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Rate Constants for the Reactions of OH with HFC-245cb ($CH_3CF_2CF_3$) and Some Fluoroalkenes (CH_2CHCF_3, CH_2CFCF_3, CF_2CFCF_3, and CF_2CF_2)

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The rate constant for the reaction of OH with HFC-245cb ($CH_3-CF_2-CF_3$) was measured by the flash photolysis resonance fluorescence technique over the temperature range 287−370 K in order to ascertain its atmospheric lifetime. Given the potential for trace levels of olefinic impurities to introduce errors into results of the rate constant measurements for low reactivity HFCs, considerable emphasis was placed on HFC purification and on demonstrating the utility of vacuum UV spectroscopy as a sensitive tool for detecting olefinic impurities in HFC samples. Measurements were also made of the OH rate constants for $CH_2{=}CH-CF_3$, $CH_2{=}CF-CF_3$, and $CF_2{=}CF-CF_3$, over the temperature range 252−370 K, and for $CF_2{=}CF_2$ at 298 K. Absorption spectra for the four fluoroalkenes as well as for ethene and propene were obtained from 160 to 220 nm.

Introduction

The internationally legislated elimination of chlorofluorocarbons (CFCs) from industrial applications, due to the established danger that they pose to Earth's ozone layer, has stimulated considerable study of the atmospheric properties of possible chemical substitutes. Partially fluorinated hydrocarbons (hydrofluorocarbons or HFCs) are among the leading environmentally acceptable CFC alternatives from the point of view of ozone depletion. Nevertheless, quantification of the possible role of HFCs as "greenhouse gases" requires accurate information on their atmospheric lifetimes, which are key parameters in determining the environmental consequences following their release into the atmosphere. HFCs typically have very low absorption cross sections at the wavelengths of solar radiation that penetrate the troposphere, and thus, their atmospheric lifetimes are dictated primarily by their reactivity with tropospheric hydroxyl radicals. This has provided the motivation for the present study of the OH reactivity toward HFC-245cb ($CH_3-CF_2-CF_3$), which is currently a candidate for replacement of CFC-12 (CF_2Cl_2) in some refrigeration applications.

Highly fluorinated alkanes are usually not very reactive toward OH, and consequently, the determination of the absolute rate constants can be easily compromised by the presence of reactive microimpurities in the samples studied. Fluorinated alkenes are the most likely reactive impurities in HFCs, being present as residual starting material from production or as decomposition products. Gas chromatography (GC) has been and currently is the principal technique for determining sample purity but, despite its high sensitivity, can have difficulties associated with incomplete separation of certain compounds. Thus, the possibility always exists that some olefinic impurities may not be chromatographically resolved from the main compound and, therefore, remain undetected. Unsaturated hydrocarbons, however, manifest very strong absorption bands in the far UV spectral region, thereby offering the possibility of using UV absorption as a sensitive diagnostic for detecting such impurities in nonabsorbing gases. We measured UV absorption spectra of several fluorinated propenes, perfluoroethene, propene, and ethene to determine the effect of fluorination on the UV absorption properties of alkenes and to ascertain the possible role of far UV absorption spectroscopy as an analytical supplement for determining the presence of unsaturated impurities in HFC samples.

To quantify the uncertainty in the rate constant due to any remaining olefinic impurities, we also measured the OH reactivity of several fluoroalkenes. The gas-phase reactions of hydroxyl radicals with alkenes are of both fundamental and practical importance. OH−alkene reactions follow a complex mechanism involving adduct formation near room temperature, with direct hydrogen atom abstraction becoming increasingly important at higher temperatures.[1] While there are many studies of OH reactions with a variety of unsaturated hydrocarbons, only limited information is available for fluorinated alkenes. For the ethenes, $CH_2{=}CHF$[2] and $CH_2{=}CF_2$[3] have slightly lower OH reactivity than that of ethylene.[4] However, in the case of hexafluoropropene ($CF_2{=}CF-CF_3$),[5] the reactivity towards OH is more than an order of magnitude less than that of propene itself.[4] There are no other studies of fluoroalkene reactivity. Hence, we present in this paper results of our measurements of rate constants for the OH reactions with three fluorinated propenes ($CH_2{=}CH-CF_3$, $CH_2{=}CF-CF_3$, and $CF_2{=}CF-CF_3$) and $CF_2{=}CF_2$.

Experimental Section[19]

Detailed descriptions of the apparatuses and the experimental methods used to measure the rate constants for the reactions of HFC-245cb and the various fluorinated olefins with OH and the olefin absorption spectra are given in previous papers.[6−9] Therefore, only brief descriptions are given here.

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 methanol 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 HFC or fluoroalkene mixtures (containing 0.1−0.2% of the reactant diluted with argon or C_2F_6) were premixed and flowed through the reactor at a total flow

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TABLE 1: Rate Constants Measured in the Present Work for the Reactions of OH with HFC-245cb and Several Fluoroalkenes[a]

	k_i, 10^{-12} cm^3 molecule^{-1} s^{-1}				k_{245cb}, 10^{-15} cm^3 molecule^{-1} s^{-1}
temp, K	$CH_2{=}CH{-}CF_3$	$CH_2{=}CF{-}CF_3$	$CF_2{=}CF{-}CF_3$	$CF_2{=}CF_2$	$CH_3{-}CF_2{-}CF_3$
252	1.72 ± 0.08 (1)	1.10 ± 0.05 (1)	2.83 ± 0.14 (2)		
277	1.59 ± 0.08 (2)	1.10 ± 0.03 (3)	2.50 ± 0.02 (3)		
287					1.23 ± 0.04 (1)
298	1.54 ± 0.05 (4)	1.12 ± 0.02 (6)	2.17 ± 0.01 (5)	1.02 ± 0.05 (3)	1.54 ± 0.04 (3)
313					2.00 ± 0.05 (1)
330	1.43 ± 0.03 (1)	1.15 ± 0.04 (2)	1.88 ± 0.04 (3)		2.54 ± 0.02 (3)
349					3.44 ± 0.04 (2)
370	1.37 ± 0.03 (2)	1.18 ± 0.05 (4)	1.73 ± 0.04 (4)		4.67 ± 0.11 (3)

[a] Error bars are levels of confidence of 95% and do not include estimated systematic errors. Numbers in parentheses indicate the number of experimental measurements.

rate between 0.5 and 1.2 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 both argon and the H_2O/argon mixture were measured by calibrated Tylan mass flow meters, whereas those of the reactant/inert gas mixtures were determined by direct measurements of the rate of pressure change in a calibrated volume. 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 (280 Pa or 2.1 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 1000−10 000 consecutive flashes. The radical decay signal at each reactant concentration was analyzed as described by Orkin et al.[7] to obtain the first-order decay rate due to the reaction under study (τ_i^{-1}).

UV Absorption Cross-Section Measurements. The absorption spectra of the pure alkenes and the gas mixtures (i.e., HFC with alkene impurities) to be analyzed were measured over the wavelength range of 160−220 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 either 0.5 or 0.1 nm at spectral slit widths of 0.5 and 0.1 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 were calculated from the differences. The complete spectra were constructed from data taken over several overlapping wavelength ranges. Data over each range were obtained at several pressures to verify adherence to the Beer−Lambert absorption law. The overall instrumental error associated with uncertainties in the path length, pressure, temperature stability, and the measured absorbance was estimated to be less than 2% over most of the wavelength range, increasing to approximately 5−10 % at the long-wavelength ends of the spectra. Mixtures containing 2%, 10%, and 100% of the olefins under study were used at pressures in the cell ranging from 4 Pa to 120 kPa (0.03−900.0 Torr).

Sample Purity. All samples were first analyzed after several freeze/pump/thaw cycles by GC and GC/MS techniques. Hexafluoropropene, $CF_2{=}CF{-}CF_3$ (PCR Corp.), was 98.8% purity with the identified impurities being C_3F_8 (0.31%), CO_2 (0.28%), and $CF_2{=}CH{-}CF_3$ (ca. 0.21%). The sample of 3,3,3-trifluoropropene, $CH_2{=}CH{-}CF_3$ (Pfaltz & Bauer, Inc.) had no detectable impurities after outgassing. The original sample of tetrafluoroethene, $CF_2{=}CF_2$ (Union Carbide Corp.), was ca. 98% purity stabilized with ca. 1% of α-terpinene. Hexafluorocyclopropane, C_3F_6 (ca. 1%), and CO_2 (0.2%) were found as the main impurities after purification of the original sample by passing through a −100 °C cold trap to remove the inhibitor. Samples of propene for UV spectrum measurements were obtained from Matheson (>99.6% purity, with 0.38% of propane as a main impurity) and Philips Petroleum Co. (>99.9% purity, with propane as a main impurity). The sample of ethene was obtained from Philips Petroleum Co. (>99.99% purity, with methane and ethane as the main impurities).

A sample of HFC-245cb ($CH_3{-}CF_2{-}CF_3$), obtained from PCR Corp., had a stated purity of ca. 99%. Nevertheless, the sample was found to contain $CH_2{=}CF{-}CF_3$ (ca. 6.5%), CH_3F (0.34%), CH_3CF_3 (0.2%), CO_2 (0.03%), CHF_2CHF_2 (0.11%), and CH_2F_2 (0.013%). (This original "mixture" was actually used to measure the rate constant for the reaction between 2,3,3,3-tetrafluoropropene and OH as well as to determine its UV cross sections.) A bromine purification/titration technique described in the Appendix was employed to prepare samples of $CH_3{-}CF_2{-}CF_3$ of acceptable purity for kinetic measurements and also to quantify the concentration of $CH_2{=}CF{-}CF_3$. UV absorption measurements were used to analyze the residual olefin concentration following bromine purification. One purified sample was sent out for independent analysis at Allied Signal Inc. using GC and GC/MS techniques.

Results and Discussion

Rate constants for the reactions of hydroxyl radicals with the four fluorinated alkenes at different temperatures are listed in Table 1 as well as those for the reaction with $CH_3{-}CF_2{-}CF_3$. The data were fit to the Arrhenius equation, and the resulting parameters are given in Table 2. The data are plotted in Arrhenius form in Figure 1 (fluoropropenes) and Figure 2 (HFC-245cb). Also presented in Table 2 and Figure 1 are the only available literature data (for $CF_2{=}CF{-}CF_3$).

Reactions of OH with Fluoroalkenes. The rate constants for the reaction between OH and $CF_2{=}CF{-}CF_3$ measured in the present work agree reasonably well with those from McIlroy and Tully,[5] the only available study for comparison. Differences range from 5 to 15% over the common temperature range. Note that the results of these investigators over an extended temperature range[5] show non-Arrhenius rate constant behavior, similar to that for other OH/alkene reactions.[1] No other measurements of the reactions between OH and fluorinated propenes are available for comparison.

All of the fluoropropenes studied here contain the $-CF_3$ group, but differ in the extent of fluorine substitution at the olefinic carbon atoms. From Table 3 it can be seen that the

TABLE 2: Arrhenius Parameters for Reactions of OH with Fluoroalkenes and HFC-245cb[a]

molecule	$A \times 10^{13}$, cm^3 molecule^{-1} s^{-1}	$E/R \pm \Delta E/R$, K	$k_{HFC}(298) \times 10^{12}$ cm^3 molecule^{-1} s^{-1}	ref
$CH_2{=}CH{-}CF_3$	$8.28^{+0.75}_{-0.69}$	−183 ± 26	1.52 ± 0.02	this work
$CH_2{=}CF{-}CF_3$	$14.1^{+1.3}_{-1.2}$	64 ± 27	1.13 ± 0.02	this work
$CF_2{=}CF{-}CF_3$	$5.66^{+1.9}_{-1.4}$	−407 ± 85	2.21 ± 0.08	this work
	$8.88^{+1.4\,b}_{-1.2}$	−281 ± 49[b]	2.28 ± 0.05[b]	McIlroy and Tully[5]
$CF_2{=}CF_2$			10.2 ± 0.05	this work
$CH_3{-}CF_2{-}CF_3$	$4.41^{+0.90}_{-0.75}$	1690 ± 60	$(1.52 \pm 0.04) \times 10^{-3}$	this work

[a] Error bars are levels of confidence of 95% and do not include estimated systematic errors. [b] An Arrhenius fit to the data over $T = 293{-}378$ K only. The rate constant was measured by McIlroy and Tully[5] over $T = 293{-}831$ K.

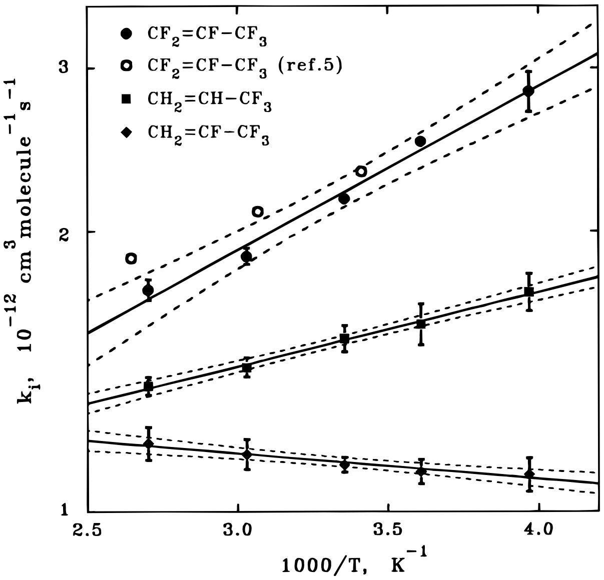

Figure 1. Arrhenius plots of rate constants for the ractions of OH with fluoropropenes. Solid lines are the least-square fits to our data; dashed lines are their 95% confidence intervals.

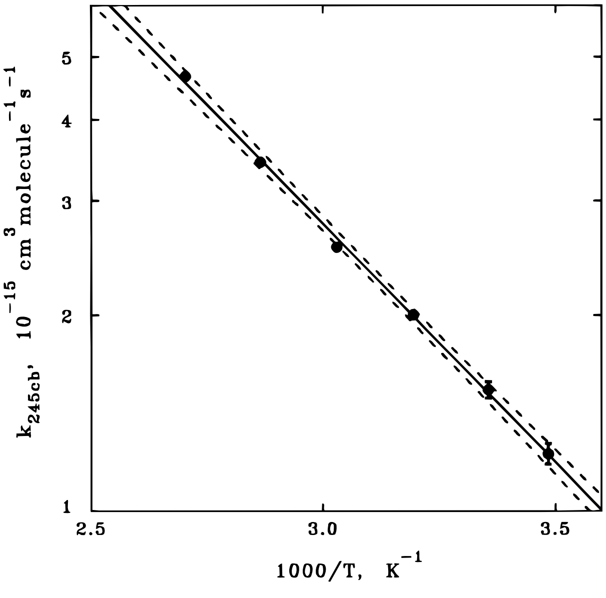

Figure 2. Arrhenius plot of the measured k_{245cb} values and the least-squares fit to our data (solid line) with its 95% confidence intervals (dashed lines).

presence of the $-CF_3$ group results in more than an order of magnitude decrease in room-temperature reactivity toward OH relative to that for propylene. Fluorination of the olefinic carbon atoms results in only small additional changes in reactivity, similar to the behavior observed for the fluorinated ethenes.[2,3] Specifically, $CH_2{=}CF{-}CF_3$ is slightly less reactive than $CH_2{=}CH{-}CF_3$, while $CF_2{=}CF{-}CF_3$ is slightly more reactive.

TABLE 3: Rate Constants at 298 K for Radical Addition to Fluorinated Propenes and Ethenes (Relative to the Propylene and Ethylene, Respectively)[a]

alkene	addition of O atoms	addition of OH radicals	addition of H atoms
$CH_2{=}CH{-}CH_3$	1.0	1.0	1.0
$CH_2{=}CF{-}CH_3$	0.5		0.95
$CF_2{=}CH{-}CH_3$	0.45		
$CH_2{=}CH{-}CH_2F$	0.21		0.67
$CH_2{=}CH{-}CF_3$	0.01	0.051	0.3
$CH_2{=}CF{-}CF_3$		0.039	
$CF_2{=}CF{-}CF_3$	0.007	0.072	<0.02
$CH_2{=}CH_2$	1.0	1.0	1.0
$CH_2{=}CHF$	0.5	0.61	0.44
$CH_2{=}CF_2$	0.3	0.44	0.33
$CHF{=}CHF$	0.4		
$CHF{=}CF_2$	0.6		0.06
$CF_2{=}CF_2$	1.4	1.13	0.07

[a] Evaluated on the basis of results of published studies listed in the NIST Kinetics Database[18] as well as on results obtained in the present work.

The fluoropropenes may also be considered as derived from ethene and fluoroethenes by substitution of CF_3 for H or F. Going from $CH_2{=}CH_2$ to $CH_2{=}CH{-}CF_3$ results in a reduction of the rate constant by a factor of 6; going from $CH_2{=}CHF$ to $CH_2{=}CF{-}CF_3$ lowers the rate constant by a factor of 5 ($k_{C_2H_4}/k_{C_3H_6} \cong 0.3^4$). Replacing the fluorine in $CH_2{=}CHF$, $CH_2{=}CF_2$, and $CF_2{=}CF_2$ by CF_3 to make $CH_2{=}CH{-}CF_3$, $CH_2{=}CF{-}CF_3$, and $CF_2{=}CF{-}CF_3$ results in reducing the reactivity by factors of approximately 4.

The effects of fluorine substitution in alkenes on their OH addition reactivity are very similar to those for O atom addition. This can be seen from Table 3, in which relative rate constants for the reactions between O and various fluoropropenes and fluoroethenes are also presented. Fluorination of any olefinic carbon results in small reactivity decreases (less than a factor of 2) in both the propenes and ethenes. However, fluorination of the $-CH_3$ group in the propenes results in a more pronounced decrease in O atom reactivity (a factor of 5 in the case of $-CH_2F$ and 2 orders of magnitude in the case of $-CF_3$). Thus, results of both the OH radical and O atom addition reactions studies suggest that fluorination of olefinic carbons does not affect π-electron density in the double bond very much, in contrast with fluorination of the carbon adjacent to the olefinic group. Relative reactivity data for H atom addition to fluorinated ethenes and propenes are also presented in Table 3. In these cases, the reactions appear to be very sensitive to complete fluorination of the olefinic carbon atoms, with more moderate decreases in reactivity caused by fluorination of the $-CH_3$ group in propylene.

Reaction of OH with HFC-245cb ($CH_3{-}CF_2{-}CF_3$). As discussed earlier, the purification procedure used in this work resulted in $CH_3{-}CF_2{-}CF_3$ samples of sufficient purity for accurate rate constant determinations. Even for the lowest temperature rate constant measurements, residual reactive impurities in the samples were at concentrations low enough to avoid any significant overestimation of the measured rate constant. For example, the fluoropropene rate constants reported here indicate that a 0.002% residual olefinic impurity could contribute a maximum of 2% to our measured room-temperature rate constant for HFC-245cb. Recall that the 0.002% upper limit for residual olefinic impurities was verified for the samples by UV analyses. The purified sample analyzed at Allied Signal Inc. contained the highest level of residual unsaturated impurities, a finding confirmed by our UV measurements. Nevertheless, even the ca. 0.006% of residual tetrafluoropropene found in that sample could result in a maximum rate constant error of approximately 6% at room temperature. The order of magnitude lower concentration of another fully halogenated unsaturated compound ($C_3F_4Br_2$) would have virtually no effect on the measured rate constant. The reactivity of $CH_2Br-CFBr-CF_3$ toward OH should be similar to the reactivity of CH_2Br-CF_3[10] and therefore is sufficiently low that any possible error due to the trace remaining concentration of this primary product of bromination (0.012% as determined in the Allied Signal analysis) is negligible.

There are no published data on the rate constant for the reaction of OH with HFC-245cb with which we can compare the present results. The A factor obtained from an Arrhenius fit to the data (4.4×10^{-13} cm^3 molecule^{-1} s^{-1}) is smaller than obtained for other OH abstraction reactions involving a $-CH_3$ group in haloalkanes. However, there is no statistically significant curvature in the temperature dependence obtained which could result in the calculation of both low A and E/R factors. The obtained temperature dependence, $E/R = 1692$ K, is similar to that reported[10] for other F_5 and higher fluorinated propanes with the exception of HFC-236fa ($CF_3-CH_2-CF_3$). The E/R for HFC-236fa is approximately 2500 K, while E/R values for other HFC-236 isomers and several HFC-235 isomers range from 1330 to 1750 K.[10]

We can compare the HFC-245cb rate constant with that for the reaction of OH with CH_3-CF_3 (HFC-143a), for which we would expect similar reactivity. However, it is first instructive to briefly examine the existing literature data for OH + HFC-143a. The Arrhenius parameters derived from a fit to our earlier HFC-143a data ($A = 0.95 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}; $E/R =$ 1980 K)[7] differ slightly from the presently recommended parameters ($A = 1.8 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}; $E/R = 2170$ K) which are based on results of two absolute[7,11] and one relative[12] reaction studies. All the data points are in good agreement but result in somewhat different Arrhenius parameters derived from the individual data sets. The highest values of the A factor and E/R come from the absolute measurements by Talukdar et al.,[11] who reported $k_{143a} = 2.12 \times 10^{-12}$ $\exp(-2200/T)$ cm^3 molecule^{-1} s^{-1}. These authors derived this value from a fitting of the data obtained in two independent sets of experiments performed by using different experimental techniques over somewhat different temperature ranges. However, analysis of the data from the two techniques independently results in slightly smaller temperature dependencies and lower A factors. For example, the flash photolysis/laser-induced fluorescence (FP/LIF) measurements result in $A = 1.01^{+0.39}_{-0.28} \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} and $E/R = 2015 \pm 93$ K with the average temperature of 289 K, while the discharge flow/laser magnetic resonance (DF/LMR) measurements result in $A = 1.21^{+0.64}_{-0.42} \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} and $E/R = 2005 \pm 132$ K with the average temperature of 313 K. The higher values of both A and E/R factors reported by authors[11] and used in data evaluations[10] appear to be the result of combined fitting to the slightly higher DF/LIF data at higher temperatures together with the slightly lower RF/LIF data at lower temperatures.

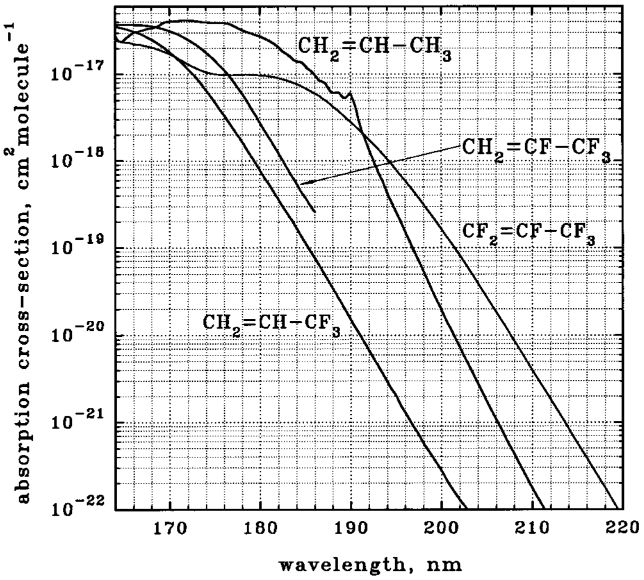

Figure 3. Ultraviolet absorption cross sections of propylene and fluoropropylenes at $T = 295$ K.

An Arrhenius fitting of the relative data by Hsu and DeMore[12] with methane as a reference compound using the latest evaluation[10] of the rate constant for the reaction of OH with CH_4 results in $A = 1.04^{+1.05}_{-0.52} \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} and $E/R = 1998 \pm 231$ K, which are both slightly lower than those presented in the original paper.[12] The relative rate data using CHF_2-CF_3 (HFC−125) as a reference compound[12] yielded $A = 1.21^{+0.28}_{-0.22} \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} and $E/R = 2070 \pm 68$ K. Thus, all of the individual absolute and relative studies of the reaction between OH and HFC-143a appear more consistent with an E/R of approximately 2000 K and an A factor of approximately 1.1×10^{-12} cm^3 molecule^{-1} s^{-1} than with the values currently recommended. An unweighted ln(k) vs $1/T$ fitting of all the available data points also results in $k_{143a} = 1.15^{+0.4}_{-0.3} \times 10^{-12} \exp\{-(2030 \pm 100)/T\}$ cm^3 molecule^{-1} s^{-1} with $k_{143a}(298) = (1.27 \pm 0.06) \times 10^{-15}$ cm^3 molecule^{-1} s^{-1}. (All uncertainties quoted above are the 95% confidence intervals).

Thus the replacement of the $-CF_3$ group (in HFC-143a) by $-CF_2-CF_3$ (to form HFC-245cb) results in a decrease in both A and E/R. The net result is a room-temperature rate constant for HFC-245cb that is actually higher by approximately 20%.

The comparative effects of CF_3 and C_2F_5 may also be derived from studies of the reactions of OH with $CF_3-CH_2-CH_2-CF_3$ (HFC-356mff)[13,14] and CF3$-CF_2-CH_2-CH_2-CF_2-CF_3$ (HFC-55-10-mcff).[13] The ratio of recommended rate constants[10] at room temperature ($k_{55-10-\mathrm{mcff}}(298)/k_{356\mathrm{mff}}(298)$) is almost identical to that for $k_{245\mathrm{cb}}(298)/k_{143\mathrm{a}}(298)$. There are no temperature dependence data for $k_{55-10-\mathrm{mcff}}$ available to compare changes in Arrhenius parameters. Additional measurements of such substituted analogs would be extremely useful to improve our understanding of the effects of fluorine substitution on molecular reactivity.

An Atmospheric Lifetime of HFC-245cb ($CH_3-CF_2-CF_3$). As mentioned earlier, reaction with tropospheric hydroxyl radicals is the primary removal process for HFCs in the atmosphere. Thus, the atmospheric lifetime of HFC-245cb ($\tau_{245\mathrm{cb}}$) can be estimated using a simple scaling procedure:

$$\tau_{245\mathrm{cb}}^{\mathrm{OH}} = \frac{k_{\mathrm{MC}}(277)}{k_{245\mathrm{cb}}(277)} \tau_{\mathrm{MC}}^{\mathrm{OH}}$$

where $\tau_{245\mathrm{cb}}^{\mathrm{OH}}$ and $\tau_{\mathrm{MC}}^{\mathrm{OH}} = 5.7$ years are the atmospheric lifetimes

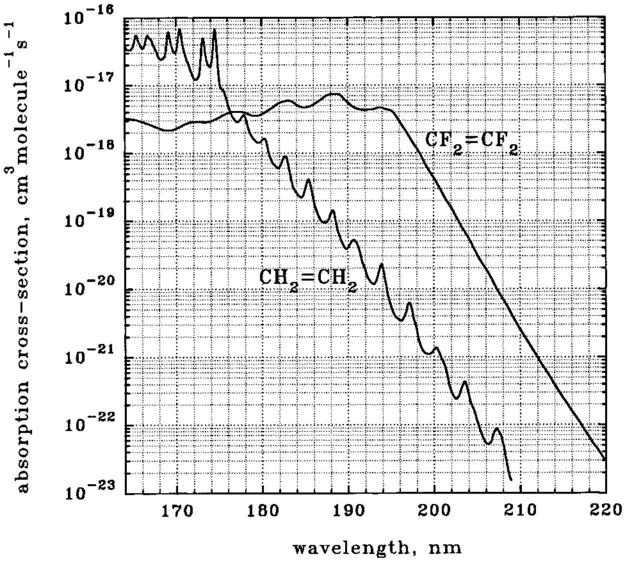

Figure 4. Ultraviolet absorption cross sections of ethylene and tetrafluoroethylene at $T = 295$ K.

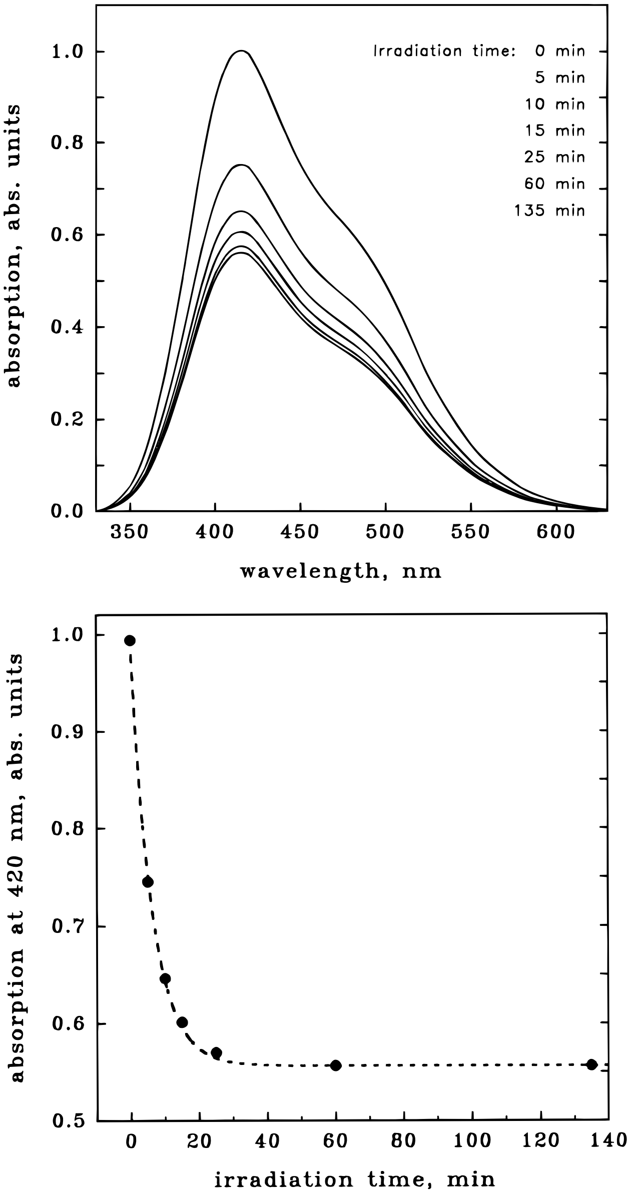

Figure 5. Absorption spectra of a mixture of 13.73 kPa (103 Torr) of an original HFC-245cb sample and 2.00 kPa (15.0 Torr) of Br_2 during irradiation. Change of the absorption maximum in Figure 1a with the time. Dashed line is a result of fitting $A = 0.56 + 0.43 \exp\{-t/6.2\}$.

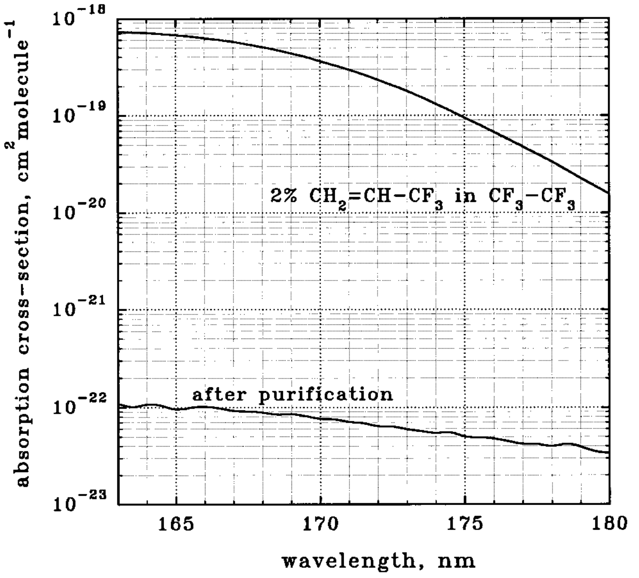

Figure 6. Absorption spectra of the "artificial" 2% mixture of 3,3,3-trifluoropropene in C_2F_6 before and after "bromine" purification.

of $CH_3-CF_2-CF_3$ and methyl chloroform (MC), respectively, due to reactions with hydroxyl radicals in the troposphere, and $k_{245cb}(277)$, $k_{MC}(277) = 6.69 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} are the rate constants for the reactions of OH with these substances at $T = 277$ K. Such estimation results in $\tau_{245cb}^{OH} = 38.9$ years. As we have discussed in previous paper,[7] the value of τ_{245cb}^{OH} thus obtained should be a reasonably good estimate for the total atmospheric lifetime of such a well-mixed atmospheric compound for which photodissociation by long-wavelength solar UV radiation is not appreciable.

UV Spectra. The UV spectra measured in the present work for propene and three fluorinated propenes are presented in Figure 3. Propene exhibits an unresolved diffuse band at wavelengths below 190 nm. Variation in the instrumental spectral resolution by a factor of 5 resulted in no change in the spectrum obtained. The measured absorption cross sections coincide well (within 10% for $\lambda < 200$ nm) with those measured by Fahr and Nayak.[15] The fluorinated propenes similarly display continuous spectra with the highest absorption occurring at short wavelengths.

Note that maximum absorption cross sections for the fluorinated propenes between 160 and 180 nm exceed 2×10^{-17} cm^2 molecule^{-1}, typical for the majority of unsaturated hydrocarbons over the 170−180 nm range (see ref 16 for example). Nevertheless, fluorination of propene suppresses the short-wavelength absorption maximum somewhat and shifts the location of the maximum to shorter wavelength. Perfluorination of ethene results in the largest change in maximum absorption cross section and a red shift in its location: $\sigma_{max} \cong 0.75 \times 10^{-17}$ cm^2 molecule^{-1} at $\lambda \cong 188.5$ nm vs $\sigma_{max} \cong 6 \times 10^{-17}$ cm^2 molecule^{-1} at $\lambda \cong 170$ nm for $CH_2{=}CH_2$ (see Figure 4).

As indicated earlier, the strong UV absorption of the fluorinated alkenes provided a convenient diagnostic for checking purified samples for the presence of residual olefinic impurities. In particular, the high absorption cross section for 2,3,3,3-tetrafluoropropene ($\sigma_{165nm} \cong 3.8 \times 10^{-17}$ cm^2 molecule^{-1}) permits its detection at the parts per million level in a 1 atm sample in our 17 cm absorption cell (every 1 ppm would result in a 1.5% absorption). Thus, detection of trace olefinic impurities at the ppm level is easily accomplished even with a single beam photometric technique using a relatively short absorption cell. Figure 6 shows an example of such application. This methodology may prove useful, particularly in industrial applications, for analyzing the purity levels of fluorinated hydrocarbons being considered as possible substitutes for CFCs and halons.

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Appendix

Bromination of the HFC-245cb Sample. A chemical titration of the olefinic group (C═C) with Br_2 was used to determine the $CH_2{=}CF{-}CF_3$ concentration in mixtures used for both the OH reaction and UV spectrum measurements. For this determination, an HFC-245cb sample containing $CH_2{=}CF{-}CF_3$ was added to a 7.5 cm long, 1.9 cm i.d., absorption cell along with an excess of Br_2 over the olefinic impurity. The molecular bromine concentration was determined from its absorption near a band maximum in the range 400−430 nm by using a Shimadzu UV-160 double-beam spectrophotometer. The pressure of Br_2 in the cell as well as the total pressure after adding the mixture to be analyzed was measured using an MKS Baratron manometer. After verifying the absence of any dark reaction, the cell was exposed to irradiation from a tungsten lamp fitted with a glass filter with a cutoff at approximately 350 nm. Molecular bromine photodissociation initiates a chain reaction by which the alkene double bonds become brominated.

$$\mathrm{Br_2} \xrightarrow{(+h\nu)} {}^{\bullet}\mathrm{Br} + {}^{\bullet}\mathrm{Br}$$

$$\begin{aligned} &{}^{\bullet}\mathrm{Br} + \mathrm{CH_2{=}CF{-}CF_3} \xrightarrow{(+\mathrm{M})} \\ &\qquad \mathrm{CH_2Br{-}{}^{\bullet}CF{-}CF_3\ ({}^{\bullet}CH_2{-}CFBr{-}CF_3)} \end{aligned}$$

$$\begin{aligned} &\mathrm{CH_2Br{-}{}^{\bullet}CF{-}CF_3\ ({}^{\bullet}CH_2{-}CFBr{-}CF_3)} + \mathrm{Br_2} \rightarrow \\ &\qquad \mathrm{CH_2Br{-}CFBr{-}CF_3} + {}^{\bullet}\mathrm{Br} \end{aligned}$$

$${}^{\bullet}\mathrm{Br} + {}^{\bullet}\mathrm{Br} \xrightarrow{(+\mathrm{M})} \mathrm{Br_2}$$

Since the irradiation light wavelengths used were capable of photodissociating Br_2 but not the bromoalkane product,[10,17] this process should result in complete olefin removal from the mixture. Thus, the change in Br_2 concentration, as measured via UV absorption after a sufficiently long period of irradiation, should be equal to the initial concentration of the olefin:

$$[\mathrm{CH_2{=}CF{-}CF_3}]_{t=0} = [\mathrm{Br_2}]_{t=0} - [\mathrm{Br_2}]_{t\to\infty}$$

The change in bromine UV absorption with irradiation time for a typical titration/purification experiment is shown in Figure 5a,b. Experiments performed with various initial Br_2 concentrations (i.e., different bromine/olefin initial concentration ratios) and irradiation intensities resulted in no significant difference in the olefin concentration determined.

To prepare samples of $CH_3{-}CF_2{-}CF_3$ acceptable for kinetic studies, the bromination process was performed in a 2 L glass bulb with an excess of molecular bromine over the olefinic impurity. Upon completion of the bromination process, the mixture contained only HFC-245cb, the saturated product of the bromination (the fluorobromoalkane), and molecular bromine. The product of bromination, $CH_2Br{-}CFBr{-}CF_3$, is a liquid at room temperature, and the condensed liquid product was removed from the bulb before further treatment. The sample was then washed with distilled water to remove the residual bromine. UV absorption measurements on both the gas sample and the outgoing water were used to determine the point at which all bromine was removed. The remaining gas-phase sample was purified via low-temperature fractional distillation to remove both water vapor and any fluorobromoalkane that remained. The efficiency of this distillation process can be easily verified by GC analysis since, unlike the alkene impurity, the heavy corresponding bromoalkane can be fully separated on the chromatographic column.

The efficiency of the whole purification process was tested on manometrically prepared mixtures of 0.2% and 2% $CH_2{=}CH{-}CF_3$ in C_2F_6 and 6.5% $CF_2{=}CF{-}CF_3$ in C_2F_6. A Shimadzu GC-9A gas chromatograph with a thermal conductivity detector was used to analyze samples before and after purification. For these mixtures, the olefinic impurity peak was sufficiently resolved from the main C_2F_6 peak that residual impurities at the ppm level could be detected. In both cases, the residual concentration of fluoropropenes in purified mixtures was less than 0.001%. We also used UV absorption measurements to analyze for the presence of residual alkenes. Figure 6 shows the result of such an analysis for the CH_2CHCF_3/C_2F_6 mixture.

Since the primary purpose of the bromine purification procedure was to prepare HFC samples of sufficient purity to be used for OH reaction studies, we measured OH decay rates using the bromine-treated test samples as a direct check on possible kinetic problems associated with residual bromoalkanes, alkenes, or molecular bromine. We first verified the efficiency of the molecular bromine wash-out by making kinetic measurements on a mixture of only C_2F_6 and Br_2 (i.e., no alkene added). The rate constants for the reactions of OH with pure C_2F_6, C_2F_6 treated with bromine, and C_2F_6 plus alkene treated with bromine were all determined as being less than ca. 2×10^{-17} cm^3 molecule^{-1} s^{-1}. This is effectively the lower limit of rate constant measurement by our technique and thus indicates the maximum possible error in a measured rate constant resulting from any residual molecular bromine.

In the case of HFC-245cb, reliable detection of small residual alkene impurities could not be achieved using our presently available gas chromatograph equipped with a thermal conductivity detector, due to the insufficient difference in chromatographic retention times of 2,3,3,3-tetrafluoropropene and the HFC itself (1,1,1,2,2-pentafluoropropane). Therefore, UV absorption technique was used to verify the extent of purification. All purified samples used for the OH reaction rate constant measurements were required to have less than a 0.002% residual impurity of $CH_2{=}CF{-}CF_3$ as determined by UV absorption in the 160−170 nm range (including possible absorption by residual water vapor).

GC with flame ionization detection and GC/MS analyses performed at Allied Signal Inc. permitted resolution between peaks of $CH_2{=}CF{-}CF_3$ and HFC-245cb high enough to detect residual alkene in the purified sample. One bromine-purified sample thus analyzed contained some residual $CH_2{=}CF{-}CF_3$ (0.0054%) as well as brominated products such as $C_3H_2F_4Br_2$ (0.0115%), $C_3F_6Br_2$ (0.0010%), and $C_3F_4Br_2$ (0.0005%). A UV analysis performed on the same sample also indicated approximately 0.006% of residual olefinic impurity. The agreement of the GC, GC/MS, and UV absorption analyses demonstrates the efficiency of our procedure in reducing olefinic impurities as well as in removing the primary bromination product ($C_3H_2F_4Br_2$).

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