

Short Communication

Atmospheric photochemistry of CF₂ClBr*

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1. Introduction

The tropospheric release of brominated organic compounds results in the formation of bromine atoms in the stratosphere. Bromine atoms, analogous to chlorine atoms, effectively destroy ozone principally through the BrO_x catalytic cycle of reactions (1) and (2) [1 - 3]:



Unlike chlorine atoms, bromine atoms do not react with hydrogen or methane to produce HBr because these reactions are highly endothermic. Bromine atoms are converted to HBr by reaction with the trace stratospheric species HO₂ and to a lesser extent with H₂O₂. Photolysis of HBr and reaction with hydroxyl radicals (reaction (3)) regenerates the bromine atoms back into the catalytic chain:



Removal of bromine atoms and BrO by reactions with stratospheric NO and NO₂ to produce BrNO [8], BrNO₂ [8 - 10], BrONO [10 - 12] and BrONO₂ [11] has been considered. However, these nitrogen oxybromides have been found to be only temporary bromine sinks due to their thermal and photochemical instability. Bromine has been detected in the stratosphere as Br⁻ using a filter paper collection method [13].

The major release of tropospheric bromine is apparently from marine aerosols [3]. There is also a substantial contribution from the agricultural fumigating agents CH₃Br and CH₂BrCH₂Br and from the combustion products of leaded gasolines that contain brominated compounds to aid in the volatilization of lead combustion products [3]. Both CH₃Br and CH₂BrCH₂Br have hydrogen bonds which react rapidly with tropospheric OH and there-

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fore only a portion of their bromine reaches the stratosphere [3]. Extensive use of the flame retardants CF_3Br and $\text{CF}_2\text{BrCF}_2\text{Br}$ results in their introduction into the atmosphere. Because these molecules are not subject to any major tropospheric removal mechanism, a large fraction of their bromine is eventually released into the stratosphere, for example by photodecomposition [11]:



CF_2ClBr (Freon 12B1, Halon 1211) is manufactured to a lesser extent than CF_3Br and $\text{CF}_2\text{BrCF}_2\text{Br}$ and is released into the troposphere through its use as a refrigerant, flame retardant, foaming agent and aerosol propellant. We measured the UV photoabsorption spectrum of CF_2ClBr in order to estimate its atmospheric photodissociation lifetime as a function of altitude.

2. Experimental

CF_2ClBr (PCR Research Chemicals, Inc.) was outgassed at 77 K on a greaseless vacuum line and the middle fraction of a distillation was saved and used. The vapor pressure [15] and the IR spectrum [16] of the purified sample were consistent with those found in the literature. The absorption was investigated using a Cary 219 UV-VIS double-beam spectrophotometer together with quartz cells having pathlengths of 2 and 10 cm. 29 samples were studied with the product of optical pathlength and pressure ranging from 24.8 to 7320 cm Torr at 295 K.

3. Results and discussion

Beer's law behavior was observed over the range of experimental conditions studied. Figure 1 shows that CF_2ClBr vapor begins to absorb at about 307 nm and reaches a maximum ($1.23 \times 10^{-18} \text{ cm}^2$) at $206 \pm 2 \text{ nm}$. Some of the photoabsorption cross sections are listed in Table 1.

Atmospheric photodissociation rate coefficients J and lifetimes J^{-1} were estimated from the photoabsorption spectrum of Fig. 1 and the solar flux intensities at a 45° zenith angle*. The photodissociation lifetimes (Table 2) are long in the troposphere, since CF_2ClBr does not absorb significant radiation with wavelengths longer than 300 nm, and therefore a substantial fraction of CF_2ClBr will mix into the stratosphere. The lifetimes in the stratosphere are much shorter than in the troposphere (Table 2) because of the existence of UV radiation at the upper altitudes. The dominant decomposition pathway during UV photolysis of CF_2ClBr is rupture of the weakest bond, *i.e.* of the C-Br bond [17]:



The bromine atoms formed in reaction (5) can then partake in the BrO_x chain-catalyzed removal of atmospheric ozone. A laboratory photo-

* $J(h) = \sum_{\lambda} \sigma(\lambda) I(\lambda, h)$ where the solar flux intensities I were obtained from the Lawrence Livermore Laboratory.

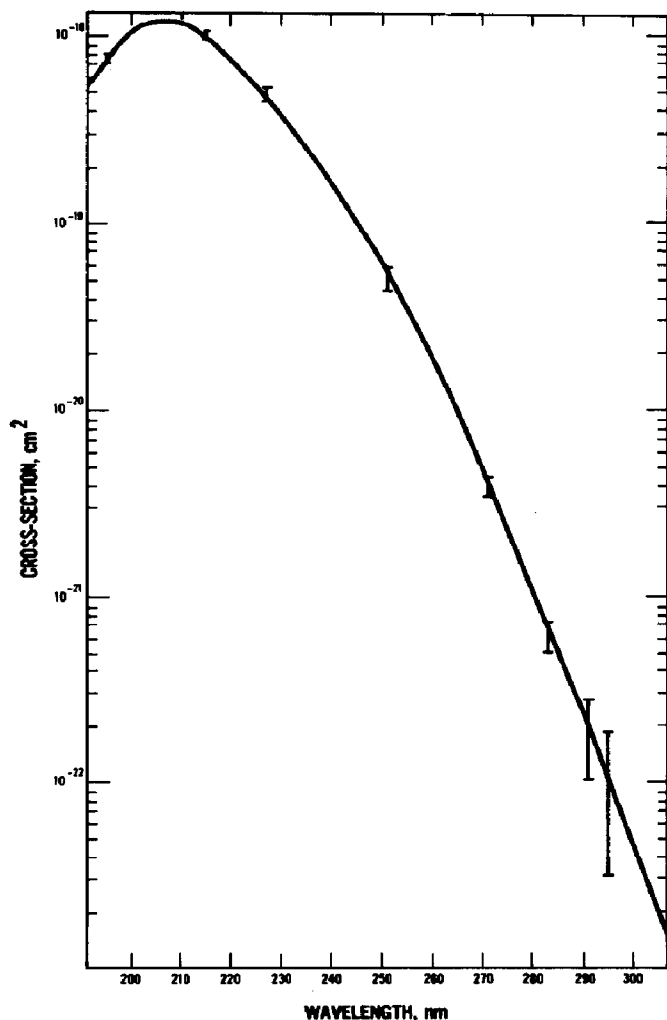
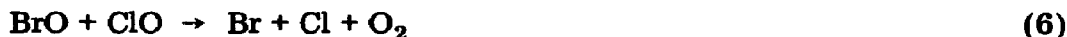


Fig. 1. The photoabsorption spectrum of CF_2ClBr vapor at 295 K.

chemical study [18] has shown that the rate of decomposition of ozone is markedly accelerated in the presence of CF_2ClBr compared with that in its absence. In the lower stratosphere, coupling between the bromine and chlorine cycles through reaction (6) contributes to the destruction of ozone [19]:



The CF_2Cl radicals produced in reaction (5) are mainly oxidized in the atmosphere by reaction with oxygen:



The ClO species formed in reaction (7) can participate in the atmospheric chlorine cycle, while photolysis of CF_2O in the stratosphere produces fluorine atoms which can contribute to the atmospheric fluorine cycle [21 - 23].

TABLE 1

Photoabsorption cross sections σ of CF_2ClBr vapor

λ (nm)	σ (cm^2)
191	5.24×10^{-19}
201	1.10×10^{-18}
211	1.15×10^{-18}
221	7.34×10^{-19}
231	3.53×10^{-19}
241	1.45×10^{-19}
251	5.25×10^{-20}
261	1.55×10^{-20}
271	3.94×10^{-21}
281	8.30×10^{-22}
291	2.04×10^{-22}
301	3.95×10^{-23}
307	1.22×10^{-23}

TABLE 2

Photodissociation rate coefficients J and lifetimes J^{-1} as functions of altitude

h (km)	J (s^{-1})	J^{-1}
0	2.2×10^{-9}	14.2 years
10	4.2×10^{-9}	7.6 years
20	2.0×10^{-8}	1.5 years
30	3.2×10^{-6}	3.6 days
40	5.7×10^{-5}	4.9 min
50	1.7×10^{-4}	1.7 min

4. Summarizing remarks

The UV photoabsorption spectrum of CF_2ClBr was measured at 295 K and its photodissociation lifetime was estimated as a function of altitude. Long tropospheric lifetimes indicate that a substantial fraction of the CF_2ClBr photodecomposes in the stratosphere, which results in its participation in the atmospheric bromine, chlorine and fluorine cycles.

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