^{-1} was assigned to the v_2 mode of free HCOBr and the 1756 cm^{-1} band to the CHOBr···HBr complex. The latter interpretation

5

requires that also HBr is mobile in the matrix just after being formed, but the isotopic shifts for these bands (Table 6) are identical to those observed in Ref. 9, where HCOBr and HBr are formed in the same matrix cage and further consistent with the shift reported in the gas phase for DCOBr.[32] The v_2 mode of free HCOBr is in Fermi resonance with the $2v_6$ mode at 1772 cm^{-1}, which in the present experiment is partly overlapped by a stronger band at 1774 cm^{-1}. Finally the 1774, 1737 (^{18}O), and 1739 (D) cm^{-1} bands, which were not observed in the similar experiments with methyl bromide, methylene bromide,[9] or cabon tetrabromide, are tentatively assigned to the HCOBr$\cdots$Br$_2$ complex.

The complex structures in HBr and CO regions are not completely assigned, and the experiments with deuterated or [18]O isotopes are of little help. As previously mentioned, the band around 2518 cm^{-1} stems from the 1:1 complex of CO$\cdots$HBr. [26,27] The corresponding CO band is found at 2154 cm^{-1}. The bands at 2498 and 2488 cm^{-1} are due to the 2:1 complex of HBr and CO.[9,27,28] After prolonged photolysis a number of absorptions appear in the spectra between 2518 and 2498 cm^{-1} (Table 7). We suggest that the 2506 and

2502 cm^{-1} bands may be due to self-association of HBr, or HBr complexed with water which is always present in trace amounts.

The most prominent features in the CO spectral region are found at 2154 and 2138 cm^{-1}, corresponding to CO complexed to HBr and free CO, respectively. The CO stretching vibrations in the CO$\cdots$HBr and CO$\cdots$HBr$\cdots$HBr complexes are very close, and they can not be separated when the bands are somewhat broadened as here. There are a number of lines between these two features. One of them at ca. 2147 cm^{-1} is most likely due to the CO$\cdots$Br$_2$ complex which was also observed in the CBr$_4$/O$_3$ experiment.

Mechanism. The experimets show that there are two mechanistic pathways in the reaction of CH$_3$Br with O([1]D): (i) the formation of H$_2$CO and HBr followed by photodecomposition to H$_2$, HBr and CO after prolonged irradiation; and (ii) direct formation of CO and HBr. With O([3]P) only route (i) seems possible (Fig. 4).

Similarly, the CBr$_4$/O experiments show that the O([1]D) reaction has two paths: One leading to COBr$_2$ and Br$_2$ followed by photodecomposition to CO and Br$_2$, the

Table 6. Intermediate product bands (in cm^{-1}) from the CHBr$_3$+O([1]D) experiments.

CHBr$_3$/[16]O$_3$	CHBr$_3$/[18]O$_3$	CDBr$_3$/[16]O$_3$	
Vib. freq.	Vib. freq.	Vib. freq.	Assignment
1825 (m)[a]	1783 (m)	1826 (m)	v(C=O) in COBr$_2\cdots$HBr
1816 (m)	1775 (m)	1816 (m)	v(C=O) in COBr$_2$
1799 (sm)	1742 (m)	1745 (m)	v(C=O) in HCOBr
1774 (sm)	1737 (m)	1739 (m)	v(C=O) in HCOBr$\cdots$Br$_2$
1756 (w)	1716 (w)	1724/21 (w)	v(C=O) in HCOBr$\cdots$HBr
	773 (mw)		v(C–Br) in COBr$_2\cdots$HBr
	766 (mw)		v(C–Br) in COBr$_2$
745 (m)	737 (m)	745 (m)	v(C–Br) in COBr$\cdots$HBr
738 (m)	729 (m)	738 (m)	v(C–Br) in COBr$_2$

[a] Abbreviations: s, strong; m, medium; w, weak.

Table 7. Final product bands (in cm^{-1}) from the CHBr$_3$+O([1]D) experiments.

CHBr$_3$/[16]O$_3$	CHBr$_3$/[18]O$_3$	CDBr$_3$/[16]O$_3$	
Vib. freq.	Vib. freq.	Vib. freq.	Assignment
2518 (m)[a]	2518 (m)	1808 (m)	v(HBr) in HBr$\cdots$CO
2515 (m)	2515 (m)	1806 (m)	
2510 (w)	2510 (w)	1804 (w)	
2507 (w)	2507 (w)	1800 (w)	
2502 (w)	2502 (w)		
2498 (m)	2498 (m)	1797 (m)	v(HBr) in (HBr)$_2\cdots$CO
2488 (w)	2488 (w)	1795 (w)	v(HBr) in (HBr)$_2\cdots$CO
2154 (sm)	2103 (m)	2155 (m)	v(CO) in CO$\cdots$(HBr)$_2$/CO$\cdots$HBr
2150 (w)			
		2150 (w)	
2149 (w)			
2147 (m)	2097 (m)	2146 (m)	v(CO) in CO$\cdots$Br$_2$
2145 (w)			
2138 (sm)	2087 (m)	2138 (sm)	v(CO)CO

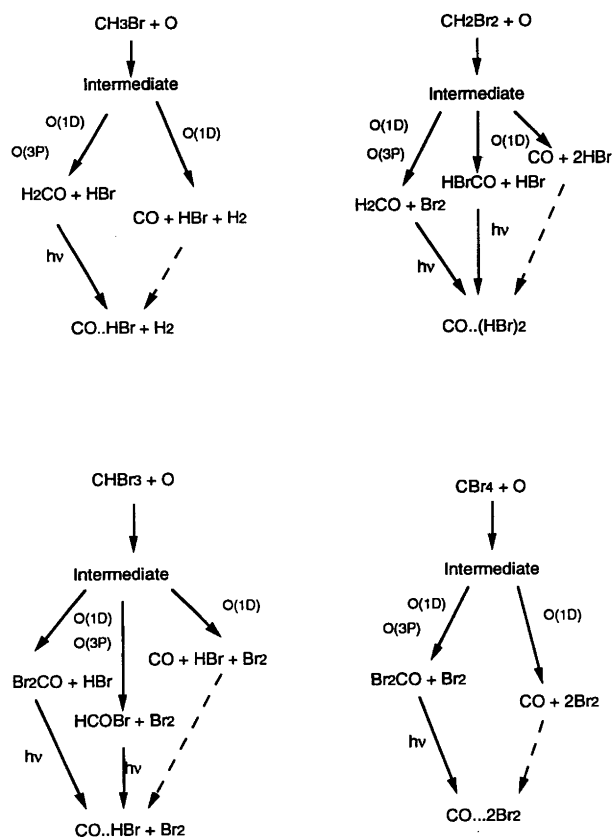[a] Abbreviations: s, strong; m, medium; w, weak.

Fig. 4. Proposed pathways for the reaction between bromo-methanes and atomic oxygen.

other leading direct to CO and Br_2. For the $O(^3P)$ reaction only the first path seems possible (Fig. 4).

For the $CHBr_3+O$ reaction there seemed to be three routes to the final products for $O(^1D)$: (i) formation of $COBr_2$ and HBr followed by decomposition to CO, Br_2 and HBr upon further photolysis; (ii) formation of HCOBr and Br_2 followed by a similar decomposition upon photolysis; and (iii) direct formation of CO and HBr. With $O(^3P)$ only paths (i) and (ii) were observed Fig. 4.

The question of how the oxygen atom initially attacks the halocarbons still remains. The primary step for the oxygen attack can be one of the following: the atomic oxygen may (i) insert into a CH bond, (ii) insert into a CBr bond, (iii) abstract a hydrogen or halogen atom, or (iv) add to the carbon forming a five-coordinated, excited intermediate. Previous studies of $O(^1D)$ insertion versus abstraction for hydrocarbons reacting indicate that the insertion mechanism dominates for the small hydrocarbons.[33,34] Insertion can also occur with the $O(^3P)$. Literature data[35] show that hydrogen or halogen atom abstraction is thermodynamically favourable with $O(^1D)$, while the reaction is endothermic with $O(^3P)$. The spectroscopic evidence obtained in this study can not conclusively indicate the initial step of these reactions.

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