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Matrix isolation study of the photochemically induced reaction of ozone with dibromochloromethane and bromodichloromethane in solid argon at 14 K. FT-IR spectra of the complexes $C(O)HCl\cdots BrX$, $C(O)HBr\cdots XCl$, $C(O)BrCl\cdots HX$, $(OC)(HCl)(Br_2)$, $(OC)(HBr)(Cl_2)$, and $(OC)(BrCl)(HX)$ (where X = Br or Cl)

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Quartz-filtered ($\lambda > 240$ nm) photolysis of either ozone/dibromochloromethane or ozone/bromodichloromethane in an argon matrix at 14 K has been shown by FT-IR spectroscopy to lead to the formation of the carbonyl$\cdots$Lewis acid complexes $C(O)HCl\cdots BrX$, $C(O)HBr\cdots XCl$, $C(O)BrCl\cdots HX$, and $C(O)Cl_2\cdots HBr$, where X = Br or Cl, depending on the trihalogenomethane used. Several of these complexes are new and are formed by either hydrogen halide or dihalogen abstraction reactions. Upon further irradiation the carbonyl complexes dissociate to form the new carbon monoxide complexes $(OC)(HCl)(Br_2)$, $(OC)(HBr)(Cl_2)$, and $(OC)(BrCl)(HX)$. Thus the photo-induced reactions of ozone with trihalogenomethanes lead to the formation of new carbonyl and carbon monoxide complexes whose vibrational properties are well characterised by FT-IR spectroscopy. Suggested pathways for the photolyses are presented.

Introduction

Matrix isolation provides an excellent means whereby photochemical reactions occurring between ozone and halogenocarbons may be analysed,[1–3] the information obtained being relevant to the mechanisms of ozone depletion from the atmosphere. Previous studies have shown that the photolysis of ozone with CH_3I,[4] CH_2X_2 (X = Cl or Br),[3] $CHCl_3$,[1] CH_2ClI[5] or CH_2BrCl[5] produces novel carbonyl$\cdots$Lewis acid complexes, for example $H_2C(O)\cdots HI$,[4] from ozone with iodomethane. The infrared spectra of such complexes differ slightly from those of isolated species on account of perturbation by the Lewis acids. The dihalide halogenocarbons CH_2XY (X and Y = Cl or Br, X and Y ≠ I) react with ozone, first *via* hydrogen halide abstraction to form the carbonyl complexes $C(O)HX\cdots HY$ *etc.* and then, on further photolysis, to form various carbon monoxide complexes (OC)(HX)(HY). By varying X and Y of the halogenoalkane, comparisons can be made between the spectra of complexes having identical carbonyls but different Lewis acids and *vice versa*, and between the spectral shifts of the carbon monoxide complexes having different Lewis acid partners.

This study is concerned with the ultraviolet induced reactions of ozone with dibromochloromethane ($CHBr_2Cl$) and bromodichloromethane ($CHBrCl_2$), with the identification of the photoproducts, and with a consideration of possible photochemical pathways.

Experimental

The infrared spectra were recorded on a Bruker IFS 113v Fourier-transform infrared spectrometer over the range 500–4000 cm^{-1} at a resolution of 0.5 or 1.0 cm^{-1} using a germanium-coated KBr beam splitter and a MCT detector cooled with liquid nitrogen. The matrices were scanned 500 times, the interferograms being added and converted to a single beam spectrum by a fast Fourier-transform algorithm using a zero filling factor of times four. The spectrum was converted to a double-beam absorbance spectrum. The band wavenumbers observed are accurate to either ±0.1 or ±0.2 cm^{-1}, depending on the resolution. Ozone was generated by Tesla coil discharge through normal oxygen at low pressures (≈38 Torr) in a 15 cm Pyrex finger immersed in liquid nitrogen, and purified by multiple freeze–thaw cycles. British Oxygen Co. supplied the research grade oxygen (>99.99%) and argon, while $CHBr_2Cl$ and $CHBrCl_2$ were used as supplied by Aldrich and were degassed by multiple freeze–thaw cycles with liquid nitrogen prior to use. The halogenocarbons were then diluted separately at species-to-argon (S/Ar) ratios in the range 1 : 400 – 1 : 600. The precursors were then separately deposited for 8 h at rates of approximately 3 mmol h^{-1} onto the CsI cold window (14 K) of a Displex closed-cycle helium cryostat (Air Products DE 202 S). The vacuum shroud surrounding the cold window could be aligned for infrared transmission studies, for gas deposition and for sample photolysis. Spectra were recorded after each matrix irradiation or warming cycle to monitor any changes caused by these processes.

The matrices were photolysed for various periods of time with an Oriel xenon mercury lamp, a 5 cm thick water filter being placed between the lamp and the sample to reduce the infrared output of the lamp. The matrices were photolysed with filtered radiation in the visible and ultraviolet regions by use of the following transmission filters: Corning 7 mm blue/green ($550 > \lambda > 350$ nm), Pyrex ($\lambda > 290$ nm) and quartz ($\lambda > 240$ nm).

Results and discussion

Precursor deposition in argon

The infrared spectra of $CHBr_2Cl$ isolated in an argon matrix ($CHBr_2Cl$/Ar = 1 : 450) and in an oxygen matrix ($CHBr_2Cl$/

Table 1 Infrared bands/cm^{-1} detected for $CHBr_2Cl$ after deposition in an argon matrix and in a solid oxygen matrix at 14 K[a]

Ar	O_2	Assignment
3070.5w	3057.2mw	ν_{C-H}
3058.9m		
3040.1w		
1361.2mw	1360.9w	$\delta_{a\ C-H}$
1353.9w		
1321.2w		
1308.6mw		
1217.0wm	1216.3w	$\delta_{s\ C-H}$
1198.7ms	1197.9m	
1160.1m	1154.1m	
1155.3ms		
1147.1w (sh)		
751.7s	751.0s	ν_{C-Cl}
737.1s	737.0s	
730.0w		
670.7vs	669.9s	ν_{C-Br}
647.6w		
573.3s	572.1ms	
529.5w		

[a] s = strong, m = medium, w = weak, v = very, sh = shoulder.

Table 2 Infrared bands/cm^{-1} detected after deposition of $CHBrCl_2$ in an argon matrix and in a solid oxygen matrix at 14 K[a]

Ar	O_2	Assignment
3058.4s	3016.0m	ν_{C-H}
3055.5m		
3040.6w		
1362.9vw (sh)		$\delta_{a\ C-H}$
1361.5w		
1354.0vw		
1320.9w		
1315.3w		
1307.8w		
1288.8w		
1266.5w		
1220.3mw	1211.6m	$\delta_{s\ C-H}$
1179.7w		
1173.9w	1169.4m	
1118.9w		
1117.5w		
821.4mw		ν_{C-Cl}
820.6mw		
767.9vs (br)	772.2 (sh)	
763.0vs	757.5vs (br)	
744.1mw		
726.8vs (br)		
723.0vs	720.3vs (br)	
696.3vw	698.6w	ν_{C-Br}
691.4vw		
687.7mw		
662.8mw		
661.4mw		
658.5mw		
607.9vs (br)	603.9s	
588.7w	586.2vw	
529.8mw		

[a] br = broad.

O_2 = 1 : 150) have been recorded (Table 1), as have the infrared spectra of $CHBrCl_2$ isolated in an argon matrix ($CHBrCl_2$/Ar = 1 : 500) and in an oxygen matrix ($CHBrCl_2/O_2$ = 1 : 150) (Table 2). In both cases the bands are assigned using as guides the assignments of bands for CH_2BrCl and other halogenomethanes in the gas phase. Ultraviolet (λ > 240 nm) photolysis of $CHBr_2Cl$/Ar or $CHBrCl_2$/Ar matrices produced no new bands.

The infrared spectra of either $CHBr_2Cl$ or $CHBrCl_2$ co-deposited with ozone in argon matrices ($CHBr_2Cl/O_3$/Ar = 1 : 2 : 400; $CHBrCl_2/O_3$/Ar = 1 : 2 : 600) exhibited bands that resemble those detected in the spectra of $CHBr_2Cl$, $CHBrCl_2$, or ozone[6] isolated separately in argon. No bands could be assigned to a complex formed between ozone and either of the two halogenomethanes; indeed even after photolysis with UV-VIS irradiation (λ > 350 nm) no new bands appeared. This situation is different from that for a monoiodoalkane co-deposited with ozone,[4,7,8] for which the spectroscopic evidence indicates that a molecular complex is formed immediately after deposition; this complex in turn breaks up after just ≈10–20 min of photolysis (λ > 800 nm or λ > 650 nm). Thus the presence of an iodine atom, as opposed to a bromine or chlorine atom, in a halogenocarbon dramatically changes the photochemistry of ozone. Irradiation of either matrix, $CHBr_2Cl/O_3$/Ar or $CHBrCl_2/O_3$/Ar, with Pyrex- (λ > 290 nm) or quartz-filtered radiation (λ > 240 nm) for tens of hours was required before a new set of bands was produced; for similar photolysis times the Pyrex-filtered irradiation cycles produced weaker bands than those detected after quartz-filtered photolysis. The most informative experiments proved to be ones in which the matrices were photolysed at fixed wavelengths (quartz-filtered) for different periods of time. The bands detected are grouped as reported below.

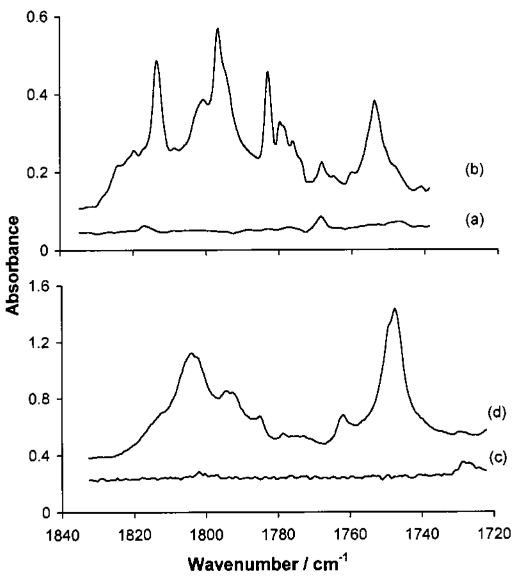


Fig. 1 Infrared spectra of $CHBr_2Cl/O_3$/Ar matrix after (a) deposition and (b) quartz-filtered photolysis (λ > 240 nm) for ≈50 h. Spectrum (b) was recorded at a resolution of 1.0 cm^{-1} and shows new bands attributed to $\nu_{C=O}$ of different carbonyl ··· Lewis acid complexes. Infrared spectra of $CHBrCl_2/O_3$/Ar matrix after (c) deposition and (d) quartz-filtered photolysis for ≈50 h. Spectrum (d) was recorded at a resolution of 0.5 cm^{-1} and shows new bands attributed to $\nu_{C=O}$ of different carbonyl ··· Lewis acid complexes.

Behaviour of deposited precursors after irradiation λ > 240 nm

Carbonyl complexes. Bands attributable to several carbonyl ··· Lewis acid complexes were detected after Pyrex- (λ > 290 nm) and quartz-filtered (λ > 240 nm) irradiation of argon matrices containing either $CHBr_2Cl/O_3$ or $CHBrCl_2/O_3$ (Tables 3 and 4). In both cases the $\nu_{C=O}$ bands of the various carbonyl ··· Lewis acid complexes produced are the most diagnostic.

C(O)HCl ··· BrX (where X = Br or Cl). Bands attributable to C(O)HCl are detected after UV irradiation of argon matrices containing either $CHBr_2Cl/O_3$ (Table 3 and Fig. 1) or $CHBrCl_2/O_3$ (Table 4 and Fig. 1). The intensities of the bands increased as the photolysis times increased up to ≈50 h, beyond which they began to decrease upon further irradiation. Employing $CHBr_2Cl$ as the initial precursor, a medium-weak band at 1779.7 cm^{-1} is assigned to $\nu_{C=O}$ of formyl chloride isolated in argon;[9] in the analogous $CHBrCl_2/O_3$ experiment this band occurs at 1785.0 cm^{-1}. In each case the $\nu_{C=O}$ bands are accom-

Table 3 Infrared bands/cm^{-1} assigned to the carbonyl products detected after photolysis ($\lambda > 240$ nm) of a mixture of ozone/argon and $CHBr_2Cl$/argon at 14 K

Complex	$\nu_{C=O}$	δ_{C-H}	ν_{C-Cl}	ν_{C-Br}	Other
$C(O)BrCl\cdots Ar$	1824.6w 1820.3w 1817.4w (sh)				
			824.1mw		626.8vw[a]
$C(O)BrCl\cdots HBr$	1813.5m 1801.4mw 1796.1m 1794.7m (sh)		820.7m 814.9m 812.0m 805.7m 797.0mw 791.2mw		
$C(O)HBr\cdots BrCl$	1783.1m	1285.9w 1279.7w 1273.1mw		642.0w [b]	1073.8vw[c]
$C(O)HCl\cdots Ar$	1779.7mw		[d]		
$C(O)HCl\cdots Br_2$	1776.3w	1307.9w	[d]		
$C(O)HCl\cdots (HX)_2$[e]	1753.7m	1302.8w 1298.5w	716.9w 712.7w		1147.1m[f]

[a] Combination $\nu_{C=O} + \delta_{C-Br-Cl}$. [b] ν_{C-Br} bands of C(O)HBr are obscured by those of $CHBr_2Cl$ at 670.7 cm^{-1}. [c] Combination $\nu_{C-Br} + \nu_5$. [d] ν_{C-Cl} bands obscured by those of $CHBr_2Cl$ at 751.7 cm^{-1}. [e] HX of the nearest neighbour. [f] Combination $\nu_{C-Cl} + \nu_5$.

Table 4 Infrared bands/cm^{-1} assigned to carbonyl products detected after photolysis ($\lambda > 240$ nm) of a mixture of ozone/argon and $CHBrCl_2$/argon at 14 K

Complex	$\nu_{C=O}$	δ_{C-H}	ν_{C-Cl}	ν_{C-Br}
$C(O)Cl_2\cdots Ar$	1813.5m (sh)		849.9m	
$C(O)Cl_2\cdots HBr$	1804.1ms 1802.4ms (sh)			
$C(O)BrCl\cdots HCl$	1794.3m 1792.6m		823.3m (sh) 821.1m	
$C(O)HCl\cdots Ar$	1785.0mw	1315.4w	726.8s[a]	
$C(O)HBr\cdots Cl_2$	1778.6w 1776.5w	1286.2w 1279.7w		662.3m 661.6m 658.8m
$C(O)HCl\cdots BrCl$	1774.8w 1772.9w			
$C(O)HCl\cdots HX$[b]	1762.0mw		767.9s[a]	
$C(O)HCl\cdots (HX)_2$[b]	1749.2s (sh) 1747.5s	1303.1w		

[a] Obscured by a broad precursor band. [b] HX of the nearest neighbour.

panied by some slightly red-shifted bands which are assigned to $\nu_{C=O}$ of formyl chloride in perturbing environments, *i.e.* complexed with Lewis acids, $C(O)HCl\cdots Br_2$ and $C(O)HCl\cdots BrCl$. Moreover, in both experiments carbonyl bands detected in the 1762–1747 cm^{-1} region (wavenumber shifts of $\nu_{C=O}$, ≈20–40 cm^{-1}) are attributed to C(O)HCl strongly perturbed by two hydrogen halides. These and other assignments for formyl chloride complexes can be found in Tables 3 and 4. Warming the matrices led to either growth or destruction of some bands; this further supports the idea that more than one formyl chloride species must be present.

C(O)HBr···XCl (where X = Br or Cl). These bands are formed after Pyrex- and quartz-filtered photolysis of matrices containing either $CHBr_2Cl/O_3$ or $CHBrCl_2/O_3$ and are attributed to formyl bromide (Tables 3 and 4, Fig. 1). Like the formyl chloride bands, their intensities increased progressively until after ≈50 h of irradiation, whereupon some of the bands began to weaken. In matrices containing $CHBr_2Cl$ and O_3, a medium band occurring at 1783.1 cm^{-1} is assigned to $\nu_{C=O}$ of the complex $C(O)HBr\cdots BrCl$, the wavenumber shift being 18.4 cm^{-1} from that (at 1801.5 cm^{-1})[5] of isolated formyl bromide. In the $CHBrCl_2/O_3$ matrix, $\nu_{C=O}$ bands detected after photolysis are considered to arise from the complex $C(O)HBr\cdots Cl_2$, due to the wavenumber shifts of 22.9 and 25.0 cm^{-1} of $\nu_{C=O}$ from that for isolated C(O)HBr. As a comparison, the corresponding shifts for $C(O)HCl\cdots Cl_2$[1] and $C(O)HCl\cdots Br_2$ are 23.5 and 7.2 cm^{-1}, respectively. Further assignments are made in Tables 3 and 4 to support the presence of C(O)HBr complexes.

C(O)BrCl···HX (where X = Br or Cl). The C(O)BrCl bands (Tables 3 and 4, Fig. 1) behave similarly, after photolysis, to those of formyl chloride and formyl bromide and were found to be at similar wavenumbers to those detected for C(O)BrCl in the gas phase.[10] Several $\nu_{C=O}$ bands were detected after photolysis of $CHBr_2Cl$ and O_3 in argon matrices, those between 1824.6 and 1817.4 cm^{-1} being attributed to C(O)BrCl isolated in argon, the least perturbing environment. The other $\nu_{C=O}$ bands were shifted to lower wavenumbers as a result of perturbation by the Lewis acid, HBr, and are considered to arise from the complex $C(O)BrCl\cdots HBr$, the shifts being of a similar magnitude to those reported for other carbonyls perturbed by HBr.[3,5] However, the three weak bands at 1824.6, 1820.3, and 1817.4 cm^{-1}, detected after 25 h of photolysis ($\lambda > 240$ nm) could, alternatively, be assigned to $\nu_{C=O}$ of $C(O)Br_2\cdots HCl$ since the $\nu_{C=O}$ band of $C(O)Br_2$ in the gas phase[11] occurs at 1828 cm^{-1}. Nevertheless formation of this complex seems unlikely, as breakage of the two strongest bonds (C–H and C–Cl) would be required while the weaker C–Br bond would need to remain intact. The large number of bands assigned to ν_{C-Cl} suggests that either further species or more than one distinct environment may be present. Photolysis of $CHBrCl_2/O_3$ matrices gave rise to $\nu_{C=O}$ bands at 1794.3 and 1792.6 cm^{-1} and are attributed to the complex $C(O)BrCl\cdots HCl$. The shift in $\nu_{C=O}$ from its value for the uncomplexed carbonyl (1817.3 cm^{-1})[5] increases with the Lewis acid strength, the complex $C(O)BrCl\cdots HCl$ exhibiting highly perturbed carbonyl bands.

C(O)Cl$_2$···HBr. Bands attributable to this species were detected after UV photolysis of a matrix containing $CHBrCl_2$ and O_3 (Table 4 and Fig. 1) and were found to be at similar wavenumbers to those detected previously for carbonyl chloride in the gas phase[12] and in solid argon.[13] The bands behaved, after photolysis, almost identically to those of the carbonyl species mentioned above. A medium band occurring at 1813.5 cm^{-1} is assigned to the isolated species $C(O)Cl_2$. Other $\nu_{C=O}$ bands attributed to $C(O)Cl_2$ were red-shifted to 1804.1 and 1802.4 cm^{-1} suggesting that a complex of the form $C(O)Cl_2\cdots HBr$ is present.

Carbon monoxide complexes. The bands in this group are attributed to several carbon monoxide···Lewis acid complexes (Tables 5 and 6) and appear to increase in intensity with increase in photolysis time at the expense of those attributed to the carbonyl···Lewis acid complexes discussed above. There-

Table 5 Infrared bands/cm^{-1} assigned to ν_{H-Cl}, ν_{H-Br} and $\nu_{C\equiv O}$ of carbon monoxide complexes detected after UV photolysis ($\lambda > 240$ nm) of a mixture of ozone/argon and $CHBr_2Cl$/argon at 14 K

Complex	ν_{H-Cl}	ν_{H-Br}	$\nu_{C\equiv O}$
$OC\cdots(HCl)_2$			2157.6mw
$OC\cdots Br_2\cdots HCl$	2813.5m		2150.7mw
	2807.6mw (sh)		
$OC\cdots HCl\cdots Br_2$	2794.6mw		2153.1m
	2791.4m		
$HBr\cdots Ar$		2541.6vw	
$(OC)_m(HBr)_n$[a]		2525.2vw	2142.3w
$OC\cdots BrCl\cdots HBr$		2510.4w	
		2507.8w	
$BrCl\cdots OC\cdots HBr$		2496.7w	2146.6mw
$OC\cdots Ar$			2138.0mw

[a] *m* and *n* are not defined.

Table 6 Infrared bands/cm^{-1} assigned to carbon monoxide complexes detected after UV photolysis ($\lambda > 240$ nm) of a mixture of ozone/argon and $CHBrCl_2$/argon at 14 K

Complex	$\nu_{C\equiv O}$	ν_{H-Cl}	ν_{H-Br}
$OC\cdots(HCl)_2$[a]	2159w (sh)	2797.7w	
		2786.3w	
		2774.9w[b]	
$OC\cdots HCl\cdots BrCl$	2156.7w	2823.8w	
$OC\cdots HCl$	2154.4w	2850.0w	
	2153.0w		
$OC\cdots HBr$	2152.1w (sh)		2540.8w[c]
			2515.8w
$OC\cdots BrCl\cdots HCl$	2151.3w	2836.9w	
$OC\cdots HBr\cdots Cl_2$	2149.5w		2494.7vw
$OC\cdots Cl_2\cdots HBr$	2143.1w		2509.3w
	2142.1w		2507.7w
			2506.3w
$OC\cdots Ar\cdots Cl_2$?	2140.6w		
$OC\cdots Ar$	2137.9w		

[a] HX of the nearest neighbour. [b] $(OC)_m(HCl)_n$. [c] $HBr\cdots Ar$.

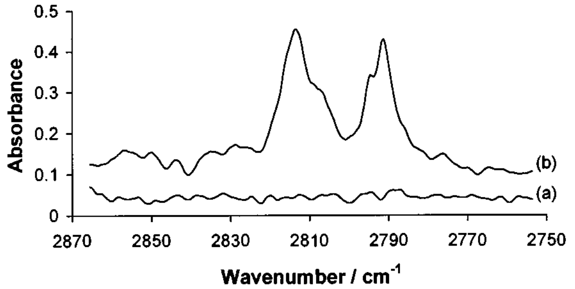


Fig. 2 Infrared spectra of an argon matrix containing $CHBr_2Cl$ and O_3 after (a) deposition and (b) quartz-filtered photolysis ($\lambda > 240$ nm) for ≈120 h. Spectrum (b) was recorded at a resolution of 1.0 cm^{-1} and shows new bands in the ν_{H-Cl} region attributed to the carbon monoxide complexes, $OC\cdots(HCl)_2$, $OC\cdots HCl$, $OC\cdots HCl\cdots BrCl$, and $OC\cdots BrCl\cdots HCl$.

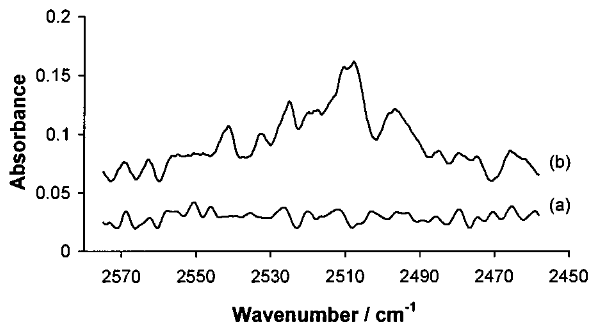


Fig. 3 Infrared spectra recorded after (a) deposition and (b) ≈120 h of quartz-filtered photolysis ($\lambda > 240$ nm) of a $CHBr_2Cl/O_3/Ar$ matrix. Spectrum (b) was recorded at a resolution of 1.0 cm^{-1} and shows new bands attributed to ν_{H-Br} of different carbon monoxide complexes, $OC\cdots HBr$, $OC\cdots HBr\cdots Cl_2$, and $OC\cdots Cl_2\cdots HBr$.

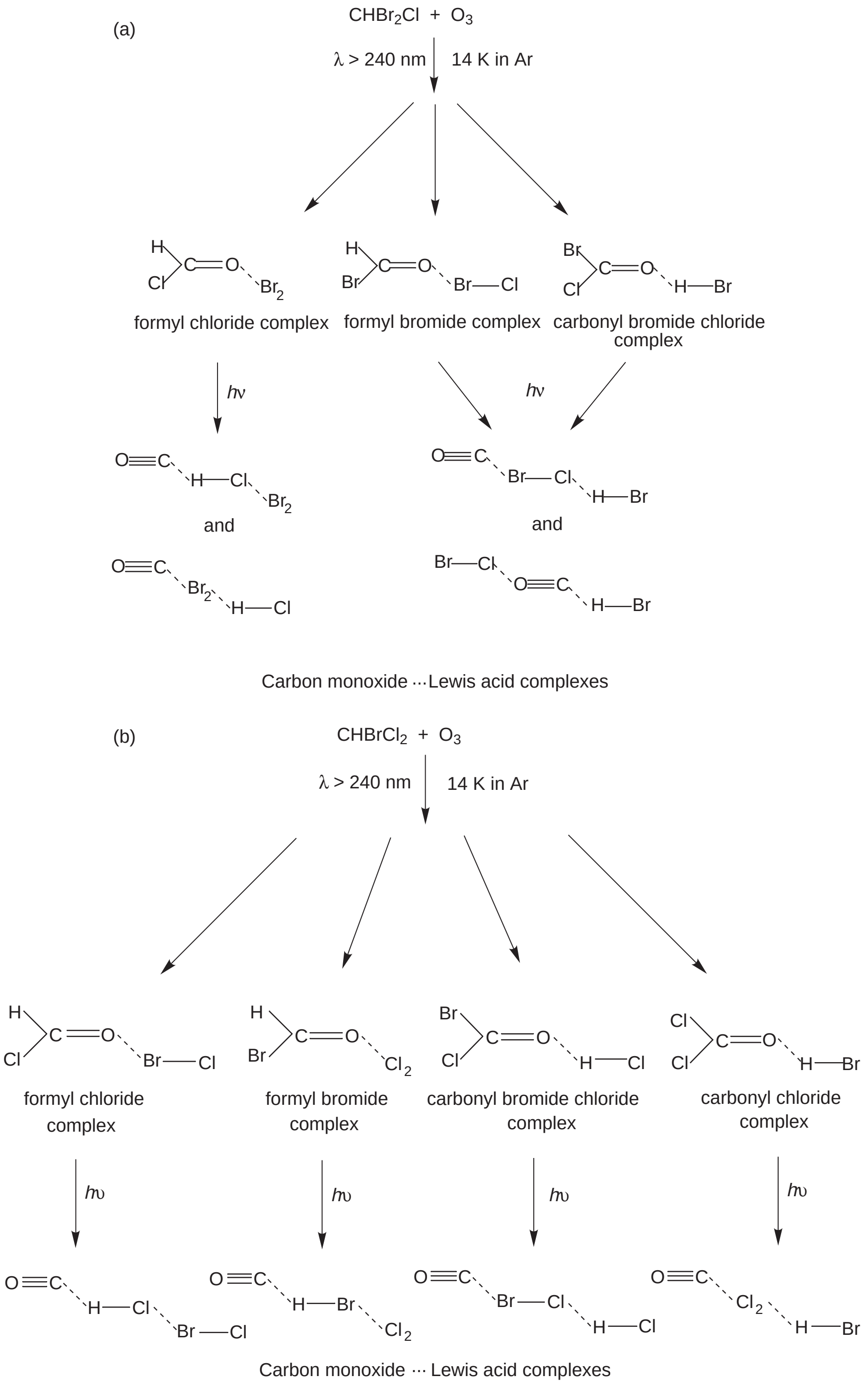
fore a mechanism in which the carbonyl ··· Lewis acid complex photodissociates to form the carbon monoxide complex is proposed.

(OC)(HX)(Y$_2$) (where X = Br or Cl and Y$_2$ = Br$_2$ or Cl$_2$). After prolonged UV photolysis of argon matrices containing either $CHBr_2Cl/O_3$ or $CHBrCl_2/O_3$, bands were detected which could be assigned to the stretches of CO, HCl, or HBr (Tables 5 and 6, Figs. 2 and 4), their intensities continuing to increase throughout the entire photolysis period (120 h). Bands are attributed to carbon monoxide species on the basis that their wavenumbers are near to that of carbon monoxide in the gas phase (≈2138 cm^{-1}) and in solid argon (2138.3 cm^{-1},[14] 2138.4 cm^{-1}[1,15]); shifts of $\nu_{C\equiv O}$ to higher wavenumbers suggest that carbon monoxide is perturbed by different species to form more than one complex (Tables 5 and 6). Similarly the large number of bands detected in both the ν_{H-Cl} and ν_{H-Br} regions indicates that either HCl or HBr forms part of more than one complex present in the matrix (HCl in solid argon absorbs at 2888.0, 2869, and 2853.3 cm^{-1};[5,14,16] HBr isolated in argon absorbs at 2568.4 and 2549.6 cm^{-1}[14]).

In previous studies[5,14] the position of HX at either *a* or *b* in complexes such as $OC\cdots HX^a\cdots HX^b$ could be distinguished by the wavenumber of the ν_{H-Cl} or ν_{H-Br} band. In the complex $OC\cdots HCl^a\cdots HCl^b$ for example, the HCl in the *a* position absorbs between 2791.3 and 2780.5 cm^{-1}, and in the *b* position between 2811.2 and 2803.0 cm^{-1}. Likewise for the $OC\cdots HBr^a\cdots HBr^b$ complex, the HBr in the *a* position absorbs at ≈2484.8 cm^{-1} and in the *b* position at ≈2509.7 cm^{-1}. Thus in the $CHBr_2Cl/O_3$ experiment the complex $OC\cdots Br_2\cdots HCl$ could be identified by the ν_{H-Cl} values of 2813.5 and 2807.6 cm^{-1}. A second group of similar bands was detected and attributed to another complex whose ν_{H-Cl} values (2794.6 and 2791.4 cm^{-1}) are typical of that of HCl in the *a* position; $OC\cdots HCl\cdots Br_2$. Also the wavenumbers of the $\nu_{C\equiv O}$ bands detected for both complexes compare reasonably well with those of related carbon monoxide complexes, *i.e.* $OC\cdots(HCl)_2$ (2157.2 cm^{-1},[14,17] 2156.7 and 2155.6 cm^{-1}[3]), $OC\cdots HCl\cdots HBr$ (2154.9 cm^{-1}),[5] $OC\cdots HCl\cdots HI$ (2151.5 and 2141.4 cm^{-1}),[5] and $OC\cdots HCl$ (2151 cm^{-1}).[16,17] The bands of complexes $OC\cdots Br_2\cdots HCl$ and $OC\cdots HCl\cdots Br_2$ have similar intensities and, since no evidence for the complex $C(O)Br_2\cdots HCl$ was detected, it is believed that they form from photodissociated $C(O)HCl\cdots Br_2$. The two structures exist because, unlike the complex $OC\cdots HCl\cdots HBr$,[5] bromine does not form a sufficiently strong hydrogen bond for one type of arrangement to dominate.

Likewise in the $CHBrCl_2/O_3$ experiment the bands observed are attributed to $OC\cdots HBr\cdots Cl_2$ and $OC\cdots Cl_2\cdots HBr$. The band at 2494.7 cm^{-1} is close to the value obtained when HBr is located in the *a* position, while those detected between 2509.3 and 2506.3 cm^{-1} are typical of HBr in the *b* position. Bands attributed to the complex $OC\cdots HBr$ were also detected. The blue-shift in $\nu_{C\equiv O}$ from its value for the uncomplexed CO in solid argon (2138.4 cm^{-1})[1,15] increases with the Lewis acid strength. This is due to the degree of removal of electron density from the antibonding orbital of CO (located primarily on the C atom),[18] leading to an increase in bond strength and therefore of $\nu_{C\equiv O}$, *cf.* the values of $\nu_{C\equiv O}$ in the related complexes $OC\cdots(HBr)_2$ (2153.1 cm^{-1}),[3] $OC\cdots HBr\cdots HCl$ (2149.0 cm^{-1}),[5] and $OC\cdots HBr$ (2152.4 cm^{-1},[14] 2150 cm^{-1}[19]).

(OC)(BrCl)(HX) (where X = Br or Cl). Once more bands assigned to perturbed $\nu_{C\equiv O}$, ν_{H-Cl}, or ν_{H-Br} could be detected after prolonged UV photolysis of $CHBr_2Cl/O_3$ and $CHBrCl_2/O_3$ matrices and are attributed to various carbon monoxide complexes (Tables 5 and 6, Figs. 3 and 4). Bands assigned to $\nu_{C\equiv O}$ and ν_{H-Br} were detected after photolysis of matrices containing



Scheme 1

$CHBr_2Cl$ and ozone. Those detected at 2510.4 and 2507.8 cm^{-1} are assigned to ν_{H-Br} in the complex $OC\cdots BrCl\cdots HBr$ on the basis that ν_{H-Br} compares well with those of the other carbon monoxide$\cdots$HBr complexes.[1,3,14,16,17,20] Other bands detected at 2496.7 and 2146.6 cm^{-1} are assigned to ν_{H-Br} and $\nu_{C\equiv O}$, respectively, for the complex $BrCl\cdots OC\cdots HBr$. These complexes are formed only weakly, possibly from the photodissociation of the complexes $C(O)HBr\cdots BrCl$ or $C(O)BrCl\cdots HBr$.

In the $CHBrCl_2/O_3$ experiment, bands attributed to CO and HCl were detected after prolonged UV photolysis. On the basis that ν_{H-Cl} in the *a* position occurs at a lower value than that in the *b* position, the ν_{H-Cl} bands at 2823.8 and 2836.9 cm^{-1} are attributed to the complexes $OC\cdots HCl\cdots BrCl$ and $OC\cdots BrCl\cdots HCl$, respectively. Both of these values for ν_{H-Cl} occur slightly higher than those referred to earlier because BrCl is a much weaker Lewis acid than HCl and thus has less effect on the shift of ν_{H-Cl} from its value for the isolated molecule.

Photochemical interconversion

The photochemical reactions of ozone with iodine-containing compounds reveal evidence for species containing $C–IO_x$ and C–O–I bonds;[4,7,8] whereas with chlorine- or bromine-containing compounds (CH_2Cl_2 or CH_2Br_2)[3] the initial products are carbonyl complexes in which insertion of an O atom into the C–H bond has taken place. Although other mechanisms have been considered for the formation of carbonyl products,[3,5,19] the favoured one in this study and elsewhere,[19] involves the insertion of an O atom (from ozone or oxygen) into either a C–H or a C–X bond of the precursors $CHBr_2Cl$ and $CHBrCl_2$, resulting in hydrogen halide (HX) or halogen (X_2 or XY) abstraction; all the required reaction products have, in fact, been detected. After prolonged periods of photolysis the band

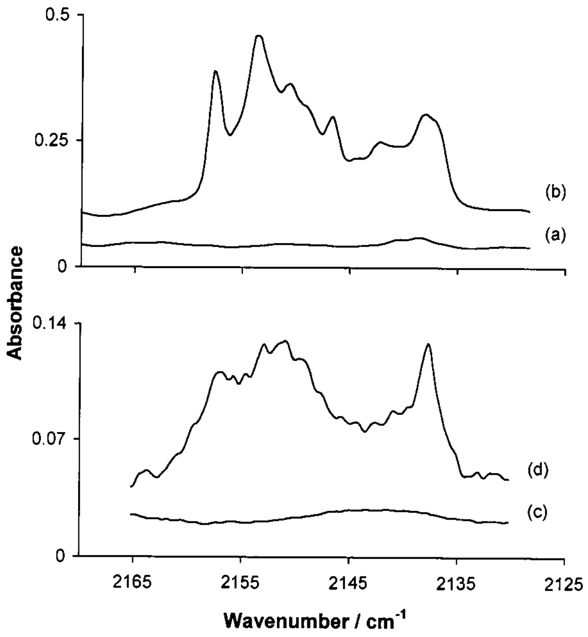


Fig. 4 Infrared spectra recorded after (a) deposition and (b) ≈120 h of quartz-filtered photolysis ($\lambda > 240$ nm) of a $CHBr_2Cl/O_3/Ar$ matrix. Spectrum (b) was recorded at a resolution of 1.0 cm^{-1} and shows new bands attributed to $\nu_{C\equiv O}$ of different carbon monoxide · · · Lewis acid complexes. Infrared spectra in the $\nu_{C\equiv O}$ region of a $CHBrCl_2/O_3/Ar$ matrix after (c) deposition and (d) quartz-filtered photolysis for ≈120 h. Spectrum (d) was recorded at a resolution of 0.5 cm^{-1} and shows new bands attributed to different carbon monoxide · · · Lewis acid complexes.

intensities of the carbonyl products decreased while new bands attributed to several carbon monoxide complexes were detected. This supports the idea that the carbonyl complexes dissociate *via* elimination of molecular CO and Lewis acids to form the carbon monoxide · · · Lewis acid complexes (Scheme 1).

Thus the photochemical reaction of ozone with either $CHBr_2Cl$ or $CHBrCl_2$ is dependent on time and photolysis wavelength and proceeds *via* the formation of a range of carbonyl · · · Lewis acid complexes that, upon further photolysis, dissociate to form several carbon monoxide complexes (Scheme 1); no evidence was obtained for the presence of species having C–Br–O or C–O–Br bonds.

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