Planet. Space Sci., Vol. 37, No. 1, pp. 105–108, 1989
Printed in Great Britain.

0032–0633/89 $3·00 + 0·00
Pergamon Press plc

ABSORPTION CROSS-SECTION OF ALTERNATIVE CHLOROFLUOROETHANES AND POTENTIAL EFFECTS ON THE OZONE LAYER

Didier GILLOTAY and Paul C. SIMON

Institut d'Aéronomie Spatiale de Belgique
Avenue Circulaire, 3, B-1180 Bruxelles, Belgium

and

Guy BRASSEUR*

National Center for Atmosphere Research
Boulder, CO 80307, USA.

(Camera-ready copy received 27 January 1989)

ABSTRACT

Ultraviolet absorption cross-sections of three chlorofluoroethanes (CH_3-CF_2Cl - HCFC 142b, CH_3-$CFCl_2$ - HCFC 141b and CF_3-$CHCL_2$ - HCFC 123) are measured with uncertainties of 2%. These compounds are photodissociated in the stratosphere. But, as shown by a one-dimensional model calculation, a substantial fraction of these molecules is destroyed in the troposphere by hydroxyl radicals. As a consequence, the lifetime and the ozone depletion potential of these 3 chlorofluoroethanes are significantly lower than those of the widely used chlorofluorocarbons 11 and 12.

1. INTRODUCTION

Odd chlorine, primarily produced in the stratosphere by the photodissociation of halocarbons released in the troposphere, plays a key role in the budget of the stratospheric ozone. The "Montreal Procotol on substances that deplete the ozone layer" limits the production of compounds such as CF_3Cl (CFC-11), CF_2Cl_2 (CFC-12), $C_2F_3Cl_3$ (CFC-113), $C_2F_4Cl_2$ (CFC-114) and C_2F_5Cl (CFC-115) because of their high ozone depletion potential. New compounds are, at the present time, under study to replace the most commonly used chlorofluorocarbons. Non-fully halogenated halocarbons are relatively easily destroyed by OH radicals in the troposphere and their lifetime is consequently shorter than the fully halogenated halocarbons which are only dissociated by solar radiation in the stratosphere.

* On leave from Institut d'Aéronomie Spatiale de Belgique, Avenue Circulaire, 3, B-1180 Bruxelles.

The purpose of this paper is to report measurements of the ultraviolet absorption cross-sections of three chlorofluoroethanes (CH_3-CF_2Cl - HCFC-142b, CH_3-$CFCl_2$ - HCFC-141b and CF_3-$CHCl_2$ - HCFC-123), performed between 170 and 250 nm, at ambient temperature. These data are used to estimate the lifetime of these compounds and their efficiency in depleting stratospheric ozone.

2. EXPERIMENTAL AND LABORATORY RESULTS

Absorption cross-sections have been determined in the ultraviolet, using a classical single beam equipment previously described by Gillotay and Simon (1988), including a Deuterium lamp, 1 m Mc Pherson 225 monochromator, a 2 m absorption cell and a EMR type 542 P-09-18 solar blind photomultiplier. The pressure inside the cell ranging from 2×10^{-3} to 10^{3} torr is measured with three capacitance manometers MKS-Baratron. The three compounds have respectively purities of 99.96% for CFC-142b, 99.72% fir CFC-142b and 98.4% for CFC-123, as determined by gas phase chromatography.

Determination of absorption cross-sections is made after more than fifteen sequential recordings of the incident and the absorbed radiation fluxes using the Beer-Lambert's law. Numerical values for selected wavelengths between 170 and 250 nm (2 nm intervals) are given in Table 1. The absorption spectra are illustrated in Figure 1.

In all cases, the Beer-Lambert's law was verified for transmittance ranging from 10 to 85%. In such conditions, and according to the error budget published by Simon et al. (1988), the absorption cross-sections given in Table 1 are determined with an accuracy of $\pm$ 2%. The three chlorofluoroethanes display continuous absorption in the region 170-250 nm, with absorption cross-sections ranging from 2×10^{-18} to 10^{-23} cm^2 $molec.^{-1}$. The only previous available values are those of Hubrich and Stuhl (1980) for HCFC-142b which are of the same order of magnitude in the 170-190 nm range and become smaller than our values in the 190-230 nm region (up to a factor of 50 at 230 nm).

3. POTENTIAL EFFECTS ON THE OZONE LAYER

The potential for a halocarbon molecule to initiate catalytic destruction of ozone in the stratosphere depends on the number of chlorine (and bromine) atoms included in the molecule, on its lifetime in the atmosphere and, more particularly, on its photolysis rate in the stratosphere and its reactivity mainly with hydroxyl radicals (OH) in the troposphere. The new measured absorption cross-sections have been used to calculate the lifetime and the ozone depletion potential (ODP) of the three chlorofluoroethanes. The values of the rate constants of the reaction of the compounds with OH radicals were taken from a recent determination made by Dogimont (1988). Calculations made using the one-dimensional model of Brasseur and De Rudder (1987) suggest that more than 90% of these compounds are destroyed in the troposphere, by reaction with OH radicals. Consequently, the calculated values of the global lifetime and the ozone depletion potential are very sensitive to the concentration of OH.

Table 2 shows that the calculated lifetime of HCFC-123, HCFC-141b and, to a lesser extent, HCFC-142b are significantly smaller than the lifetime of CFC-11 (about 70 yrs) and CFC-12 (about 140 yrs).

TABLE 1.- Absorption cross-section [$\sigma(\lambda)$ x 10^{21} (cm^2 $molec.^{-1}$)] at 2 nm interval, at room temperature

(nm)	CH_3-CF_2Cl HCFC-142b	CH_3-$CFCl_2$ HCFC-141b	CF_3-$CHCL_2$ HCFC-123
170	264	1310	1858
172	212	1361	1889
174	168	1474	1948
176	136	1562	1903
178	100	1631	1878
180	84.3	1657	1727
182	66.2	1608	1515
184	47.0	1505	1285
186	35.6	1244	1015
188	28.5	1074	800
190	22.5	863	603
192	18.1	671	455
194	14.8	499	332
196	11.9	364	245
198	9.34	257	175
200	7.13	183	122
202	5.45	126	89.0
204	4.12	84.9	61.4
206	3.06	55.5	42.4
208	2.32	36.5	29.5
210	1.83	23.5	20.3
212	1.42	15.4	14.1
214	1.15	9.84	9.57
216	0.995	6.25	6.51
218	0.763	4.10	4.46
220	0.584	2.67	3.16
222	0.443	1.76	2.20
224	0.335	1.15	1.48
226	0.251	0.728	1.12
228	0.185	0.490	0.797
230	0.140	0.333	0.586
232	0.107	0.222	0.443
234	0.0839	0.148	0.336
236	0.0651	0.103	0.250
238	0.0471		0.190
240	0.0345		0.148
242	0.0222		0.109
244	0.0135		0.0782
246			0.0603
248			0.0404

As a consequence, the ozone depletion potential of the three compounds relative to that of CFC-11 is of the order of 0.01 for HCFC-123, 0.1 for HCFC-141b and 0.05 for HCFC-142b. These values are determined with an uncertainty of a factor of $\pm$ 2 because of the difficulty in modelling accurately the tropospheric OH density.

In conclusion, the impact of HCFC-123, 141b and 142b on the ozone layer is significantly smaller than that of the chlorofluorocarbons regulated by the Montreal Protocol. The contribution of these species to the greenhouse effect of the atmosphere remains however to be determined accurately.

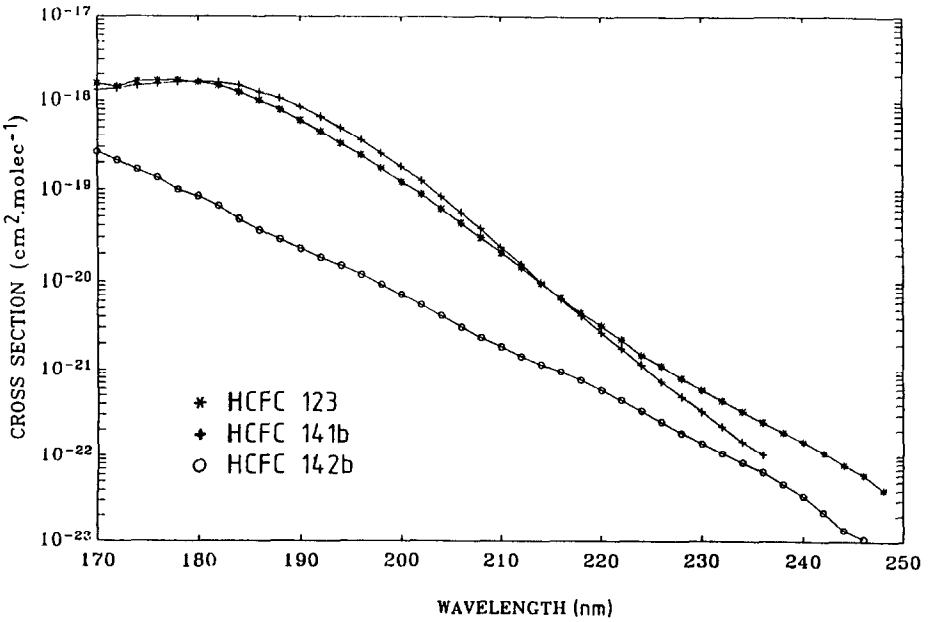

Figure 1. Ultraviolet absorption cross-sections of HCFC-123, HCFC-141b and HCFC 142b with respect to wavelength at 295 K.

TABLE 2.- Calculated lifetime of chlorofluoroethanes

Compound	Global lifetime (years)
HCFC-123	2
HCFC-141b	8.5
HCFC-142b	21

ACKNOWLEDGEMENTS

The authors wish to thank Drs. G. Martens and J. Franklin from SOLVAY S.A. for helpful discussions and for providing the samples studied in this work. The National Center for Atmospheric Research is sponsored by the U.S. National Science Foundation.

REFERENCES

BRASSEUR, G. and A. DE RUDDER, 1987, The potential impact on atmospheric ozone and temperature of increasing trace gas concentrations, J. Geophys. Res., 92, 10903-10920.

DOGIMONT, C., 1988, Private communication.

GILLOTAY, D. and P.C. SIMON, 1988, Ultraviolet absorption cross-sections of methyl bromide at stratospheric temperatures, Ann. Geophysicae, 6, 211-215.

HUBRICH, C. and F. STUHL, 1980, The ultraviolet absorption of some halogenated methanes and ethanes of atmospheric interest, J. Photochem., 12, 93-107.

SIMON, P.C., D. GILLOTAY, N. VANLAETHEM-MEUREE and J. WISEMBERG, 1988, Ultraviolet absorption cross-sections of chloro- and chlorofluoro-methanes at stratospheric temperatures, J. Atmos. Chem., 7, 107-135.

MONTREAL PROTOCOL ON SUBSTANCES THAT DEPLETE THE OZONE LAYER, Final act, 1987, United Nations Environment Programme.