Photochemical Reaction of Ozone with Chloroiodomethane and Bromochloromethane in Solid Argon at 14 K. FTIR Spectra of the Intermediate, CH_2ClIO, and the Complexes $HC(O)Cl\cdots HI$, $HC(O)Cl\cdots HBr$, $HC(O)Br\cdots HCl$, COBrCl, (CO)(HCl)(HI), and (CO)(HBr)(HCl)

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The photolysis (visible and ultraviolet) of low-temperature argon matrices containing either chloroiodomethane/ozone or bromochloromethane/ozone has been studied by FTIR spectroscopy. Codeposition of ozone and chloroiodomethane in an argon matrix led to the formation of a weak complex, $CH_2ClI\cdots O_3$, which, on irradiation with near infrared/visible light ($\lambda > 650$ nm), formed iodosochloromethane CH_2ClIO. Subsequent photolysis at shorter wavelength ($\lambda > 350$ nm) produced hypoiodochloromethane CH_2ClOI, a formyl chloride complex $HC(O)Cl\cdots HI$, and a carbon monoxide complex $OC\cdots HCl\cdots HI$. Subsequent Pyrex- ($\lambda > 290$ nm) and quartz- ($\lambda > 240$ nm) filtered irradiation increased the yield of the formyl chloride and carbon monoxide complexes. The photolysis of matrices containing bromochloromethane and ozone required much harsher conditions, i.e. ultraviolet irradiation for tens of hours, to produce any products, the first of which being the carbonyl complexes, $HC(O)Cl\cdots HBr$, $HC(O)Br\cdots HCl$, and $COBrCl\cdots H_2$. Subsequent photolysis produced the carbon monoxide complexes $OC\cdots HCl\cdots HBr$ and $OC\cdots HBr\cdots HCl$. Thus by studying the reactions of ozone with these two disubstituted halomethanes it has been possible to extend the number of known species having $I-O_x$ bonds and to detect a number of carbonyl···HX and carbon monoxide···(HX)(HY) complexes in which the halogen atoms (X and Y) differ.

Introduction

Chloroiodomethane is believed to be a possible source of atmospheric iodine and hence, like other halocarbons, it leads to the destruction of atmospheric ozone. In a matrix environment ozone can form weak complexes with iodine-containing compounds ICl,[1] CH_3I,[2] CF_3I,[3] C_2H_5I,[4] $C_2F_xH_{5-x}I$,[5] and $(CH_3)_2CHI$,[5] which can lead to the photodissociation of the ozone part of the complex and the transfer of an oxygen atom to the iodine-containing compound (ZI) to form an iodoso-intermediate (Z−IO). The latter, on further photolysis, can rearrange to the hypoiodide species (Z−OI). Finally loss of the iodine atom can yield a carbonyl···Lewis acid complex. These photodissociation processes can be achieved with longer wavelength radiation (visible and near-infrared) than is required to bring about any significant dissociation of isolated ozone.[6]

The ozone photolysis reactions with CH_3I,[2] CH_2X_2,[7] (X = Cl or Br), and $CHCl_3$[8] have been shown to produce a number of novel carbonyl···Lewis acid complexes, for instance $CH_2O\cdots HI$[2] by treating iodomethane with ozone. Such complexes are of interest because their spectra are devoid of features attributable to either parent species. In previous studies, the parent halocarbon has contained two identical halogen atoms, e.g. CH_2X_2 (where X = Cl or Br),[7] whose reactions with ozone have led to the formation of the complexes $HC(O)X\cdots HX$ and $OC(HX)_2$. In this study the use of halocarbons having two different halogen atoms, CH_2XY, is expected to produce complexes such as $HC(O)X\cdots HY$, $HC(O)Y\cdots HX$, and various OC(HX)(HY). Comparisons could then 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.

Experimental Section

The infrared spectra were recorded on a Bruker IFS 113v Fourier transform infrared spectrometer over the range 560−4000 cm^{-1} at a resolution of 1 cm^{-1} using a germanium-coated KBr beam splitter and an MCT detector cooled with liquid nitrogen. The matrices were scanned 500 times, the interferograms being coadded 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 bands observed are accurate to ±0.2 cm^{-1}.

Ozone was generated from research grade oxygen (>99.99%) and oxygen-18 (>97.7%) supplied by British Oxygen Co. and Enritech Enrichment Technologies Ltd., respectively. Argon, chloroiodomethane, and bromochloromethane were used as supplied by Aldrich, the halocarbons being degassed by multiple freeze−thaw cycles with liquid nitrogen prior to use and then diluted separately at species-to-argon (S/Ar) ratios in the range 1:100 to 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).[4,9] The vacuum shroud surrounding the cold window can be aligned for infrared transmission studies, for gas deposition, and for sample photolysis. Spectra were recorded after each matrix irradiation or warming cycle in order to monitor changes caused by these processes.

The matrices were photolysed for varying periods of time with an Oriel xenon mercury lamp, a 5 cm water filter being placed between the lamp and sample to reduce the infrared output of the lamp. The matrices were photolysed with various bands of near-infrared, visible, and ultraviolet radiation by use of the following optical filters: 8 mm thick deep red ($\lambda > 650$ nm), 2 mm thick green ($\lambda > 410$ nm), Corning 7 mm blue/green ($550 > \lambda > 350$ nm), Pyrex ($\lambda > 290$ nm), and quartz (λ

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TABLE 1: The Infrared Bands/cm^{-1} of Chloroiodomethane, CH_2ClI, Trapped in a Variety of Matrices at 14 K

Ar	O_2	$^{16}O_3$/Ar	$^{18}O_3$/Ar	assignment
4448.1w	4434.6m	4435.6s	4464.0mw	$\nu_{a\,CH} + \delta_{CH_2}$
4171.3w	4165.1m	4162.3s	4168.9mw	$\nu_{a\,CH} + \omega_{CH_2}$
3727.2m		3846.3w	3857.9mw	$\nu_{s\,CH} + \rho_{CH_2}$
3068.1m	3059.4m	3059.2vs	3070.0m	$\nu_{a\,CH_2}$
2996.7w	2989.0m	2990.0m	3001.6mw	$\nu_{s\,CH_2}$
	2582.5w	2584.5w	2589.3w	$\delta_{CH_2} + \omega_{CH_2}$
2179.0w	2180.4w	2178.5w	2183.8w	$\delta_{CH_2} + \rho_{CH_2}$
1598.9m	1594.1w		1470.2w	$2\rho_{CH_2}$
1450.4w	1453.3w	1442.7w	1461.0w	$2\nu_{CCl}$
			1450.9w	
1398.8mw	1397.8m	1396.4s	1400.7mw	δ_{CH_2}
1384.8w	1386.7w	1385.3sh	1384.8w	$\omega_{CH_2} + \delta_{ClCI}$[a]
1374.2w	1372.8w		1356.4w	
1322.5w		1321.6m	1323.6mw	
1187.1s	1182.3s	1185.2vs	1186.7vs	ω_{CH_2}
1146.1mw	1146.6m	1145.7m	1141.3m	
1120.6mw	1118.7mw	1140.4m	1114.3w	
1103.7w		1114.3m	1104.7mw	
1065.6w	1049.7w	1066.1w	1061.8w	$2\nu_{CI}$
1050.7w				
942.7w	939.3m			$\nu_{CCl} + \delta_{ClCI}$
924.3w	922.9m	923.9wm	923.9mw	
918.1w	917.1m	918.1sh	919.0w	
808.6w	806.7m			ρ_{CH_2}
792.2m	790.3s	793.9vs	792.2s	
		744.0s		
733.6vs	733.6vs	731.7s	735.6vs	ν_{CCl}
		728.1m		
540.0mw	541.0w	543.4w	541.0w	ν_{CI}

[a] $\delta_{ClCI} \approx 200$ cm^{-1}.

> 240 nm). In this way the threshold wavelength of formation of each photoproduct was established.

Results

A. Chloroiodomethane and Ozone in Argon. The spectrum of chloroiodomethane was recorded in an argon and in an oxygen matrix (Table 1) and is consistent with the vapor phase spectrum[10] recorded previously. Codeposition of chloroiodomethane/argon (CH_2ClI/Ar = 1:600) and ozone/argon (O_3/Ar = 1:300) in matrices, and the subsequent photolysis and warming of these matrices, produced a variety of bands, which have been grouped below according to their photolytic and thermal behavior in the matrix.

$CH_2ClI\cdots O_3$ Complex. The bands formed on codeposition of chloroiodomethane and ozone in argon matrices resemble those assigned previously to isolated chloroiodomethane (Table 1) and ozone,[11] but with slight perturbations. The most obvious shifts occur to the bands assignable to the ozone moiety (Table 2), and in particular the ν_3 bands detected at 1035.7 and 1033.3 cm^{-1} for the complex, as compared to 1039.1 cm^{-1} for the isolated molecule. In the experiments involving $^{16}O_{3-x}{}^{18}O_x$, the bands (Table 2) arising from ν_1, ν_2, ν_3 and $\nu_1 + \nu_3$ each consist of six components. The latter arise from the six possible isotopomers 16−16−16, 16−18−18, 18−18−18, etc., which would be expected to be present if the ozone moiety were bound via the central oxygen atom. If the ozone moiety were bound via a terminal oxygen atom, then eight components would be expected. In these studies, varying the initial CH_2ClI/O_3/Ar ratios had no effect on the subsequent photochemical reactions, only on the relative intensities of the precursor bands. Near-infrared ($\lambda > 650$ nm) photolysis of argon matrices reduced the band intensities, producing new bands assigned below to the iodoso-species.

TABLE 2: Infrared Bands/cm^{-1} Assigned to Ozone after Deposition of Mixed Isotopomer Ozone, $^{16}O_{3-x}{}^{18}O_x$, and Chloroiodomethane in Argon at 14 K

ν_1	ν_2	ν_3	$\nu_1 + \nu_3$	assignment[b]
1105.2vw	704.0w	1039.1ms	2111.0w	16−16−16
		1035.7m	2108.1w	*c*
		1033.3m	2140.9sh	*c*
			2138.5w	
1090.2w	687.6w	1025.6s	2090.2w	16−16−18
		1019.8m	2087.3w	*c*
		1017.9m		*c*
	671.2vw	1016.4m	2059.9w	18−16−18
		1013.1mw	2057.0w	*c*
		1010.2mw		*c*
	696.3vw	1005.8m	2049.7w	16−18−16
		1002.4mw	2047.3vw	*c*
		1000.0mw		*c*
1061.3w	680.4w	991.4s	2027.1w	18−18−16
		a	2024.2w	*c*
		986.5br,m		*c*
1040.1	667.8 w	982.2m		18−18−18
		978.8mw		*c*
		976.4mw		*c*

[a] Obscured band. [b] Represents the isotopomer arrangement of ozone. [c] Complex bands.

TABLE 3: Infrared Bands/cm^{-1} Assigned to Iodosochloromethane, CH_2ClIO, Formed after Near-Infrared ($\lambda > 650$ nm) Photolysis of an Argon Matrix Containing Chloroiodomethane and Ozone

$^{16}O_3$/Ar	$^{16}O_{3-x}{}^{18}O_x$/Ar	$^{18}O_3$/Ar	assignment
2962.0m	2966.8w	2965.9m	ν_{CH}
	2960.1w	2959.1w	
1215.1m		1213.2mw	δ_{CH_2}
1211.2m			
1205.4m			
1202.6m			
1201.1m,sh			
1198.7sh,m			ω_{CH_2}
1195.3sh,m			
1157.7m	1156.7m	1157.2m	δ_{CH_2}
748.1m	755.1m	754.1ms	ν_{CCl}
723.5s	728.3m	690.0s	ν_{IO}
	690.5m		
542.9w		539.6w	ν_{CI}
532.8w			
528.9w			

Iodoso-Species. Bands due to iodoso-species are formed after near-infrared irradiation of argon matrices containing the codeposited precursors CH_2ClI and O_3. Shorter wavelength visible ($\lambda > 450$ nm) irradiation increased the band intensities by a further 10%, subsequent UV−vis ($\lambda > 350$ nm) photolysis reduced the band intensities by a further 10%, and Pyrex-filtered photolysis reduced them by yet a further 50%. Finally, quartz-filtered irradiation destroyed the bands completely. The bands detected (Table 3) for this group are assigned as follows. The medium band at 2962.0 cm^{-1} is assigned to a C−H stretch. A group of five medium intensity bands between 1215.1 and 1201.1 cm^{-1} are assigned to C−H bends. Two bands at 1198.7 and 1195.3 cm^{-1}, which appear as shoulders on the existing C−H bands, are assigned to CH_2 wags. A broadening of the precursor band at 793.9 cm^{-1} indicates some perturbation of the CH_2 rock. A medium band at 748.1 cm^{-1} is assigned to a new C−Cl vibration. The strong precursor band at 731.7 cm^{-1} broadens and shifts to 723.5 cm^{-1} (690.0 cm^{-1} for the ^{18}O isotopomer, i.e. the ^{18}O-shift is 33.5 cm^{-1}) and displays a photochemical behavior resembling that of bands reported elsewhere;[1−4] it is assigned to an I−O stretch (Figure 1). A further three bands were detected at 542.9, 532.8, and 528.9 cm^{-1} and are assigned to perturbed C−I vibrations. The bands detected in the $^{18}O_3$ and $^{16}O_{3-x}{}^{18}O_x$ experiments can be assigned to either ^{16}O or ^{18}O isotopomers, indicating the presence of only one oxygen atom in the species responsible for these bands.

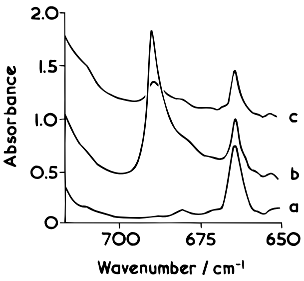


Figure 1. Infrared spectra in the region 700−650 cm^{-1} of an argon matrix containing chloroiodomethane and $^{18}O_3$ after (a) deposition, (b) near-infrared photolysis (λ > 650 nm), and (c) UV−vis photolysis (λ > 350 nm) showing the development of the I−^{18}O band of iodosochloromethane, $CH_2ClI^{18}O$, at 690.0 cm^{-1} in part b.

TABLE 4: Infrared Bands/cm^{-1} Attributed to Hypoiodochloromethane, CH_2ClOI, Formed after Visible Irradiation (λ > 450 nm)[a]

$^{16}O_3$/Ar	$^{16}O_{3-x}{}^{18}O_x$/Ar	$^{18}O_3$/Ar	assignment
1062.2m	1054.5w	1034.8m	ν_{CO}
579.6sh,w	578.6w	549.7w	ν_{OI}
576.7w	554.5w		

[a] δ_{CH_2} bands are too weak to be detected because of overlap from the CH_2ClIO bands.

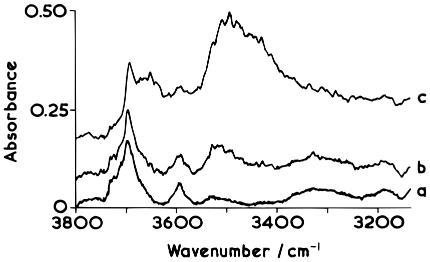


Figure 2. Infrared spectra of an argon matrix containing chloroiodomethane and $^{18}O_3$ after (a) deposition, (b) visible photolysis (λ > 450 nm), and (c) Pyrex-filtered photolysis (λ > 290 nm). The spectra show the band at ~3500 cm^{-1} attributed possibly to the ^{18}O−H stretch of hydrogen hypoiodide, HOI.

Hypoiodo-Species. Bands at 1062.2, 579.6, and 576.7 cm^{-1} attributable to hypoiodo-species are formed after visible (λ > 450 nm) irradiation, are increased in intensity by 20% after UV−vis photolysis, and are destroyed by Pyrex-filtered irradiation (Table 4). The medium band at 1062.2 cm^{-1} with an ^{18}O-shift of 27.4 cm^{-1} (the predicted shift for C−O is 28 cm^{-1}) is assigned to the C−O vibration. Some confusion surrounds this assignment, due to the presence of an additional band at 1054.5 cm^{-1} detected in the mixed-ozone experiment and also assigned to a C−O stretch. The band at 576.7 cm^{-1} exhibited an ^{18}O-shift of 27.0 cm^{-1} (the predicted O−I diatomic shift is 29 cm^{-1}) and is assigned to an O−I stretch, as is the weak shoulder band at 579.6 cm^{-1}. In the mixed-ozone experiments the two bands detected at 578.6 and 554.5 cm^{-1} were assigned to O−I stretches of the ^{16}O- and ^{18}O-isotopomers, respectively (^{18}O-shift of 24.1 cm^{-1}). Detection of bands attributable to O−I and C−O stretches in this group suggests the presence of a C−O−I unit. Bands assigned to C−H bends were too weak to be detected in the presence of overlapping bands arising from iodoso-species. After considerable photolysis (~20 h) a weak band around 3500 cm^{-1} was detected in the $^{18}O_3$ experiment and has been tentatively assigned to an O−H stretch of $H^{18}OI$ (Figure 2).

TABLE 5: Infrared Bands/cm^{-1} Attributed to Several Formyl Chloride Complexes, HC(O)Cl···HI [···HCl][a]

O_2	$^{16}O_3$/Ar	$^{16}O_{3-x}{}^{18}O_x$/Ar	$^{18}O_3$/Ar	assignment
2985.2mw	2987.6s	2967.3w		ν_{CH}
		2959.6w		
		2945.0w		
1773.0m	1778.3s	1778.3m		$\nu_{C=O}$
	1769w	1770.6w		
	1762.8s	1761.9s		
		1738.7m	1739.2s	
		1730vw	1728.3w[b]	
		1720.9s	1721.4vs	
1747.9s	1756.6w		1710.8sh	$\nu_{C=O}$[a]
	1748.9w			
			1686.2m	
		1311.0w	1311.0w	δ_{CH}
1307.2w	1306.2w	1308.6w		
	1244.5w	1242.1w		δ_{CH}
			1142.3m	
			951.3w	ν_{o-o-p}
			935.9w	
792.2s	794.4vs		799.0m	δ_{CClO}
	770.0mw			
	748.1m	749.3s	748.8s	ν_{CCl}

[a] HC(O)Cl···HCl. [b] Band wavenumber deduced following deconvolution of the very strong band at 1721.4 cm^{-1}.

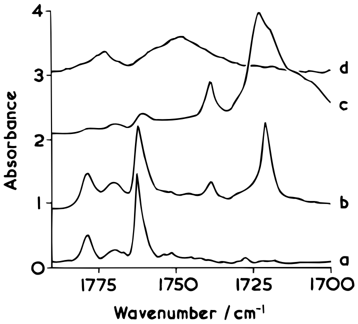


Figure 3. Infrared spectra recorded after Pyrex-filtered photolysis (λ > 290 nm) of chloroiodomethane in the following matrices: (a) $^{16}O_3$/Ar, (b) $^{16}O_{3-x}{}^{18}O_x$/Ar, (c) $^{18}O_3$/Ar, and (d) a solid oxygen matrix. The spectra show the bands attributed to the carbonyl stretches of the ^{16}O- and ^{18}O-isotopomers of the formyl chloride···HI complexes.

Formyl Chloride. Bands attributable to formyl chloride are formed after visible photolysis and doubled in intensity after UV−vis photolysis, while subsequent Pyrex- and quartz-filtered irradiation increased the intensities of the bands by a further 100% and 40%, respectively. The band at 2987.6 cm^{-1} (Table 5) is assigned to a C−H stretch. The strong bands at 1778.3 and 1762.8 cm^{-1} and the weak band at 1769 cm^{-1} (^{18}O-isotopomer bands at 1739.2 and 1721.4 cm^{-1}) are assigned to the carbonyl stretch (Figure 3). These bands exhibit ^{18}O-shifts of between 39.1 and 42 cm^{-1}, confirming their assignment to C═O stretches. In the mixed-ozone experiment, bands were detected at 1778.3, 1770.6, 1761.9, 1738.7, 1730, and 1720.9 cm^{-1}, these being assigned to either ^{16}O- or ^{18}O-isotopomers, confirming that only one oxygen atom is involved. Heating the matrix to 25 K for 20 min reduced slightly the intensities of the bands at 1778.3 and 1762.8 cm^{-1}, while that of the band at 1769 cm^{-1} increased.

The weak band at 1306.2 cm^{-1} is assigned to a C−H bend, and those at 951.3 and 935.9 cm^{-1} for the ^{18}O-isotopomer are assigned to the out-of-plane vibration. The medium band at 748.1 cm^{-1} is assigned to the C−Cl stretch, though no evidence for the ^{37}Cl band could be found. In one set of experiments, weak bands were detected at 1756.6 and 1748.9 cm^{-1} (^{18}O at 1710.8 cm^{-1}), and these have been assigned to an additional carbonyl stretch, most likely from a different complex from that described above.

Carbon Monoxide. Weak bands attributable to carbon monoxide complexes are formed after visible irradiation (Table 6, Figure 4), and these intensified steadily by 10−20% with each successive photolysis (λ > 350, 290, and 240 nm) cycle.

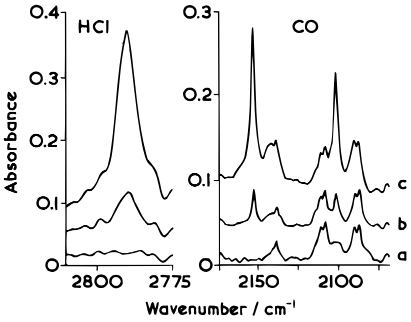


Figure 4. Infrared spectra of argon matrices containing CH_2ClI and $^{16}O_{3-x}{}^{18}O_x$ after (a) deposition, (b) visible photolysis (λ > 410 nm), and (c) Pyrex-filtered photolysis. The spectra show the ν_{HCl} (2800−2775 cm^{-1}) and ν_{CO} regions (2175−2075 cm^{-1}) of the complex OC···HCl···HI.

TABLE 6: Infrared Bands/cm^{-1} Assigned to the Carbon Monoxide Complex OC···HCl···HI

O_2	$^{16}O_3$/Ar	$^{16}O_{3-x}{}^{18}O_x$/Ar	$^{18}O_3$/Ar	assignment
	2787.5m	2789.9m	2790.4m	ν_{HCl}
2142.8mw	2151.5m	2152.4m	2100.8m	ν_{CO}
	2141.4m	2101.3m	2087.3m	

This group consisted of a medium band at 2787.5 cm^{-1} assigned to a HCl stretch (with the ^{18}O counterpart at 2790.4 cm^{-1}) and two other medium bands at 2151.5 and 2141.4 cm^{-1}, having ^{18}O-shifts of 50.3 and 54.1 cm^{-1}, respectively, assigned to C−O stretches of carbon monoxide (isolated CO in an argon matrix absorbs at 2138.4 cm^{-1}).[12]

B. Bromochloromethane and Ozone in Argon. The spectra of CH_2BrCl in argon ($CH_2BrCl/Ar = 1:500$) and solid oxygen ($CH_2BrCl/O_2 = 1:200$) matrices are in good agreement (Table 7) with that reported for the liquid phase.[13] Ultraviolet (λ > 240 nm) photolysis of CH_2BrCl in an argon matrix produced no new bands.

The spectra recorded after codeposition of bromochloromethane and ozone in argon matrices ($CH_2BrCl/O_3/Ar = 1:3:600$) exhibited bands that could be assigned to either precursor (Table 7). Thus, unlike the situation with iodomethane[2] and chloroiodomethane (above) and the other single-iodine-containing precursors,[1,3,4] no initial complex was formed on deposition. UV−vis (λ > 350 nm) photolysis of these matrices for 40 min produced no detectable bands, while Pyrex-filtered photolysis, for similar periods, produced only weak bands. Quartz-filtered photolysis, for ~40 min, doubled the intensities of the bands, in part due to the higher photon throughput of the quartz-filtered than the Pyrex-filtered arrangement). Various matrix experiments were performed in order to increase the intensities of the product bands; the first, varying the deposition ratio $CH_2BrCl/O_3/Ar$, made no difference to the photochemistry, only to the intensities of the precursor bands, due simply to the reduced or increased concentrations of precursors. The most diagnostic experiments concerned photolysis at fixed wavelengths, for varying time intervals; the evolution of the products with time has been studied in order to elucidate the mechanism. The bands listed in Tables 8 and 9 were detected after quartz-filtered photolysis. For clarity they are grouped according to the product species to which they can be attributed, i.e. HC(O)Cl, HC(O)Br, COBrCl, HBr, HCl, or CO.

TABLE 7: Infrared Bands/cm^{-1} Assigned to Bromochloromethane, CH_2BrCl, Deposited in an Oxygen Matrix and in an Ozone/Argon Matrix at 14 K

O_2	O_3/Ar	assignment
3067.0w	3077.7w	$\nu_{a\ CH_2}$
3061.4w	3040.6vw	
	3006.4w	$\nu_{s\ CH_2}$
2998.1w	2997.7w	
	1465.8w	$\delta_{HCCl} + \nu_6$[a]
1420.1mw	1457.1w	
1415.7mw	1415.2w	δ_{CH_2}
1411.4mw		
1381.8mw	1371.9w	$\delta_{t\ CH_2} + \nu_6$
1368.3mw		
1346.9mw	1346.7w	
1338.3mw	1321.2w	
1330.0mw	1307.7w	
1319.9w		
1230vs	1230.9s	δ_{HCCl}
	1229.0s	
	1197.5w	$2\nu_{CBr}$
	1130.7w	$\delta_{t\ CH_2}$
	1125.3w	
	1076.3w	$\nu_6 + \rho_{CH_2}$
	1070.0w	
1051.0w	1059.6w	
	903.6w	$\nu_{CCl} + \nu_{CBr}$
	896.9w	
	889.6w	
854.4w	856.8sh	ρ_{CH_2}
853.0m	849.1m	
738vs	745.0s	ν_{CCl}
	740.0s	
	738vs	
	732.5s	
613.5s	658.2w	ν_{CBr}
	612vs	

[a] The band assigned to the ν_6 mode of CH_2BrCl absorbs at ~240 cm^{-1}.

TABLE 8: Infrared Bands/cm^{-1} Attributed to the Carbonyl Products of the Photochemical Reaction (λ > 240 nm) of CH_2BrCl with Ozone in Argon at 14 K

complex	$\nu_{C=O}$	δ_{CH}	ν_{o-o-p}	ν_{CCl}	ν_{CBr}
HC(O)Cl···HBr	1761.8w	1315.8w	962.9w	756.0mw	
	1756.6s	1313.6vw	941.2w	745.1s	
	1748.9w	1302.8vw[a]		742.4s	
HC(O)Cl···Ar	1781.5vw				
HC(O)Br···HCl	1753.0m,sh	1287.4w	867.4vw		685.2vw
		1283.3w			681.8vw
		1279.7w			
		1272.6w			
HC(O)Br···Ar	1801.5w				
COBrCl	1817.3vw			817.3w	
				809.1w	
				805.2mw	
				800.0w	
				797.5mw	
combinations					
$2\nu_6$ HC(O)Br			1775.7vw		
			1190.0w		
$\nu_{CCl} + \nu_5$ HC(O)Cl			1153.9w		
			1117.9w		
$\nu_{CBr} + \nu_5$ HC(O)Br			1090.2w		
			1067.0w		

[a] Obscured by a precursor band.

Formyl Chloride. Bands due to formyl chloride are formed after photolysis with Pyrex- and quartz-filtered radiation (Table 8, Figure 5). They increased in intensity as the photolysis times increased up to ~50 h, at which point they began to decrease (Figure 6). This group of bands, attributed to a formyl chloride species, is assigned as follows: the bands at 1761.8, 1756.6, and 1748.9 cm^{-1} are assigned to carbonyl stretches. Weak bands at 1315.8 and 1313.6 cm^{-1} are assigned to CH_2 bends, while weak bands at 962.9 and 941.2 cm^{-1} are assigned to out-of-plane vibrations. A medium-weak band at 756.0 cm^{-1} and strong bands at 745.1 and 742.4 cm^{-1} (possibly attributable to ^{37}Cl components) are assigned to C−Cl stretches. Additional, weak combination bands were detected at 1190.0, 1153.9, and 1117.9 cm^{-1}. Detection of this first group of bands suggests that the carbonyl responsible is formyl chloride, HC(O)Cl.

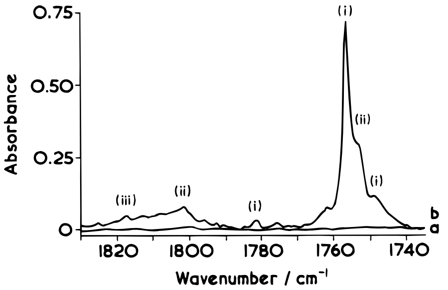


Figure 5. Infrared spectrum in the $\nu_{C=O}$ region of an argon matrix containing CH_2BrCl and ozone after (a) deposition and (b) photolysis with UV ($\lambda > 240$ nm) radiation for 71 h, showing bands assigned to (i) HC(O)Cl, (ii) HC(O)Br, and (iii) COBrCl.

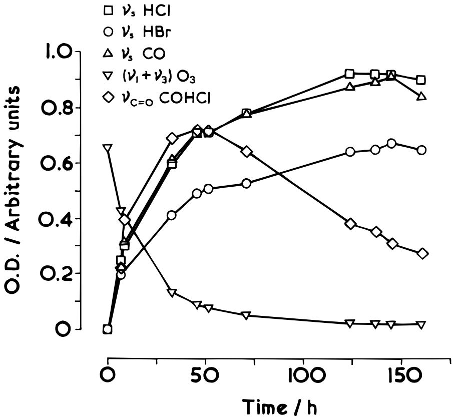


Figure 6. Plot of optical density *versus* time showing the destruction of the ozone ($\nu_1 + \nu_3$) band, the formation and destruction of the carbonyl band of HC(O)Cl, and the growth of the ν_{HCl}, ν_{HBr}, and ν_{CO} bands.

TABLE 9: Infrared Bands/cm^{-1} Assigned to HCl, HBr, and CO in Several Complexes, Detected after Photolysis ($\lambda > 240$ nm) of Ozone and Bromochloromethane in Argon Matrices at 14 K

complex	ν_{HCl}	ν_{HBr}	ν_{CO}
HCl···CO	2828.5vw		
OC···HBr···HCl	2812.5w	2492.0w 2479.0w	2149.0w
OC···HCl···HBr	2783.6s	2507.3s	2154.9s
HCl···CO···HBr		2500.6m	2156.7m
$(CO)_2HX$			2142.5vw
CO			2138.1w

Formyl Bromide. Formyl bromide bands behave almost identically to the formyl chloride bands after photolysis for varying periods of time (Figure 6), except for their weakness under similar photolytic conditions. The weak and medium bands detected at 1801.5 and 1753.0 cm^{-1}, respectively, are assigned to carbonyl stretches (Table 8, Figure 5). Weak bands at 1287.4, 1283.3, 1279.7, and 1272.6 cm^{-1} are assigned to CH_2 bends. A very weak band at 867.4 cm^{-1} is assigned to the out-of-plane vibration, and the very weak bands at 685.2 and 681.8 cm^{-1} to C−Br stretches. A very weak overtone band at 1775.7 cm^{-1} and combination bands at 1090.2 and 1067.0 cm^{-1} are also detected.

Carbonyl Bromide Chloride. Bands attributable to carbonyl bromide chloride (Table 8) behave, after photolysis, in a manner similar to those of formyl chloride and formyl bromide referred to above. A weak band at 1817.3 cm^{-1} is assigned to a carbonyl stretch, while weak to medium-weak bands at 817.3, 809.1, 805.2, 800.0, and 797.5 cm^{-1} are assigned to C−Cl stretches; the number of such bands detected suggests that other species or distinct environments may also be present.

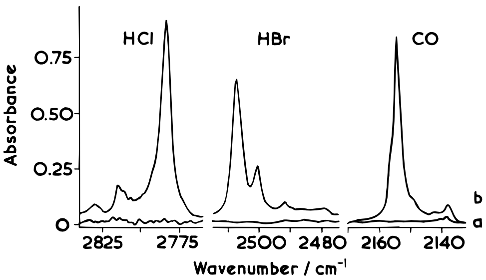


Figure 7. Infrared spectrum of an argon matrix containing CH_2BrCl and ozone after (a) deposition and (b) quartz-filtered ($\lambda > 240$ nm) photolysis for 160 h, showing bands in the ν_{HCl} (2850−2750 cm^{-1}), ν_{HBr} (2510−2480 cm^{-1}), and ν_{CO} (2170−2140 cm^{-1}) regions attributed to the various carbon monoxide complexes.

HBr and HCl. Bands attributable to HBr and HCl are formed after UV irradiation (Table 9, Figure 7). The strong and medium HBr bands at 2507.3 and 2500.6 cm^{-1}, respectively, and the weak bands at 2492.0 and 2479.0 cm^{-1} suggest that hydrogen bromide is present in a number of environments and hence in different complexes (HBr isolated in argon absorbs at 2560 cm^{-1}).[14] Similarly the strong, weak, and very weak bands at 2783.6, 2812.5, and 2828.5 cm^{-1}, respectively, in the ν_{HCl} region indicate that various HCl complexes are formed.

Carbon Monoxide. Like the HCl and HBr bands, bands attributable to CO (Table 9 and Figure 7) are formed after UV photolysis, and these increase in intensity after successive irradiation cycles (Figure 6). The spectra of these CO complexes gave rise to a strong band at 2154.9 cm^{-1} and weak bands at 2149.0, 2142.5, and 2138.1 cm^{-1}. The last has been assigned to isolated CO in an argon matrix,[12] the others to $(CO)_x(HCl)_y(HBr)_z$ complexes. Warming of the matrix to 25 K appeared to have no effect on any of these bands, indicating that the complexes are formed in a thermally stable environment. This result supports the assumption, made later, that the two OC···(HCl)(HBr) complexes are strongly hydrogen-bonded.

Discussion

The various bands reported above are grouped below according to the chemical species to which they refer and their photolytic and thermal behavior.

Precursor···Ozone Complex. These bands are detected after codeposition of CH_2ClI and O_3 in argon matrices and resemble the bands detected for the isolated precursors (Tables 1 and 2), except for small perturbations which are most apparent for those attributed to ozone. In the mixed isotopomer experiments, six sets of bands were assigned for each of the fundamental modes (only four for the weak ν_1 mode). These bands indicate that ozone has retained its symmetry, i.e. is symmetric about the central O atom, and therefore that any bonding must occur to this atom. This spectral evidence, combined with the effective photodissociation after near-infrared photolysis producing the iodoso-species bands, confirms the assignment to modes of a weak ozone···chloroiodomethane complex, which is believed to be very similar to those reported elsewhere;[1−4,15] production of bands due to iodoso-species occurs via a light-induced charge-transfer mechanism, in which an oxygen atom is transferred from ozone to the iodine atom of chloroiodomethane.

The bands detected directly after codeposition of the precursors, CH_2BrCl and ozone,[11] are assigned (Table 7) to modes of the precursors. Ultraviolet irradiation for tens of hours was required before any product bands were detected; this behavior differs markedly from that of ozone with the mono-iodinated precursors in which a complex with ozone is formed after deposition, and products are detected after ∼10−20 min of near-infrared photolysis. Thus the presence of an iodine atom in a halocarbon dramatically changes the photochemistry of ozone.

Iodoso-Species. These bands, formed after near-infrared ($\lambda > 650$ nm) irradiation of matrices containing CH_2ClI and O_3, and destroyed by Pyrex-filtered irradiation, are assigned to perturbed C−H stretches and bends, a C−Cl stretch, C−I stretches and, most diagnostically, an I−O stretch. The species accounting for these bands is iodosochloromethane, CH_2Cl-IO. Several similar iodoso-species have been reported (ClIO,[1] CH_3IO,[2] CF_3IO,[3] C_2H_5IO,[4] and HIO[16]) to have this Z−IO structure.

Hypoiodo-Species. The hypoiodo-species bands were formed, after UV−vis ($\lambda > 350$ nm) photolysis of CH_2ClI and O_3 in argon matrices, at the expense of the iodoso-species bands, thus indicating a connection between the two. The bands detected (Table 4) are assigned to C−O and O−I stretches. On this basis a COI unit must be present, and hence the species must be hypoiodochloromethane, CH_2Cl-OI. Several other hypoiodo-species (Z−OI) have been detected previously, and this interconversion between the iodoso- and hypoiodo-species has been studied using semiempirical calculations, MOPAC[17] (see the Photochemical Interconversion section). Of prime interest here is the presence of hydrogen hypoiodide and to a lesser extent chlorine hypoiodide, ClOI, which was not detected. Interestingly, the lack of any strong HOI bands detected in this experiment matches the results reported for the reaction of ozone with iodomethane in argon matrices[2] and in the gas phase,[18] lending extra weight to the interconversion between the iodoso- and hypoiodo-species proposed below. Other workers[19,20] using O_2 as the oxygen atom source have, however, reported the formation of HOI in the reactions with iodomethane. This can be accounted for by the shorter wavelength ($\lambda < 280$ nm) photolysis and increased photolysis times (1−2 h) required to produce O atoms in sufficient quantity from oxygen, which may cause iodomethane to photodissociate into CH_2 and HI; the hydrogen iodide then reacts with oxygen atoms to produce HOI.[16] This method of producing HOI is the assumed route by which the weak ν_{OH} bands (Figure 2) were formed in the $^{18}O_3$ experiment.

Carbonyl Complexes. Bands attributable to several carbonyl···Lewis acid complexes were detected after Pyrex- and quartz-filtered irradiation of argon matrices containing either CH_2ClI/O_3 or CH_2BrCl/O_3. In all cases the carbonyl stretching bands are the most diagnostic. The various carbonyl···Lewis acid complexes are discussed below.

(i) HC(O)Cl···HX (where X = Br or I). The most diagnostic bands for these two complexes occur in the carbonyl stretching region. The $\nu_{C=O}$ bands for the HC(O)Cl···HI complex (Table 5 and Figure 3) were detected after photolysis of CH_2ClI and ozone in argon matrices, while those for the HC(O)Cl···HBr complex (Table 8 and Figure 5) were detected after photolysis of CH_2BrCl and O_3 in argon. In the latter case detection of bands assignable to HBr supports the formation of a HC(O)Cl···HBr complex, but in the former case no bands assignable to HI were detected. This is not unusual given the low infrared absorption of hydrogen iodide.

The wavenumbers of the $\nu_{C=O}$ bands of these formyl chloride···Lewis acid complexes can be compared (Table 10): HC(O)Cl···HCl[7] (1756.7, 1754.6, and 1751.3 cm^{-1}), ···HBr (1761.8 and 1756.6 cm^{-1}), and ···HI (1778.3, 1769, and 1762.8 cm^{-1}). The shift in wavenumber of the carbonyl band from its value for the uncomplexed carbonyl (isolated HC(O)Cl in argon absorbs at 1783.5 cm^{-1})[8] increases with the Lewis acid strength; thus the HC(O)Cl···HCl complex exhibits the most highly perturbed carbonyl bands.

TABLE 10: Infrared Bands/cm^{-1} Assigned to the Formyl Chloride Moiety in Several Complexes

complex[a]	ν_{CH}	$\nu_{C=O}$	δ_{CH}	ν_{CCl}	δ_{CCl}	ν_{o-o-p}
HC(O)Cl[26]	2933.5	1783.5	1307.0	738.6	458.0	932.3
···Cl_2[8]		1780.6				
···Br_2[29]		1779.7	1307.9			
		1768.1	1302.8			
			1298.5			
···HI	2987.6	1778.3	1306.2			935.9
		1769				
		1762.8				
···HBr		1761.8	1315.8	766−740.3		941.2
		1756.6	1313.6			
			1302.8			
···HCl[7]	2960.5	1756.7		753		
		1754.6				
		1751.3				

[a] The complexes are listed in order of increasing perturbation; that is, the HC(O)Cl···HCl complex is the most perturbed.

Carbonyl bands were also detected that could be attributed to other formyl chloride complexes (Tables 5 and 8), in particular those detected near 1748.9 cm^{-1} after photolysis of both CH_2ClI/O_3 and CH_2BrCl/O_3. They can be attributed to the carbonyl in a more highly perturbing environment, such as with two hydracids, the second hydracid coming from a second carbonyl complex, or with another complex in a neighboring matrix site.

(ii) HC(O)Br···HCl. Bands attributable to this species were detected after photolysis of ozone and bromochloromethane and were formed in much lower intensities than those attributed to the formyl chloride complexes. Again the most diagnostic bands (Table 8 and Figure 5) are those assigned to the carbonyl stretch, in particular the medium band at 1753.0 cm^{-1} assigned to the complex HC(O)Br···HCl. For comparison, the $\nu_{C=O}$ bands of the complex HC(O)Br···HBr occur at 1756.3 and 1754.9 cm^{-1}.[7]

(iii) COBrCl. Bands attributable to this complex (Table 8) were formed after photolysis of ozone and CH_2BrCl and detected at 1817.3 cm^{-1} and between 817.3 and 797.5 cm^{-1}; *cf.* the closely similar values found for bromide chloride, COBrCl, in the gas phase.[21] The bands are significantly weaker than those of either formyl chloride or formyl bromide. Assuming that the carbonyl stretch of each of these three compounds has a similar infrared absorption coefficient, then formyl chloride can be assumed to be present in the greatest quantity. This result parallels that obtained for the gas phase reaction of bromochloromethane and ozone,[22] in which >70% of the product was formyl chloride.

We can also compare the range of products detected here with those detected in the reactions of dichloro- and dibromomethane[7] with ozone; in all cases the dissociation of HX and the formation of formyl halide is the favored product. However, with dibromomethane, methanal was reported as a minor product, whereas in the current studies none was detected; instead, using CH_2BrCl as a precursor, evidence for carbonyl bromide chloride was obtained.

Carbon Monoxide Complexes. The following bands attributed to several carbon monoxide···Lewis acid complexes appeared to increase in intensity while those of the carbonyl complexes discussed above decreased, providing support for a mechanism in which the carbonyl···Lewis acid complex was photodissociated and formed the carbon monoxide complex.

(i) OC···HCl···HI. The bands for this group—detected after photolysis of matrices containing CH_2ClI and O_3—are assigned to stretches of CO and HCl (Table 6, Figure 4), suggesting that a complex of the form $(OC)_n(HX)_m$ is present. In previous

studies[23] it has been suggested that it is possible to distinguish between the ν_{HCl} bands in the complex $OC\cdots H{-}Cl^{a}\cdots H{-}Cl^{b}$, the HCl in the *a* position absorbing between 2791.3 and 2780.5 cm^{-1}, and in the *b* position between 2811.2 and 2803.0 cm^{-1}. Thus in this experiment the ν_{HCl} band at 2787.5 cm^{-1} can be assigned to HCl in the *a* position of the complex. Similarly the wavenumber of the ν_{CO} band of this carbon monoxide complex can be compared with that of other carbon monoxide···hydrogen halide complexes, i.e. OC···HI (2152, 2147.5, and 2137.5 cm^{-1}),[24] $OC\cdots(HCl)_2$ (2156.7 and 2155.6 cm^{-1}),[7] $OC\cdots(HBr)_2$ (2153.1 cm^{-1}),[7] and OC···HCl (2151 cm^{-1}).[24] The band detected at 2151.5 cm^{-1} in this study seems to relate to CO perturbed by either HCl or HI. Although no HI bands were detected, examination of the mechanism and stoichiometry of the reaction suggests that these bands can best be attributed to the complex OC···HCl···HI. This assignment is supported further by the detection, discussed below, of an OC···HCl···HBr complex in which the ν_{HCl} and ν_{CO} bands are even more perturbed than for OC···HCl···HI, due to the greater hydrogen bond strength of HBr relative to HI.

(ii) OC···HCl···HBr. Bands attributed to CO, HCl, and HBr were detected after photolysis of matrices containing CH_2BrCl and ozone and are attributed to either the complex OC···HCl···HBr or OC···HBr···HCl (Table 9 and Figure 7). As noted above, the position—either *a* or *b*—of the HCl moiety in the complex $OC\cdots(HCl)^{a}\cdots(HCl)^{b}$ can be determined by its wavenumber. For the complex $OC\cdots(HBr)_2$,[7,25] a similar behavior has been noted, with HBr bands in the *a* position absorbing at ∼2484.8 cm^{-1} and in the *b* position at ∼2509.7 cm^{-1}. Thus the strong bands detected at 2783.6 and 2507.3 cm^{-1} in this study are attributed to HCl in the *a* position and HBr in the *b* position, respectively, of the complex OC···HCl···HBr. The band attributed to CO (2154.9 cm^{-1}) in this complex has, as would be expected, a wavenumber intermediate between that of the CO band in the complexes[7] $OC\cdots(HCl)_2$ and $OC\cdots(HBr)_2$ at 2156 and 2153 cm^{-1}, respectively. For comparison, the wavenumbers of the HCl bands in the *a* position of the following complexes can be noted, OC···HCl···HCl[7,14,23–26] (2781.1 cm^{-1}),[7] OC···HCl···HBr (2783.6 cm^{-1}), and OC···HCl···HI (2787.5 cm^{-1}); again the trend is observed that the wavenumber of HCl in the *a* position is more perturbed from its value when isolated in argon (2869 cm^{-1})[14] when the stronger Lewis acid is in the *b* position; similarly, the band due to HBr in the *b* position of OC···HCl···HBr is 2.4 cm^{-1} lower than that in $OC\cdots(HBr)_2$, due to the greater perturbation by a central HCl as compared to a central HBr.

(iii) OC···HBr···HCl. A second group of weak bands at 2812.5, 2479.0, and 2149.0 cm^{-1} is attributed to HCl in the *b* position, HBr in the *a* position, and CO, respectively, and hence to the complex OC···HBr···HCl. The relative wavenumbers of the HCl and HBr bands are consistent with the discussion in the previous section.

(iv) Other Carbon Monoxide Complexes. The remaining HCl, HBr, and CO bands are assigned (Tables 6 and 9) by analogy with previous results.[24] Interestingly, the medium intensity HBr band at 2500.6 cm^{-1} would be expected to belong to either of the $OC\cdots HX^{a}\cdots HX^{b}$ complexes involving HCl and HBr in either *a* or *b* positions; however the wavenumber is intermediate between the two, and comparison of the relative intensities suggests that the bands arise from a third complex having a different geometric arrangement, i.e. HBr···CO···HCl.

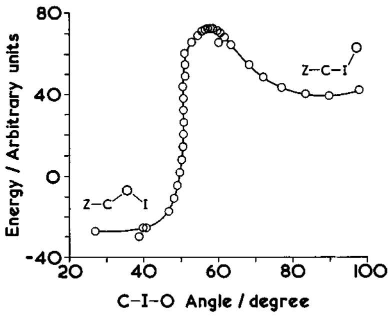
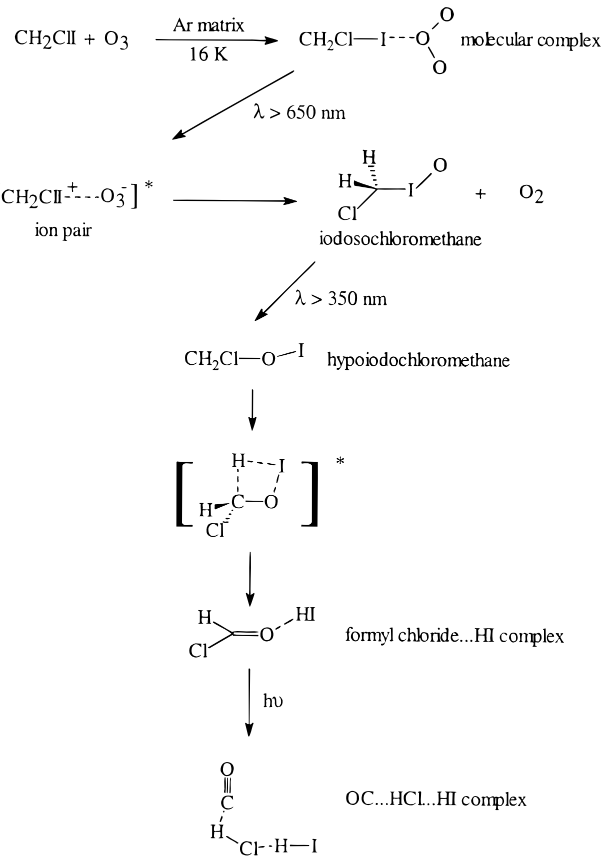


Figure 8. Plot of energy *versus* C−I−O angle calculated using MOPAC.[17] The plot shows the energy path between the two species iodosochloromethane (C−I−O angle ∼99°) and hypoiodochloromethane (C−I−O angle ∼28°) via a simple change in the position of the IO unit relative to the rest of the molecule.

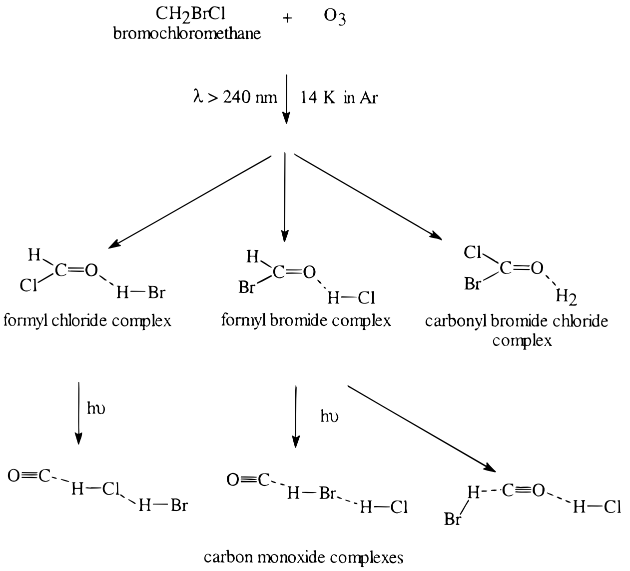
SCHEME 1



Photochemical Interconversion

CH_2ClI with O_3. The first step in the photochemical interconversion (see Scheme 1) is the formation of a weak complex between ozone and chloroiodomethane after codeposition of chloroiodomethane and ozone in argon. Photolysis of the matrix with near-infrared radiation ($\lambda > 650$ nm) causes the transfer of an oxygen atom from ozone to chloroiodomethane via a charge-transfer type intermediate to produce iodosochloromethane, $CH_2Cl{-}IO$. Visible ($\lambda > 350$ nm) photolysis causes a conversion of the iodoso-species into hypoiodochloromethane, $CH_2Cl{-}OI$. On shorter wavelength irradiation, the hypoiodo-bands increase in intensity at the expense of iodoso-bands, thus demonstrating a link between iodosochloromethane and hypoiodochloromethane. The interconversion between the iodoso-(XC−IO) and hypoiodo-species (XC−OI) has been the subject of semiempirical calculations. Using MOPAC[17] the change in the C−I−O angle between the two species was shown to range from 99° for the iodoso-species to 28° for the hypoiodo-species, revealing an energy barrier (Figure 8). This transition between the two can be viewed as a consequence of reduction of the C−I−O angle until a new C−O bond is formed and then rupture

SCHEME 2



of the existing C−I bond to form XC−OI. This proposed transformation from XC−IO to XC−OI is corroborated by a calculated increase of the C−I bond length from 2.12 to 2.82 Å and decrease of the C−O bond length from 3.09 to 1.40 Å. An alternative mechanism involving radicals has been proposed[2] for the conversion of CH_3IO to CH_3OI, in which the former dissociates into the radicals $CH_3^\bullet$ and $IO^\bullet$, with subsequent rotation of $IO^\bullet$ and recombination producing the hypoiodo-species, CH_3OI. At this stage no evidence is available to distinguish between the two.

Further Pyrex-filtered photolysis destroyed the bands attributed to the hypoiodo-species and produced the formyl chloride complexes. Since the C−O bond is already in place in the hypoiodo-species, the mechanism to form the carbonyl simply involves the rupture of the O−I bond and the formation of a new H−I bond to form the complex HC(O)Cl···HI. This same photolysis wavelength and the subsequent shorter UV irradiation led to the production of the carbon monoxide complex OC···HCl···HI.

CH_2BrCl with O_3. Unlike the reaction between ozone and CH_2ClI, which is wavelength-dependent, that between ozone and CH_2BrCl is time-dependent (Figure 6 and Scheme 2). Thus, for photolysis times of 0−50 h, carbonyl complexes are formed, but the latter decay to form the carbon monoxide complexes on longer photolysis (50−150 h). There was no evidence for the formation of species having C−Br−O or C−O−Br bonds. There are several possible reactions that could lead to the observed products in this study, the most likely of which involve the insertion of O atoms (from ozone or oxygen) into one of the C−H, C−Cl, or C−Br bonds. It would seem likely that an O atom would insert into the C−Br bond in preference to the C−Cl bond on bond energy grounds; but no distinction can be made between any of these possibilities, except that insertion into the C−H bond would produce HC(O)Cl, HC(O)Br, and COBrCl, as detected, whereas insertion into the C−Br bond would produce HC(O)Cl and H_2CO, and insertion into the C−Cl bond would produce HC(O)Br and H_2CO.

Alternatively, photodissociation of a C−halogen bond (probably Br) of CH_2BrCl may occur, to give CH_2Cl and Br atoms, with the former reacting with oxygen atoms to form formyl chloride. This mechanism may account for the very weak and weak bands at 826.5 and 817.3 cm^{-1}, respectively, which although assigned to ν_{CCl} of COBrCl (Table 8) could possibly be attributed to CH_2Cl.[27] However, the lack of detection of bands assignable to BrO[28] makes this mechanism seem unlikely. Previously, an unidentified band at 817 cm^{-1} was detected in the photochemical reaction of ozone with $CHCl_3$[8] and $CHBr_2Cl$,[29] and this may be attributed to the radical CHCl.[27] However, due to the low intensity, any reaction producing this band must be minor. A final possibility is that an oxygen atom could add directly to the carbon atom of CH_2BrCl to form a five-centered intermediate, which could subsequently rearrange to form a variety of products. This possibility has not been considered in any great detail due to the broad range of previous studies in which insertion into the C−X bond (X = H or halogen) seems to be the prevalent mechanism.

Previous *ab initio* calculations carried out for the reaction of CH_2Cl_2/CH_2Br_2[7] with oxygen atoms predicted that the carbonyl product HC(O)X···HX would be favored over the products COX_2···H_2 and COH_2···X_2. This calculation fits our experimental results in that the overwhelming product is HC(O)Cl···HBr, with low concentrations of HC(O)Br···HCl and COBrCl···H_2 being formed but no methanal. Interestingly, for the reaction of dibromomethane[7] and diiodomethane[5] with O atoms, methanal is formed as an additional product, whereas in the cases of CH_2I_2 and CH_2ClI, formyl iodide was not detected directly. Thus there is some measure of disagreement with theoretical work. Further calculations, e.g. on CH_2BrCl, CH_2ClI and CH_2I_2, might yield interesting results.

After long periods of photolysis another type of product is formed, which has been attributed to carbon monoxide···hydracid complexes, formed after dissociation of the formyl halide complexes. The detection of the carbon monoxide complexes confirms that the carbonyl complexes dissociate via elimination of molecular CO and HX.

Conclusions

The reactions of ozone with chloroiodomethane and bromochloromethane have produced several novel carbonyl and carbon monoxide complexes of the form HC(O)X···HY and OC···HY···HX. Chloroiodomethane also produced some iodoso- and hypoiodo-species. Interestingly the final carbonyl and carbon monoxide Lewis acid complexes produced were very similar, despite initial differences in the reaction pathway (i.e. formation of −IO bonds).

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