Photochemistry of Bromine-Containing Fluorinated Alkenes: Reactivity toward OH and UV Spectra

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The rate constants for the reactions of OH radicals with the fluorinated alkenes containing one Br atom ($CFBr{=}CF_2$, $CHBr{=}CF_2$, $CH_2{=}CBr{-}CF_3$, $CH_2{=}CBr{-}CF_2{-}CF_3$, and $CH_2{=}CH{-}CF_2{-}CF_2Br$), as well as $CF_2{=}CF_2$, were measured using the flash photolysis resonance fluorescence technique over the temperature range 250−370 K to give the following Arrhenius expressions: $k_{C_2F_3Br}(T) = (2.02^{+0.12}_{-0.12}) \times 10^{-12} \exp\{(396 \pm 18)/T\}$ cm^3 molecule^{-1} s^{-1}; $k_{C_2HF_2Br}(T) = (1.30^{+0.22}_{-0.18}) \times 10^{-12} \exp\{(370 \pm 47)/T\}$ cm^3 molecule^{-1} s^{-1}; $k_{C_3H_2F_3Br}(T) = (1.36^{+0.17}_{-0.14}) \times 10^{-12} \exp\{(317 \pm 34)/T\}$ cm^3 molecule^{-1} s^{-1}; $k_{C_4H_2F_5Br}(T) = (0.98^{+0.35}_{-0.26}) \times 10^{-12} \exp\{(369 \pm 90)/T\}$ cm^3 molecule^{-1} s^{-1}; $k_{C_4H_3F_4Br}(T) = (0.85^{+0.15}_{-0.12}) \times 10^{-12} \exp\{(201 \pm 46)/T\}$ cm^3 molecule^{-1} s^{-1}; $k_{C_2F_4}(T) = (3.39^{+0.22}_{-0.12}) \times 10^{-12} \exp\{(323 \pm 11)/T\}$ cm^3 molecule^{-1} s^{-1}. Ultraviolet absorption spectra of these brominated fluoroalkanes and bromoethene were measured between 164 and 276 nm. On the basis of these results, the atmospheric lifetimes were estimated to be 1.4, 2.4, 2.8, 3.2, 7.0, and 1.1 days, respectively. The general pattern of halolalkene reactivity toward OH is discussed.

Introduction

Despite their excellence as fire suppressants, the production of bromofluorocarbons (Halons) is being phased out because of the danger they pose to the Earth's stratospheric ozone layer. A number of nonbrominated substances have been proposed and tested, but the effort to find replacements continues to return to bromine-containing compounds because of the properties of bromine as a chemically active flame suppressant. One class of suppressants currently under consideration is the family of bromofluoroalkenes.[1] The presence of a carbon−carbon double bond is expected to render these substances highly reactive toward the hydroxyl radical, OH, resulting in an extremely short tropospheric lifetime, thereby limiting their delivery of bromine to the stratosphere where it can participate in ozone-destroying catalytic reactions. To quantify their atmospheric lifetimes, we have investigated the reactivity toward OH of five singly brominated fluoroalkenes, chosen to represent a variety of possible relative placements of bromine, fluorine, and hydrogen in relation to the double bond: $CFBr{=}CF_2$, $CHBr{=}CF_2$, $CH_2{=}CBr{-}CF_3$, $CH_2{=}CBr{-}CF_2{-}CF_3$, and $CH_2{=}CH{-}CF_2{-}CF_2Br$. Rate constants were measured over the temperature range 250 to 370 K. We also investigated the reactivity of $CF_2{=}CF_2$ toward OH over this temperature range. In addition, we have measured the ultraviolet absorption spectra of all of these compounds and bromoethene, $CHBr{=}CH_2$ down to 164 nm.

Experimental Section

Detailed descriptions of the apparatuses and the experimental methods used to measure the rate constants for the reactions of the various fluorinated alkenes with OH and the alkene absorption spectra are given in previous papers.[2−4] Therefore, only brief descriptions are given here.[23]

OH Reaction Rate Constant Measurements. The principal component of the flash photolysis−resonance fluorescence (FPRF) apparatus is a Pyrex reactor (of approximately 50 cm^3 internal volume) thermostated with water or ethanol circulated through its outer jacket. Reactions were studied in argon carrier gas (99.9995% purity) at a total pressure of 13.33 kPa (100.0 Torr). Flows of dry argon, argon bubbled through water thermostated at 276 K, and fluoroalkene mixtures (containing 0.01%−0.1% of the reactant diluted with argon) were premixed and flowed through the reactor at a total flow rate between 0.6 and 1.4 cm^3 s^{-1}, STP. The concentrations of the gases in the reactor were determined by measuring the mass flow rates and the total pressure with a MKS Baratron manometer. Flow rates of argon, the H_2O/argon mixture, and reactant/inert gas mixtures were measured by calibrated Tylan mass flow meters. Hydroxyl radicals were produced by the pulsed photolysis (1−4 Hz repetition rate) of H_2O (introduced via the 276 K argon/H_2O bubbler) by a xenon flash lamp focused into the reactor. The radicals were then monitored by their resonance fluorescence near 308 nm, excited by a microwave-discharge resonance lamp (330 Pa or 2.5 Torr of a ca. 2% mixture of H_2O in UHP helium) focused into the reactor center. The resonance fluorescence signal was recorded on a computer-based multichannel scanner (channel width 100 μs) as a summation of 1000−5000 consecutive flashes. The radical decay signal at each reactant concentration was analyzed as described by Orkin et al.[3] to obtain the first-order decay rate coefficient due to the reaction under study. At each temperature, the rate constant was determined from the slope of the decay rate versus haloalkene concentration plot using at least seven different concentrations.

All samples, except tetrafluoroethene, were used as supplied after several freeze/pump/thaw cycles. Bromoethene ($CHBrCH_2$,

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TABLE 1: Rate Constants Measured for the Reactions of OH with Haloalkenes

	$k(T)$,[a] 10^{-12} cm^3 molecule^{-1} s^{-1} (haloalkene concentration range, 10^{13} molecule/cm^3)					
T, K	$CF_2{=}CF_2$	$CFBr{=}CF_2$	$CHBr{=}CF_2$	$CH_2{=}CBr{-}CF_3$	$CH_2{=}CBr{-}CF_2{-}CF_3$	$CH_2{=}CH{-}CF_2{-}CF_2Br$
250	**12.3 ± 0.20** (0.39−2.96)	**9.79 ± 0.22** (0.39−2.96)	**5.79 ± 0.15** (0.77−6.60)	**4.87 ± 0.08** (0.78−4.52)	**4.23 ± 0.10** (1.56−5.40)	**1.92 ± 0.06** (3.12−15.2)
272		**8.67 ± 0.21** (0.36−2.72)	**5.05 ± 0.10** (1.43−5.44)	**4.33 ± 0.15** (1.43−5.44)	**3.87 ± 0.10** (0.35−4.48)	
298	**10.0 ± 0.15** (0.65−2.48)	**7.59 ± 0.15** (0.33−3.05)	**4.43 ± 0.08** (0.65−6.09)	**3.88 ± 0.15** (1.31−7.59)	**3.51 ± 0.07** (0.66−5.23)	**1.65 ± 0.04** (2.62−21.9)
330		**6.63 ± 0.13** (0.59−2.51)	**4.06 ± 0.05** (1.19−5.52)	**3.55 ± 0.10** (0.59−5.50)	**2.92 ± 0.06** (3.36−11.0)	
370	**8.09 ± 0.10** (0.26−2.45)	**5.89 ± 0.37** (0.26−1.53)	**3.55 ± 0.05** (1.06−4.92)	**3.22 ± 0.08** (2.11−9.82)	**2.68 ± 0.08** (2.11−9.82)	**1.48 ± 0.03** (2.63−17.7)

[a] Uncertainties represent statistical levels of confidence of 95% and do not include an estimated uncertainty of 4% associated with possible systematic errors.

99.5% purity, Matheson Gas Products), 1-bromo-2,2-difluoroethene ($CHBrCF_2$, 99.5+% purity, Ozone, St. Petersburg, Russia), and bromotrifluoroethene ($CFBrCF_2$, 99.5+% purity, Ozone, St. Petersburg, Russia) were used without any further purification. Tetrafluoroethene (CF_2CF_2, Union Carbide Corp.) was ca. 98% purity stabilized with ca. 1% of α-pinene with hexafluorocyclopropane (1%) and CO_2 (0.2%) as the main impurities. 2-Bromo-3,3,3-trifluoropropene (CH_2CBrCF_3) and 2-bromo-3,3,4,4,4-pentafluoro-1-butene ($CH_2CBrCF_2CF_3$) were at least 98% purity with corresponding bromine-free fluorinated alkenes as the main impurities (SynQuest Labs., Inc.). They could also contain corresponding 1-bromoalkenes and 1,2-dibromoalkanes as minor impurities. 4-Bromo-3,3,4,4-tetrafluoro-1-butene ($CH_2CHCF_2CF_2Br$, SynQuest Labs., Inc.) was at least 98% purity with $CH_2CHCF_2CF_2Cl$ and 2-methoxyethanol ($CH_3{-}O{-}CH_2{-}CH_2OH$) as possible impurities. The presence of the above-mentioned halogenated hydrocarbon impurities could not result in a noticeable overestimation of the measured rate constant because they are less reactive than the target compound. There are two impurities that cause concern: α-pinene and $CH_3{-}O{-}CH_2{-}CH_2OH$. Their OH reaction rate constants at room temperature are ca. 6×10^{-11} and 1.1×10^{-11} cm^3 molecule^{-1} s^{-1}, respectively,[5] and exceed the measured reaction rate constants of the target compounds, C_2F_4 and $CH_2{=}CHCF_2CF_2Br$. A sample of CF_2CF_2 was purified by passing through a −100 °C cold trap to decrease the α-pinene concentration from ca. 1% to below 0.03% (determined by UV absorption analysis near 220 nm). GC analysis of a $CH_2CHCF_2{-}CF_2Br$ sample for the presence of 2-methoxyethanol indicated less than ca. 0.1% of this impurity. Thus, these impurity levels are low enough to result in no noticeable overestimation of the measured rate constants (less than 0.2% and 1% for C_2F_4 and $CH_2CHCF_2CF_2Br$, respectively).

UV Absorption Cross Section Measurements. The absorption spectra of the bromofluoroalkenes were measured over the wavelength range of 160−280 nm using a single beam apparatus consisting of a 1-m vacuum monochromator equipped with a 600 lines/mm grating. The radiation source was a Hamamatsu L1385 deuterium lamp, and the detector was a Hamamatsu R166 photomultiplier. Spectra were recorded at increments of 0.5 nm at a spectral slit width of 0.5 nm. The pressure inside the 16.9 ± 0.05 cm absorption cell was measured by a MKS Baratron manometer at $T = 295 \pm 1$ K. Absorption spectra of the evacuated cell and of the cell filled with a gas sample were alternately recorded several times, and the absorption cross sections at the wavelength λ were calculated as

$$\sigma(\lambda) = \frac{\ln\{I_0(\lambda)/I_{[HA]}(\lambda)\}}{[HA]L}$$

where [HA] is the concentration of haloalkene in the absorption cell with the optical path length L. $I_0(\lambda)$ and $I_{[HA]}(\lambda)$ are the radiation intensities measured after the absorption cell when the haloalkene concentration was zero and [HA], respectively. The complete spectrum of each compound was constructed from data taken over several overlapping wavelength ranges. Data over each spectral range were obtained at several pressures to verify adherence to the Beer−Lambert absorption law. The coincidence of the contiguous parts of spectra taken over overlapping wavelength ranges was usually better than ca. 1%. The overall instrumental error associated with uncertainties in the path length, pressure, temperature stability, and measured absorbance was estimated to be less than 2% over most of the wavelength range, increasing to ca. 10%−20% at the long-wavelength ends of the spectra because of increased uncertainty in measuring low absorbance values. Different manometrically prepared mixtures containing 2%, 10%, and 100% of haloalkenes were used at total pressures in the cell ranging from 4 Pa to 120 kPa (0.03−900 Torr). There was no difference in the absorption cross sections obtained with different mixtures, and their use allowed a wider dynamic range in absorption measurements.

Results and Discussion

Kinetics. Rate constants measured for the reactions of hydroxyl radicals with the five bromofluoroalkenes and $CF_2{=}CF_2$ at different temperatures are listed in Table 1. The data are presented graphically in Figure 1, and the derived Arrhenius parameters are listed in Table 2, along with available data from the literature. To the best of our knowledge, there are no other results available on the reactivity of the bromofluoroalkenes studied in the present work. The $CF_2{=}CF_2$ reaction was studied at room temperature in two previous investigations[6,7] (see Table 2). A previous measurement from our laboratory[6] coincides with the present result. Acerboni et al.[7] measured the reaction by a relative rate technique with two different reference reactions. While their reported average value of the rate constant exceeds the present results, the quoted uncertainty is much larger than the disagreement.

The effect of fluorination on alkene reactivity is quite complicated. Nevertheless, one can speculate on the correlation between reactivity and structure of these halogenated alkenes. The room-temperature rate constants for the reactions of these and some other bromine/fluorine-substituted alkenes with the hydroxyl radical are listed in Table 3. Asymmetric fluorination of the olefinic carbon atom tends to lessen reactivity, whereas

TABLE 2: Arrhenius Parameters for OH Reactions of Br-Containing Fluoroalkenes and Their Estimated Atmospheric Lifetimes[a]

molecule	$A \times 10^{12}$, cm^3 molecule^{-1} s^{-1}	$E/R \pm \Delta E/R$, K	$k(298) \times 10^{12}$ cm^3 molecule^{-1} s^{-1}	atmospheric lifetime, days[b]
CF_2=CF_2	3.39 ± 0.22	-323 ± 11	9.98 ± 0.15 10.2 ± 0.5[6] 11.3 ± 3.3[7]	1.1
CFBr=CF_2	2.02 ± 0.12	-396 ± 18	7.62 ± 0.15	1.4
CHBr=CF_2	$1.30^{+0.22}_{-0.18}$	-370 ± 47	4.53 ± 0.10	2.4
CH_2=CBr$-CF_3$	$1.36^{+0.17}_{-0.14}$	-317 ± 34	3.94 ± 0.15	2.8
CH_2=CBr$-CF_2-CF_3$	$0.98^{+0.35}_{-0.26}$	-369 ± 90	3.39 ± 0.14	3.2
CH_2=CH$-CF_2-CF_2$Br	$0.85^{+0.15}_{-0.12}$	-201 ± 46	1.68 ± 0.05	7.0

[a] Uncertainties represent statistical levels of confidence of 95% and do not include estimated systematic errors. [b] Atmospheric lifetimes were estimated in the manner typically used for long-lived compounds. Such estimations assume a uniform tropospheric distribution that is not correct for short-lived compounds.

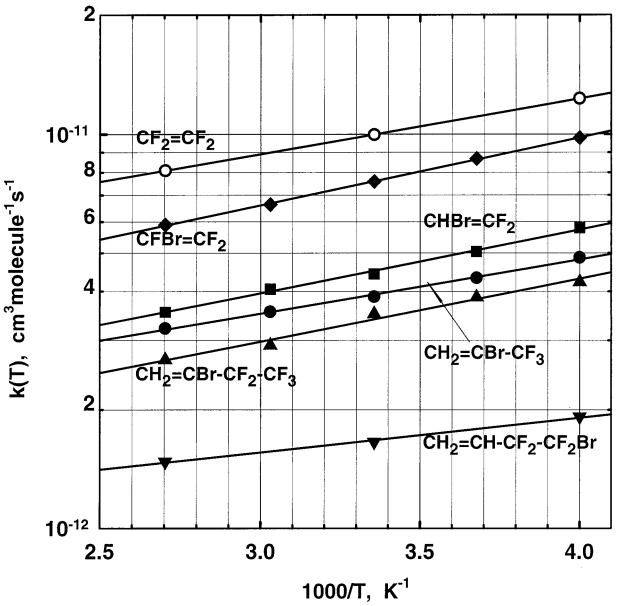

Figure 1. Arrhenius plot showing the average rate constants for the reactions of OH with halogenated alkenes obtained at each temperature. The solid lines are the least-squares fits to the data points with the Arrhenius parameters presented in Table 2.

TABLE 3: Hydroxyl Radical Reactivity toward Haloalkenes

molecule	$k(298) \times 10^{12}$, cm^3 molecule^{-1} s^{-1}	ref
CH_2=CH_2	9.0	20
CH_2=CHF	5.5	21
CH_2=CF_2	2.0	22
CF_2=CF_2	10.	this work
CHBr=CH_2	7.0	21
CFBr=CF_2	7.6	this work
CHBr=CF_2	4.5	this work
CH_2=CH$-CH_3$	30.	20
CH_2=CH$-CF_3$	1.5	6
CH_2=CF$-CF_3$	1.1	6
CF_2=CF$-CF_3$	2.2	6
CH_2=CBr$-CF_3$	3.9	this work
CH_2=CBr$-CF_2-CF_3$	3.4	this work
CH_2=CH$-CF_2-CF_2$Br	1.7	this work

further fluorination (yielding more symmetric substitution) compensates for the original deactivation. This can be seen from the reactivities of CH_2CH_2, CH_2CF_2, $CHFCH_2$, and CF_2CF_2. This suggests that the alkene reactivity toward OH depends mainly on the geometrical localization of π-electron density. The π-electron localization in the center of the C=C bond (CH_2=CH_2, CF_2=CF_2) promotes the OH addition reaction,

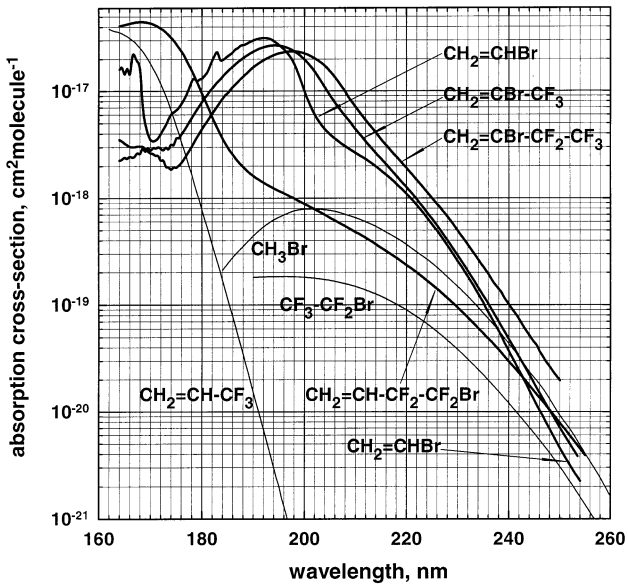

Figure 2. Ultraviolet absorption spectra of several CH_2=CBr$-$ containing haloalkenes and CH_2=CH$-CF_2-CF_2$Br at T = 295 K. Absorption spectra of CH_3Br,[8] CF_3-CF_2Br,[9] and CH_2=CH$-CF_3$[6] are shown for comparison purposes.

while the shift of the electron density toward the carbon atom (due to the high electron affinity of the F atom) obstructs it. It is interesting that the $-CF_3$ group adjacent to the double bond causes an even more pronounced deactivating effect than the F-atom despite the smaller electron affinity of $-CF_3$ and longer distance from the C=C double bond. This suggests the importance of a geometrical factor, as well as the electron affinity of the substitute, on the delocalization of π-electrons.

Bromination of the olefinic carbon located between the double bond and a fluorinated alkyl group increases the reactivity of fluorinated $C_{n\geq 3}$ alkenes, while Br on a remote carbon has essentially no effect. This suggests that the large electron rich Br atom shields the deactivating adjacent $-CF_3$ ($-C_2F_5$) group.

Ultraviolet Spectra. The ultraviolet absorption spectra of the halogenated alkenes obtained in this work are presented in Figures 2 and 3. The spectral data are provided in the Supporting Information and at www.nist.gov/kinetics/spectra/index.htm. These UV spectra reflect the interaction between π-electrons of the C=C double bond and the electrons of the bromine atom. The CH_2=CBr$-$ group has a very strong absorption with a maximum at 190$-$200 nm (see spectra for CH_2CHBr, CH_2-$CBrCF_3$, and $CH_2CBrCF_2CF_3$), which suppresses the distinctive shorter wavelength absorption of CH_2=CH$-$ group (see spectrum for CH_2CHCF_3 in Figure 2). The absorption in the

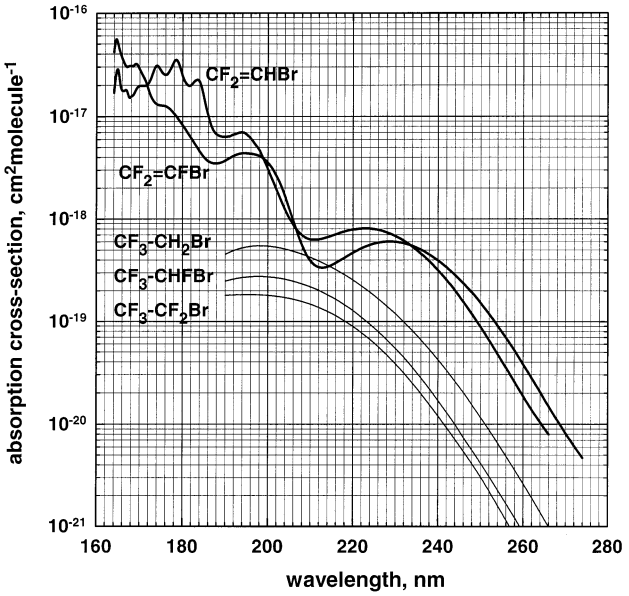

Figure 3. Ultraviolet absorption spectra of CF_2═CFBr and CF_2═CHBr at $T = 295$ K. Absorption spectra of bromofluoroalkanes[9,10] are shown for comparison purposes.

maximum is about 1.5 orders of magnitude higher than that of a bromoalkane such as CH_3Br[8] and is the strongest absorption exhibited by any brominated hydrocarbon in the region of the stratospheric transparency window near 200 nm. In contrast, the spectrum of CH_2═CH−CF_2−CF_2Br appears to be a superposition of absorption by a fluoroalkene[6] (such as CH_2-$CHCF_3$) and a bromofluoroalkane (such as CF_3CF_2Br[9]). The absorption spectra of Br-containing fluorinated ethenes (CHBr═CF_2 and CFBr═CF_2) are presented in Figure 3. In contrast with the CH_2═CBr− group, they exhibit a less-pronounced absorption at 190−200 nm while showing much stronger absorption at the shorter wavelengths. Their longest wavelength absorption bands are of slightly higher intensity than those of bromofluoroethanes[9,10] and are about 20−30 nm red-shifted (see Figure 3).

Atmospheric Implications. The atmospheric lifetimes of the alkenes under study can be estimated on the basis of the photochemical properties obtained in the present work. All of the compounds are very reactive toward OH, while their absorption cross sections for tropospheric UV radiation (above 290 nm) are negligible. Therefore, the reactions with hydroxyl radicals in the troposphere dictate their atmospheric lifetimes. A simple scaling procedure has proven to be valid for relatively long-lived compounds that are well-mixed throughout the troposphere. For such chemicals, lifetimes can be estimated using the equation[11]

$$\tau_i^{OH} = \frac{k_{MC}(270)}{k_i(270)}\tau_{MC}^{OH}$$

where τ_i^{OH} and τ_{MC}^{OH} are the atmospheric lifetimes of the compound of interest and methyl chloroform (MC), respectively, due to reactions with hydroxyl radicals in the troposphere only and $k_i(270)$ and $k_{MC}(270) = 5.78 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} (ref 8) are the rate constants for the reactions of OH with these substances at $T = 270$ K. The value of τ_{MC}^{OH} was obtained following the procedure used by Prinn et al.[12] from the measured lifetime of MC, $\tau_{MC} = 4.8$ years, when an ocean loss of 85 years and a stratospheric loss of 37 years are taken into account. Applying this method to the alkenes of this study yields the estimated atmospheric lifetimes listed in Table 2. As can be seen, the lifetimes derived here are very short, much shorter than the characteristic time of mixing processes in the troposphere, and hence are only crude estimates. The correct residence time of the compounds in the atmosphere will depend on the emission location and season, as well as local atmospheric conditions. Nevertheless, these estimations give a useful scaling among these alkenes and demonstrate that they are extremely short-lived in the atmosphere.

Note that these calculated lifetimes reflect the globally averaged sink for a compound due to its reaction with OH in the troposphere and, therefore, lie between the shortest local lifetimes in the tropical region and longest ones at high latitudes. Such lifetimes have clear physical meaning for long-lived chemicals that are well mixed in the troposphere following their emission. Such lifetimes can be used for quantitative analysis of chemical concentrations in the atmosphere. In the case of short-lived compounds, these calculated parameters should lie between the atmospheric lifetimes in the tropical and high latitude areas. Calculation of the entire range of real atmospheric lifetimes requires detailed 3-D modeling. In two recent papers, 3-D modeling was performed to study the atmospheric fate of 1-bromopropane, a short-lived compound with an estimated lifetime of 14.4 days using the above-mentioned scaling procedure. The detailed calculations resulted in lifetime ranges of 8−24 days[13] and 9−19.5 days[14] with the shorter values corresponding to tropical emission and the longer ones to emission at higher latitudes.

Using these rough lifetime estimates together with the measured UV absorption spectra, one can calculate approximate ozone depletion potentials (ODPs) for these chemicals. On the basis of an ODP for CF_3Br of 13 and a lifetime of 65 years,[15] ODP values considerably smaller than 0.01 are obtained for the bromofluoroalkenes studied. The determination of the correct ODP values requires 3D modeling calculations that consider local emission conditions. Moreover, based on the shortness of the lifetimes of the alkenes themselves, correct ODP values must take into account the lifetimes of any bromine-containing products resulting from the tropospheric oxidation of the alkenes. Therefore, it is important to estimate the total lifetime of Br atoms in the form of volatile degradation products produced in the oxidation processes initiated by the reactions of OH with Br-containing fluoroalkenes.

We can speculate on a possible degradation mechanism for Br-containing fluorinated alkenes in the atmosphere. It is worthwhile to point out that the production of a relatively long-lived bromine-containing degradation product is not likely for a compound with a brominated olefinic carbon (i.e., all of the bromoalkenes studied in the present work, except CH_2═CH−CF_2−CF_2Br). Because of the relatively weak C−Br bound, the Br atom can be quickly ejected to form either a carbonyl (C═O) or a hydroxyalkene (C═C−OH), depending on which olefinic carbon acquired OH in the initial addition reaction. Note that analogous processes are known in the oxidation of chlorinated compounds. Thus, C═O formation and Cl atom release are a part of kinetic scheme for the decomposition of hydrochlorofluoroalkanes (HCFCs) in the atmosphere.[16] Along similar lines, the release of Cl atom following the reaction of OH with *trans*-1,2-dichloroethene (CHCl═CHCl) has been directly observed.[17] In accordance with the kinetic scheme shown in Figure 4, the Br atom will probably be released immediately after the initial reaction between OH and brominated alkene in the lower troposphere (probably within minutes in the case of the C═O formation channel). Furthermore,

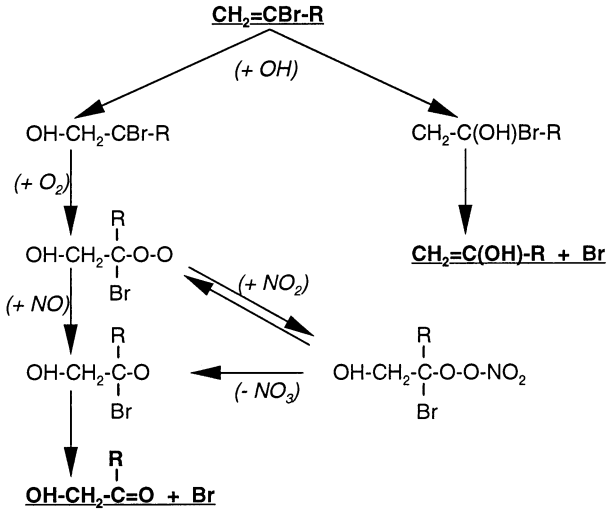

Figure 4. Kinetic scheme for the degradation of bromoalkenes of the form C═C−Br in the atmosphere.

haloalkylperoxynitrate formation cannot significantly increase the lifetime of bound bromine and therefore its transport to the stratosphere because of the short lifetime of such compounds due to thermal decomposition.[18,19]

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Supporting Information Available: The ultraviolet absorption cross sections of halogenated alkenes are presented in Table 4. This material is available free of charge via the Internet at http://pubs.acs.org.

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(23) Certain commercial equipment, instruments, or materials are identified in this article to adequately specify the experimental procedure. Such identification does not imply recognition or endorsement by the National Institute of Standards and Technology, nor does it imply that the material or equipment identified is necessarily the best available for the purpose.