

Ultraviolet Absorption Cross Sections of Several Brominated Methanes and Ethanes of Atmospheric Interest

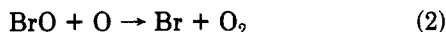
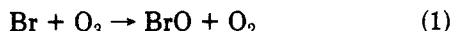
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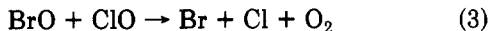
The ultraviolet absorption spectra have been measured for CH₃Br, CH₂Br₂, and five bromofluorocarbons to determine their rates of interaction with solar radiation in both the troposphere and the stratosphere. Dibromomethanes such as CH₂Br₂ and CBr₂F₂ have appreciable photon cross sections for λ > 295 nm and consequently have average lifetimes against direct solar photoexcitation of 1 yr or less. The photoexcitation of CBr₂F₂ leads to its decomposition in air, and the short lifetime ensures no appreciable accumulation in the atmosphere. The cross sections between 295 and 340 nm correspond to average photoexcitation lifetimes of 20 yr for CBrClF₂, 25–40 yr for CBrF₂CBrF₂, and >10² yr for CBrF₃, CBrF₂CF₃, and CH₃Br. Both CH₃Br and CH₂Br₂ have tropospheric sinks involving reaction with OH radicals which reduce their average atmospheric lifetimes to less than 2 yr. The only brominated molecules for which tropospheric removal is *not* the dominant process are expected to be the monobromoperfluoro compounds such as CBrF₃ and CBrF₂CF₃.

Introduction

The release of bromine atoms in the stratosphere initiates the ozone-depleting BrO_x chain reaction of eq 1 and 2 by analogy with the well-studied ClO_x chain reaction.^{1–4}



The presence of the BrO_x species also introduces additional cross interactions among the various free-radical chains, as illustrated by chemical processes such as those involving the ClO_x and NO_x chains in reactions 3⁵ and 4.^{6,7} Reac-



tions such as reaction 3 followed by attack on O₃ by each halogen atom furnish an alternate catalytic cycle which converts 2O₃ → 3O₂ without requiring O atoms and which can therefore operate well in the lower stratosphere below the altitudes important for the Br/BrO and Cl/ClO chains. Current atmospheric measurements indicate that tropospheric bromine levels are in the 10⁻¹¹ mole fraction range,^{2,3,8} more than 2 orders of magnitude below the existing chlorine levels in the troposphere, and the present importance of BrO_x reactions is minor in comparison to ClO_x effects. However, the BrO_x chain appears to be at least as effective per atom as that of ClO_x in its efficiency for removal of ozone, and the calculations of cross interactions with the ClO_x chain indicate nonlinear effects at bromine mole fractions of 10⁻¹⁰ or 10⁻⁹ by volume.⁴ Estimates of the lifetimes and sinks for various bromine-containing compounds are therefore needed in order to evaluate possible future changes in atmospheric bromine levels from increased usage of such compounds, together with the other chemical changes which might follow from increases in bromine levels. Among the bromine-containing molecules of particular interest in this respect are the commercially available fire retardants CBrF₃ (Fluorocarbon 13B), CBrF₂CBrF₂ (Fluorocarbon 114B2), and CBrClF₂ (Fluorocarbon 12B1).

The ultraviolet absorption characteristics of bromine-containing molecules have some apparent similarity to those of the corresponding chlorine-containing molecules,

with broad unstructured absorption bands, except that the bands are shifted toward the red by several tens of nanometers. Consequently, the long-wavelength tails of such absorptions extend toward 280 nm and beyond, and the possibility of significant tropospheric photochemical sinks beyond 290 nm must be considered in every case. Our current experiments have been directed toward determination of absorption cross sections both in the λ > 290 nm region important for tropospheric photochemistry and in the 200–230-nm region important for midstratospheric photochemistry.

Experimental Section

Measurement of Ultraviolet Cross Sections. The ultraviolet absorption cross sections for seven bromocarbon molecules have been measured with a Cary 219 double-beam spectrophotometer using a 10-cm and a 180-cm cell, as described previously.⁹ The measurements were carried out at pressures ranging from 6 to 40 torr for CH₂Br₂, from 5 to 300 torr for CBr₂F₂, CBrF₂CBrF₂, and CBrF₂CF₃, and from 10 to 500 torr for the other three compounds. Beer's law was obeyed at all pressures for each of the seven molecules. The initial measurements made with CBr₂F₂ as obtained directly from the Chemical Procurement Co. showed a wing in the 300-nm region. An initial purification by distillation reduced the intensity of the wing, and then triple distillation at -90 °C removed almost all of what remained. Double distillation of CBrF₂CBrF₂ (Chemical Procurement Co.) caused no change in its absorption characteristics. The other five gases were obtained with good initial purity, as confirmed by measuring the UV spectra of successive distillation fractions; hence, they were

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TABLE I: Ultraviolet Absorption Cross Sections for Seven Bromocarbon Molecules at 298 K

λ , nm	σ , ^a cm ² molecule ⁻¹						
	CH ₃ Br	CH ₂ Br ₂	CBrF ₃	CBr ₂ F ₂	CBrClF ₂	C ₂ BrF ₅	C ₂ Br ₂ F ₄
190	4.41 (-19)		6.71 (-20)	1.16 (-18)	4.24 (-19)	1.81 (-19)	1.09 (-18)
195	6.75 (-19)		9.61 (-20)	9.77 (-19)	7.11 (-19)	1.84 (-19)	1.19 (-18)
200	7.85 (-19)	2.31 (-18)	1.18 (-19)	7.68 (-19)	9.62 (-19)	1.81 (-19)	1.22 (-18)
205	7.63 (-19)	2.20 (-18)	1.29 (-19)	7.86 (-19)	1.09 (-18)	1.69 (-19)	1.16 (-18)
210	6.49 (-19)	2.42 (-18)	1.23 (-19)	1.10 (-18)	1.05 (-18)	1.48 (-19)	1.01 (-18)
215	5.06 (-19)	2.74 (-18)	1.03 (-19)	1.63 (-18)	8.96 (-19)	1.20 (-19)	8.31 (-19)
220	3.60 (-19)	2.83 (-18)	7.50 (-20)	2.16 (-18)	7.00 (-19)	8.94 (-20)	6.48 (-19)
225	2.38 (-19)	2.58 (-18)	4.83 (-20)	2.44 (-18)	5.13 (-19)	6.13 (-20)	4.78 (-19)
230	1.45 (-19)	1.98 (-18)	2.70 (-20)	2.31 (-18)	3.42 (-19)	3.83 (-20)	3.28 (-19)
235	8.05 (-20)	1.37 (-18)	1.48 (-20)	1.86 (-18)	2.33 (-19)	2.22 (-20)	2.11 (-19)
240	4.11 (-20)	8.65 (-19)	6.95 (-21)	1.33 (-18)	1.44 (-19)	1.20 (-20)	1.27 (-19)
245	2.04 (-20)	5.08 (-19)	3.25 (-21)	8.65 (-19)	8.87 (-20)	6.20 (-21)	7.30 (-20)
250	9.49 (-21)	2.76 (-19)	1.39 (-21)	5.32 (-19)	5.29 (-20)	3.05 (-21)	3.98 (-20)
255	4.05 (-21)	1.37 (-19)	5.89 (-22)	2.96 (-19)	2.97 (-20)	1.35 (-21)	2.02 (-20)
260	1.63 (-21)	6.31 (-20)	2.34 (-22)	1.55 (-19)	1.56 (-20)	5.90 (-22)	9.57 (-21)
265	6.22 (-22)	2.82 (-20)	9.05 (-23)	7.81 (-20)	7.91 (-21)	2.60 (-22)	4.40 (-21)
270	2.36 (-22)	1.21 (-20)	3.48 (-23)	3.84 (-20)	3.92 (-21)	1.12 (-22)	2.06 (-21)
275	9.0 (-23)	5.11 (-21)	1.38 (-23)	1.85 (-20)	1.90 (-21)	5.05 (-23)	9.28 (-22)
280	3.3 (-23)	2.16 (-21)	5.5 (-24)	8.45 (-21)	8.83 (-22)	2.18 (-23)	4.07 (-22)
285	1.1 (-23)	9.1 (-22)	2.2 (-24)	3.81 (-21)	3.98 (-22)	1.00 (-23)	1.75 (-22)
290	3 (-24)	3.5 (-22)	8 (-25)	1.69 (-21)	1.82 (-22)	4.5 (-24)	7.4 (-23)
295		1.2 (-22)	3 (-25)	7.73 (-22)	8.21 (-23)	2.0 (-24)	3.3 (-23)
300		3 (-23)	1 (-25)	3.56 (-22)	3.61 (-23)	9 (-25)	1.6 (-23)
305				1.74 (-22)	1.65 (-23)		8 (-24)
310				9.2 (-23)	6.6 (-24)		4 (-24)
315				5.5 (-23)	2.6 (-24)		2 (-24)
320				2.9 (-23)	9.8 (-25)		1 (-24)
325				1.3 (-23)	3.7 (-25)		
330				7 (-24)	1.5 (-25)		
335				4 (-24)			
340				2 (-24)			

^a Exponent for base 10 in parentheses.

not treated further. The chemical sources were Eastman Organic Chemical (CH₂Br₂), Matheson (CH₃Br, CBrF₃), and PCR Research Chemicals, Inc. (CBrClF₂, CBrF₂CF₃).

Temperature-dependent measurements were judged to be unnecessary because the wings of the absorption bands, where temperature effects are expected to be most pronounced, do not fall in the stratospherically important 190–220-nm wavelength region.

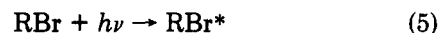
Tropospheric decomposition is determined by absorption beyond 290 nm, but almost 25% of the tropospheric burden of these molecules is present at temperatures above 0 °C, so that the 25 °C measurements are reasonably satisfactory there as well.

Results

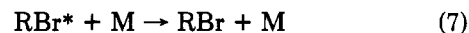
The photoabsorption cross sections for seven bromocarbon molecules are listed in Table I and illustrated in Figure 1. All of these compounds exhibit absorption maxima between 200 and 230 nm, with long-wavelength absorption decreasing beyond these maxima by a factor of 10 for every 12–15 nm. Both CBr₂F₂ and CBrF₂CBrF₂ exhibit small changes in slope vs. wavelength for cross sections of <10⁻²² cm², which might represent trace concentrations of an impurity in either. The absorption spectra show a steady progression toward longer wavelengths as F in CBrF₃ is replaced by H, CBrF₂, Cl, and Br, and can be conveniently considered as monobromo (-CBrXY) and dibromo (-CBr₂X) spectra in terms of the number of bromine atoms attached to an individual carbon atom; i.e., CBrF₂CBrF₂ has a monobromo spectrum. Note, however, that this progression is toward shorter wavelengths as F is replaced by H in going from CBr₂F₂ to CH₂Br₂.

The similarities in the smooth continuous absorption spectra suggest that the electronic nature of the absorption process may well be the same for all of these molecules.

Observations with mixed halogenated hydrocarbons indicate that the absorption of ultraviolet radiation is followed by the rupture of the weakest carbon-halogen bond,¹¹ so that the expected decomposition sequence is that given by eq 5 and 6. However, both CBr₂F₂ at 265



nm^{12,13} and CBrCl₃ at 366 nm¹⁴ are reported to exhibit pressure-dependent yields of Br atoms, implying that RBr* is not formed in a repulsive electronic state, but in an excited state long-lived enough to permit collisional stabilization, as in reaction 7. The excitation energies fol-



lowing photon absorption are in both cases well above the threshold energies for reaction 6, with 108 kcal/mol (corresponding to 265 nm) for CBr₂F₂ vs. estimated C-Br bond dissociation energy of about 67 kcal/mol,¹¹ and 78 kcal/mol (corresponding to 366 nm) for CBrCl₃ vs. estimated¹¹ 55 kcal/mol.

Calculations of Average Tropospheric Photoexcitation Lifetimes. The absorption cross sections of Table I and Figure 1 have been combined with estimates of the solar flux for wavelengths longer than 290 nm to obtain tropospheric photoexcitation rates for each molecule, as given in Table II. Two separate sets of such estimated tropospheric solar ultraviolet fluxes have been used in these calculations—those of Peterson,¹⁵ corresponding to

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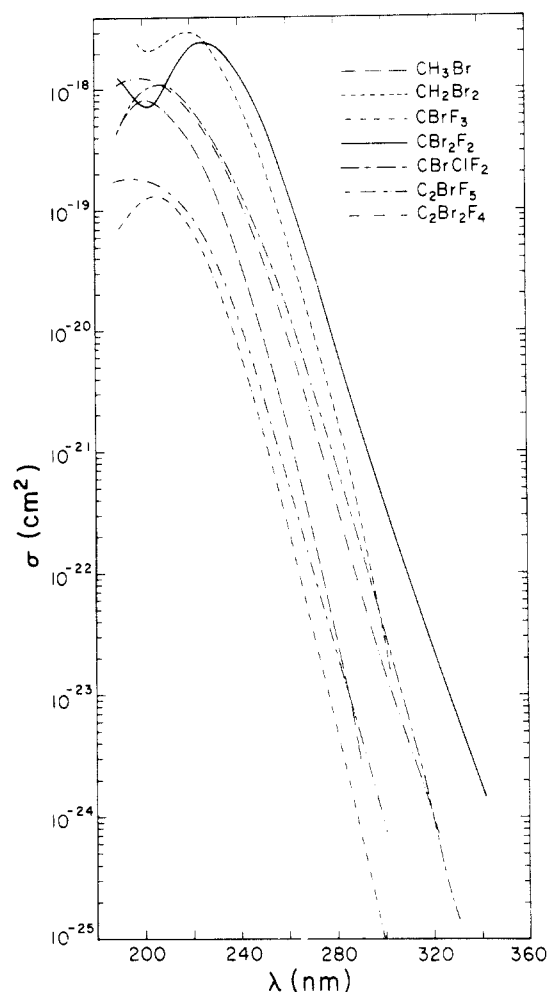


Figure 1. Ultraviolet absorption cross sections for seven bromocarbon compounds.

TABLE II: Estimated Tropospheric Photoexcitation Rates (J) and Average Tropospheric Lifetimes (T)

molecule	case I ^c		case II ^c	
	$10^9 J, s^{-1}$	T, yr	$10^9 J, s^{-1}$	T, yr
CBr_2F_2 ^a	110	0.9	170	0.6
CBr_2F_2 ^b	67	1.4	101	0.9
$CBrClF_2$	4.5	21	6.7	14
$CBrF_2CBrF_2$ ^a	4.1	23	6.2	15
$CBrF_2CBrF_2$ ^b	2.4	40	3.5	27
$CBrF_2CF_3$	<0.2	>500	<0.3	>400
$CBrF_3$	<0.1	>10 ³	<0.1	>10 ³

^a Using cross sections from Table I. ^b Using cross sections for $\lambda > 300$ nm extrapolated by straight line on Figure 1 of data for $\lambda < 300$ nm. ^c Cases I and II: computed by using solar fluxes from ref 15 and 16, respectively.

"best-estimate" surface albedos and zero zenith angle; and those of Wuebbles and Chang,¹⁶ corresponding to noon, midlatitude equinox conditions. The estimated photoexcitation rates are about a factor of 1.5 smaller when the former is used.

The reported pressure dependence of RBr dissociation¹²⁻¹⁴ raises the question of whether the calculated photoexcitation rates are substantially larger than the actual photodecomposition rate through effective quantum

yields for decomposition much less than unity. None of the literature studies have been carried out in the presence of O_2 as is appropriate for consideration for photoexcitation processes in the troposphere. However, current experiments in our laboratories have shown the formation of the decomposition product CF_2O with a quantum yield of approximately unity from the 250-nm photolysis of CBr_2F_2 in the presence of O_2 .¹⁷ While further experiments are desirable to clarify the details of CBr_2F_2 photolysis in the presence and the absence of O_2 , the new observations indicate that calculated photoexcitation rates for CBr_2F_2 can be essentially converted directly into photodecomposition rates. Table II gives average tropospheric lifetimes, estimated by assuming a diurnally and latitudinally averaged photoexcitation rate equal to one-third of the value given in the table and assuming unit quantum yield for decomposition. This factor of $1/3$ is only a rough approximation but should be adequate for the purpose of this work. The photodestruction of CBr_2F_2 in the troposphere thus requires about 1 yr, and no appreciable accumulation of this compound in the atmosphere is expected.

The photochemistry of the other bromofluorocarbon molecules is largely unexplored, but the similarity among the spectra suggests similarity in chemical reactions after photoexcitation, and excitation probably leads to efficient decomposition reactions for these molecules in the presence of O_2 . Although quantum yield measurements in O_2 mixtures are desirable for molecules such as $CBrClF_2$ and $CBrF_2CBrF_2$, the general conclusion is indicated from Table II that only the monobromoperfluoro molecules $CBrF_3$ and $CBrF_2CF_3$ do not have major tropospheric photochemical sinks.

Calculations of Stratospheric Lifetimes. The expected steady-state distributions of the longer-lived bromocarbon compounds have been calculated by using a one-dimensional (1-D) vertical diffusion model, as described earlier.^{1,18} These calculations have been carried out with two representative vertical transport coefficient—i.e., K_z —profiles. One (labeled II in the figures) is that of Chang and Dickinson,³ who calculated a K_z profile intended to give reasonable agreement with the vertical mixing ratio profiles of N_2O and CH_4 , using the best estimates of chemical reaction rate constants and solar fluxes in mid-1979. This K_z profile tended somewhat to underestimate the rapidity with which the experimentally determined mixing ratios of CCl_3F and CCl_2F_2 decreased with increasing altitude.

During the past 2 years several developments in laboratory chemistry have led to atmospheric model calculations indicating lower OH concentrations in the lower stratosphere than previously estimated. Since the primary removal process for CH_4 in the atmosphere is reaction with OH, the procedure of fitting to CH_4 and N_2O could be carried out again with the new laboratory data, and a new K_z profile would be obtained which would give generally slower vertical mixing and longer atmospheric lifetimes than characteristic of the Chang-Dickinson 1979 model. However, considerable uncertainty still remains in the lower-stratospheric chemistry, and this process has not been carried out. Instead, another K_z profile (labeled I in the figures) has been chosen which is simply a "test" function (devised by Wuebbles and Chang)¹⁹ generally typical of the kind that provides a better fit to the measured vertical profiles of CCl_3F and CCl_2F_2 .

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(18) Rowland, F. S.; Molina, M. J. *J. Phys. Chem.* 1976, 80, 2049.

(19) K_z profiles described in: Chang, J. S.; Wuebbles, D. J. "Annual Report of Lawrence Livermore National Laboratory to the FAA on the High Altitude Pollution Program—1980"; Luther, F. M., Ed.; Lawrence Livermore Laboratory: Livermore, CA 1980; UCRL-50042-80.

(15) Peterson, J. T. "Calculated Actinic Fluxes (290–700 nm) for Air Pollution Photochemistry Applications", Report EPA-600/4-76-025, June 1976.

(16) Wuebbles, D. J., personal communication, 1981.

TABLE III: Estimated Atmospheric Lifetimes against Stratospheric Photodecomposition

compd	lifetime, ^a yr	
	case I ^b	case II ^c
CBrF ₃	112	62
CBrClF ₂	42	29
CBrF ₂ CF ₃	103	58
CBrF ₂ CBrF ₂	44	30
CCl ₃ F	83	49
CCl ₂ F ₂	148	81

^a Estimated by using the solar flux values of Wuebbles and Chang (ref 16) and assuming unit quantum yield for decomposition. ^b Computed with the test K_z profile of Wuebbles and Chang (ref 19). ^c Computed with the Chang-Dickinson K_z profile of ref 3.

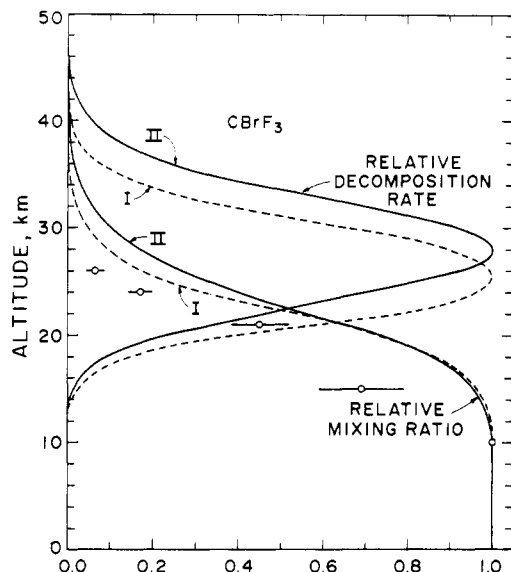


Figure 2. Vertical mixing ratio and decomposition rate profiles normalized to the maximum value, calculated for CBrF₃ with a 1-D model: (I) using the K_z profile of ref 19; (II) using the K_z profile of ref 3; (O) measured mixing ratios (ref 21).

Table III gives the average atmospheric lifetime for each of the bromofluorocarbon molecules against stratospheric photodecomposition alone, that is, the average residence time that the molecule would spend in the atmosphere if photolysis in the stratosphere were the only sink (This "atmospheric lifetime against stratospheric decomposition" is not the average time spent in the stratosphere as a whole, or at a specific altitude before photolysis, but the average time before photodecomposition spent by the molecule throughout the atmosphere, including large amounts of time in the troposphere. The "stratospheric lifetime" is much shorter, e.g., about 1 mo at 30-km altitude for CCl₃F for either case I or case II. Replenishment from the troposphere is slower in case II so the average steady-state concentration of CCl₃F at 30 km is less.) The expected mixing ratio profile vs. altitude from a one-dimensional calculation for 30° N latitude is shown in Figure 2 for CBrF₃ for both of the profiles described above. The lack of difference in these two mixing ratio profiles simply reflects that the 190–230-nm ultraviolet flux increases very rapidly with altitude in the 20–35-km range (e.g., a factor of 4 between 20 and 25 km). Profile I represents considerably slower diffusion around 25 km such that less penetration to higher altitudes by undissociated molecules occurs. The maximum decomposition and release of Br is calculated to occur in the 25–27-km altitude range, with the higher altitude attached to the model in which upward diffusion is faster.

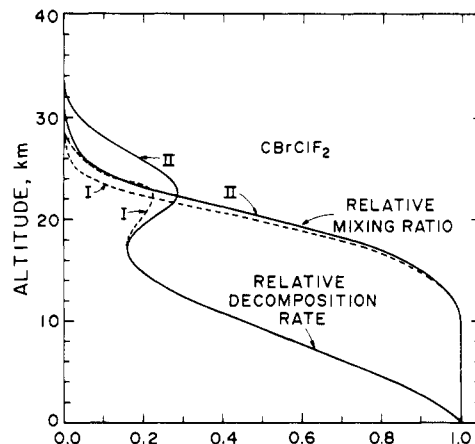


Figure 3. Vertical mixing ratio and decomposition rate profiles normalized to the value at the surface, calculated for CBrClF₂ with a 1-D model: (I) using the K_z profile of ref 19; (II) using the K_z profile of ref 3.

The tropospheric mixing ratio of CBrF₃ has been measured²⁰ as 0.7×10^{-12} , with a second measurement of 1.0×10^{-12} by a second group.²¹ The mixing ratios have also been measured in the stratosphere to an altitude of 26 km²¹ and are displayed in Figure 2 as ratios relative to the 10-km value. The stratospheric measurements were made at 44° N latitude and therefore do not correspond directly to the vertical profiles calculated for 30° N. In general, the measured mixing ratio profiles for halocarbons in the stratosphere progressively fall off more rapidly with altitude as the latitude moves poleward from the equator. The calculated vertical profiles of the different halocarbons in Table III arrange themselves in the same order as the calculated lifetimes (CBrClF₂ \approx CBrF₂CBrF₂ < CCl₃F < CBrF₂CF₃ \approx CBrF₃ < CCl₂F₂) with the slowest falloff with altitude attached to CCl₂F₂, the longest lived. The measured altitudes at which the mixing ratio is reduced to 0.1 times the tropospheric value in the 44° N measurements occur in the same order given above:²¹ CCl₃F, 23 km; CBrF₃, 25 km; CCl₂F₂, 28 km.

Comparable calculations for CBrClF₂ are displayed in Figure 3. The indicated decomposition below 18 km occurs almost entirely for wavelengths > 295 nm. No measurements of CBrClF₂ in the atmosphere have yet been reported.

Discussion

The absorption spectrum of CBr₂F₂ has previously been measured in the 220–310-nm region,¹³ with results which are in reasonable agreement with our cross sections listed in Table I. (The published spectrum does not permit quantitative comparison for the wavelengths beyond 295 nm.) Both dibromomethanes (CH₂Br₂, CBr₂F₂) have significant absorption cross sections of 3×10^{-23} and 3×10^{-22} cm², respectively, at 300 nm and therefore have the possibility of important photochemical decomposition sinks throughout the troposphere. If the observed absorption spectrum for CBr₂F₂ is indeed attributable entirely to that molecule, then the calculated tropospheric lifetime toward photoexcitation and decomposition is 6–9 mo. If the true absorption spectrum is represented instead by an exponential extrapolation of the observed cross sections between 250 and 300 nm, the tropospheric absorption is still significant, with an atmospheric lifetime of 1–1.5 yr.

(20) Penkett, S. A.; Prosser, N. J. D.; Rasmussen, R. A.; Khalil, M. A. K. *J. Geophys. Res.* 1981, 86, 5172.

(21) Fabian, P.; Borchers, R.; Penkett, S. A.; Prosser, N. J. D. *Nature (London)* 1981, 294, 733.

The photoabsorption cross sections for CH_2Br_2 are less than those for CBr_2F_2 by about a factor of 10 on the long-wavelength side, and the corresponding calculated tropospheric lifetime toward photoexcitation is longer in the same ratio, estimated as about 6 yr. No information appears to be available on the appropriate quantum yields for photodissociation from this photoexcited state. However, CH_2Br_2 can also be readily attacked by tropospheric OH radicals, as in reaction 8, for which we estimate a



removal time of less than 2 yr by comparison with the laboratory OH reaction rates for CH_3Br and CH_3CCl_3 ,²² and an estimated atmospheric lifetime of 7 yr for the latter.²³ The overall tropospheric removal rate for CH_2Br_2 is the sum of the photolysis and OH removal rates and therefore corresponds to a tropospheric lifetime of about 1 yr.

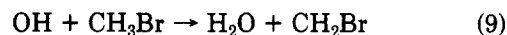
Although we have not measured the absorption spectra of any additional complex molecules containing the CBr_2X group, we anticipate by analogy with the current measurements that all such molecules (plus all containing CBr_3) will have appreciable absorption cross sections for $\lambda > 295$ nm and therefore will very probably be subject to photodecomposition in the troposphere on the time scale of a few months to a year or two.

Both CBrClF_2 and $\text{CBrF}_2\text{CBrF}_2$ have absorption cross sections $> 10^{-23} \text{ cm}^2$ at 300 nm, and appreciable rates of tropospheric photoexcitation. The cross sections for CBrClF_2 have been previously published down to 307 nm in experiments with a 10-cm cell.²⁴ Our measurements are generally about 20% lower than those over the range 285–305 nm. For the purpose of estimation of tropospheric photoexcitation lifetimes, the agreement in cross section measurements is quite satisfactory. Our calculated tropospheric lifetimes against photoexcitation for CBrClF_2 and $\text{CBrF}_2\text{CBrF}_2$ are 15–20 and 16–40 yr, respectively. The 30–40-yr lifetime for $\text{CBrF}_2\text{CBrF}_2$ corresponds to an exponential extrapolation to longer wavelengths of the cross sections measured between 250 and 300 nm, while the 16–23-yr lifetime utilizes the actual cross sections of Figure 1. No quantum yields for photodissociation have been measured for either of these molecules, but we assume by analogy with CBr_2F_2 that photoexcitation leads to decomposition in air with a quantum yield approaching unity.

As shown in Table III, we estimate 30–45-yr lifetimes in the atmosphere for both CBrClF_2 and $\text{CBrF}_2\text{CBrF}_2$, if stratospheric photolysis is assumed to be the only sink, and if the quantum yield for decomposition is unity. These lifetimes are comparable to the tropospheric lifetimes given

in Table II, and hence stratospheric removal should account for at least 30% of the total photolytic removal in the atmosphere for these two compounds.

Of the seven brominated molecules measured here, the only ones definitely lacking any appreciable direct tropospheric photoexcitation are those containing Br atoms: CH_3Br , CBrF_3 , and CBrF_2CF_3 . Our measurements for CH_3Br are in agreement with those of Robbins²⁵ over his range out to 270 nm and extend beyond them to 290 nm. The direct photochemistry of CH_3Br is not particularly important, however, since methyl bromide has a tropospheric removal process through attack by OH, as in reaction 9. This reaction controls the removal of CH_3Br



from the atmosphere, with an estimated tropospheric lifetime of about 1.7 yr by analogy with CH_3CCl_3 .^{22,23}

The measured absorption spectrum for CBrF_2CF_3 shows essentially exponential falloff from 240 to 300 nm, with a cross section of $9 \times 10^{-25} \text{ cm}^2$ at 300 nm. Continued extrapolation leads to an estimated tropospheric removal rate of $1.6 \times 10^{-10} \text{ s}^{-1}$, or an atmospheric lifetime against even photoexcitation of 500 yr, with most of the excitation occurring between 300 and 320 nm. Stratospheric photodissociation calculations show a lifetime of 60–100 yr, with the altitude of maximum decomposition around 25–27 km. A figure depicting the vertical mixing ratio profile and altitudes of decomposition for CBrF_2CF_3 is essentially identical with Figure 2, which describes the corresponding calculations for CBrF_3 . With both eddy diffusion models, the lifetimes of CBrF_2CF_3 and CBrF_3 are calculated to be bracketed between the shorter-lived CCl_3F and the longer-lived CCl_2F_2 .

The measured absorption cross sections for CBrF_3 are about a factor of 10 lower than those for CBrF_2CF_3 near 300 nm, leading to an estimated tropospheric lifetime against direct solar photoexcitation in excess of 10^3 yr. The calculated stratospheric lifetimes are nearly identical with those for CBrF_2CF_3 , and the mixing ratio profiles vs. altitude are shown in Figure 2.

In summary, these ultraviolet absorption measurements have the following significance toward atmospheric reactions: (a) no important direct photochemical removal process exists within the troposphere for CBrF_3 or CBrF_2CF_3 ; (b) stratospheric removal is important ($>30\%$) for CBrClF_2 and $\text{CBrF}_2\text{CBrF}_2$; (c) tropospheric removal in about 1 yr is calculated for CBr_2F_2 , as is expected for other molecules containing two or more Br atoms attached to the same carbon atom; (d) CH_3Br and CH_2Br_2 are rapidly removed from the troposphere by reaction with OH radicals, making the question of possible additional direct photochemical removal of relatively minor importance with regard to possible stratospheric release of atomic bromine.

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(22) The reaction rate for $\text{OH} + \text{CH}_3\text{Br}$ is about 4 times faster than for $\text{OH} + \text{CH}_3\text{CCl}_3$ over the tropospheric region in which reaction with OH primarily occurs (lowest 5 km), as given in: Baulch, D. L.; Cox, R. A.; Hampson, R. F.; Kerr, J. A.; Troe, J.; Watson, R. T. *J. Phys. Chem. Ref. Data* 1980, 9, 295. The rate of OH reaction with CH_2Br_2 is expected by analogy with other reaction systems to be as fast as or faster than that of OH with CH_3Br .

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