J. Phys. Chem. A **2003,** *107,* 2239−2246

An Investigation of the Reactivity of OH with Fluoroethanes: CH_3CH_2F (HFC-161), CH_2FCH_2F (HFC-152), and CH_3CHF_2 (HFC-152a)

Sergey N. Kozlov,[†] Vladimir L. Orkin,*[,‡] and Michael J. Kurylo

Physical and Chemical Properties Division, National Institute of Standards and Technology,
Gaithersburg, Maryland 20899

Received: September 18, 2002; In Final Form: January 13, 2003

Rate constants for the reactions of OH radicals with fluoroethane (CH_3CH_2F), 1,2-difluoroethane (CH_2FCH_2F), and 1,1-difluoroethane (CH_3CHF_2) were measured using the flash photolysis resonance−fluorescence technique over the temperature range of $T = 210-480$ K. Arrhenius plots for all three reactions exhibit noticeable curvature, and the rate constants are well represented by three-parameter modified Arrhenius expressions over the full experimental temperature range, with better than 3% precision: $k_{CH_3CH_2F}(T) = 3.14 \times 10^{-13}(T/298)^{2.45} \exp\{-103/T\}$ cm^3 molecule^{-1} s^{-1}, $k_{CH_2FCH_2F}(T) = 4.33 \times 10^{-14}(T/298)^{3.85} \exp\{+247/T\}$ cm^3 molecule^{-1} s^{-1}, and $k_{CH_3CHF_2}(T) = 7.72 \times 10^{-14}(T/298)^{3.02} \exp\{-247/T\}$ cm^3 molecule^{-1} s^{-1}. For the temperature range of atmospheric interest ($T < 300$ K), the rate constants can be well represented by standard (two-parameter) Arrhenius expressions. On the basis of all the available low-temperature data, the following rate constants are recommended for atmospheric modeling: $k_{CH_3CH_2F}(T < 300\text{ K}) = 2.55 \times 10^{-12} \exp\{-730/T\}$ cm^3 molecule^{-1} s^{-1}, $k_{CH_2FCH_2F}(T < 300\text{ K}) = 1.12 \times 10^{-12} \exp\{-730/T\}$ cm^3 molecule^{-1} s^{-1}, and $k_{CH_3CHF_2}(T < 300\text{ K}) = 0.94 \times 10^{-12} \exp\{-990/T\}$ cm^3 molecule^{-1} s^{-1}. Using these recommendations, atmospheric lifetimes were estimated to be ca. 2.4 months, 5.5 months, and 1.4 years for CH_3CH_2F, CH_2FCH_2F, and CH_3CHF_2, respectively.

Introduction

Concerns about the detrimental effects of chlorinated hydrocarbons on the Earth's ozone layer have focused attention on the environmental acceptability of non-chlorinated substitutes for many industrial chemicals. The hydrofluorocarbons (HFCs) are a class of chemicals that have been introduced as ozone-friendly alternatives for many of the refrigeration, foam blowing, and aerosol propellant usages that were formerly satisfied by the now-regulated chlorofluorocarbons (CFCs). However, such fluorinated hydrocarbons can be strong absorbers of infrared radiation, thus raising concern about their possible roles as greenhouse gases. To assess this potential, accurate determinations of the atmospheric lifetimes of these gases are required.

HFCs are not appreciably photolyzed by solar radiation in the visible and near UV portion of the spectrum; therefore, their residence times in the Earth's atmosphere are primarily controlled by reactions with the OH radical in the troposphere. We report, herein, results of our investigations of such reactions for three fluorinated ethanes: HFC-161 (CH_3CH_2F), HFC-152 (CH_2FCH_2F), and HFC-152a (CH_3CHF_2). These chemicals currently have limited use as CFC and hydrochlorofluorocarbon (HCFC) replacements in some of the aforementioned applications, and their OH reactions have been studied to various degrees of completeness by both absolute and relative rate techniques.[1−10] Unfortunately, these earlier studies have been unable to provide the basis for reducing the uncertainty in the rate-constant recommendations for use in atmospheric modeling.[11] For example, the rate-constant recommendations for HFC-161 and HFC-152a have been based on the only two published studies of the temperature dependence of the OH reactions for these chemicals. In each case, a relative rate investigation (Hsu and DeMore[9]), conducted at or above room temperature, yielded a temperature dependence considerably stronger than that derived from an absolute rate study (Gierczak et al.,[7] Schmoltner et al.[10]) using data obtained at or below room temperature. These unresolved differences have led to uncertainties in the calculation of the tropospheric lifetimes of these chemicals. For HFC-152, the rate-constant recommendation has been based on a single room-temperature investigation by Martin and Paraskevopoulos,[12] combined with an estimated temperature dependence.

The aforementioned uncertainty in the rate constants for HFC-152a and HFC-161 have resulted in further complications in producing an evaluated database for OH reactions with HCFCs and other HFCs, because they have been used as reference reactants in relative rate studies. This has led to a propagation of uncertainty and even inconsistencies in the recommended database, depending on one's choice for the temperature dependence of the reference rate constant. Hence, resolution of the apparent differences between the earlier relative and absolute rate studies will provide a firmer basis for the rate-constant evaluations of a large number of reactions between OH and halogenated hydrocarbons.

Finally, the three subject HFCs constitute the simplest sequence of fluorine substitution in ethane. Thus, the accurate determination of the OH reaction rate constants over a wide temperature range might provide insight into the effects of fluorine substitution on reactivity and on the possible differences in reactivity of the different H atoms in the molecules. Therefore, we decided to conduct a study of the temperature dependence of the OH reaction rate constant for all three HFCs over a wider

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* To whom correspondence should be addressed. Author can be contacted by E-mail (vladimir.orkin@nist.gov).

[†] Present address: Institute of Chemical Physics, Russian Academy of Sciences, Moscow 117334, Russia.

[‡] Also associated with the Institute of Energy Problems of Chemical Physics, Russian Academy of Sciences, Moscow 117829, Russia.

10.1021/jp022087b

temperature range (210−480 K) than those encompassed by both the previous absolute and relative rate studies, in an attempt to resolve the apparent disparities and provide accurate data for atmospheric lifetime calculations.

Experimental Section[13]

OH Reaction Rate Constant Measurements. Detailed descriptions of the apparatus and the experimental method used to measure the OH reaction rate constants have been given in previous papers.[14,15] The principal component of the flash photolysis−resonance fluorescence apparatus is a Pyrex reactor (internal volume of ~70 cm^3) thermostated with methanol, water, or mineral oil circulated through its outer jacket. Reactions were studied in argon carrier gas (99.9995% purity) at a total pressure of 4.00 kPa (30.0 Torr). Flows of dry argon, argon bubbled through water thermostated at 276 K, and fluoroethane mixtures (containing 0.2%, 0.5%, or 1% of HFC-161; 0.4% or 1% of HFC-152; 1%, 2%, 3%, or 6% of HFC-152a) diluted with argon were premixed and flowed through the reactor at a total flow rate of 0.3−0.6 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 using calibrated Tylan mass flow meters. Hydroxyl radicals were produced by the pulsed photolysis (repetition rate of 1−4 Hz) of H_2O (introduced via the 276 K argon/H_2O bubbler) by a xenon flash lamp focused into the reactor. The radicals were monitored by their resonance fluorescence near 308 nm, excited by a microwave-discharge resonance lamp (330 Pa (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 of 100 μs) as a summation of 500−5000 consecutive flashes. The radical decay signal at each reactant concentration was analyzed as described by Orkin et al.[14b] to obtain the first-order decay rate coefficient due to the reaction under study. The minimum reaction decay rate in our measurements was 11.5 s^{-1} whereas the maximum decay rate was 420 s^{-1}. At each temperature, the rate constant was determined from the slope of a plot of the decay rate versus fluoroethane concentration. The temperature points for the measurements were chosen to be approximately equally distant along the Arrhenius 1/T scale to have them properly and equally weighted in the following fitting procedure. An exception was made only for the two lowest temperatures that were chosen because $T = 210$ K is the lowest temperature where our experiments with H_2O precursor can be conducted. Experiments were also performed at the two temperatures that are widely used in other studies: 298 and 272 K. The first value is the standard temperature used in the evaluations and presentations of the rate constants, whereas the second value is the "best" temperature for use in estimations of the compound's atmospheric lifetime.[22]

Reactants. For most experiments, fluoroethane samples were used as supplied after several freeze/pump/thaw cycles. Two samples of HFC-161 (CH_3CH_2F) were used. One sample, of 99.8% purity (PCR, Inc.), contained ca. 0.1% ethane, <0.005% ethene with traces of $CHCl_2F$, CO_2, and water and was mainly used to obtain the data presented in this paper. Another sample, with a stated purity of 99.25% (SynQuest Laboratories, Inc.), contained 0.63% $CHFClCH_3$, ca. 0.1% ethane, ca. 0.01% ethene, and <0.06% chloroethane and chloromethane. It was used for a test experiment at $T = 210$ K. A sample of HFC-152 (CH_2FCH_2F), with a stated purity of 99.62% (SynQuest Laboratories, Inc.), contained 0.17% dichloro-1,2-difluoroethane and 0.10% 1,2-difluorotetrachloroethane as the main impurities, with traces of fluoroethane, $CHFClCH_2Cl$, and water. Neither ethene nor vinyl fluoride was detected. A sample of HFC-152a (CH_3CHF_2), with a stated purity of 99.9% (PCR, Inc.), contained no detectable reactive impurities. Our gas chromatography−mass spectroscopy/flame ionization detection (GC-MS/FID) analysis indicated only water, air, and ca. 0.02% of CF_3CF_2Cl in the original sample.

TABLE 1: Rate Constants Measured in the Present Work for the Reactions of OH with Fluoroethane (CH_3CH_2F), 1,2-Difluoroethane (CH_2FCH_2F), and 1,1-Difluoroethane (CH_3CHF_2)

	$k(T)$,[a] 10^{-14} cm^3 molecule^{-1} s^{-1}		
temp., K	CH_3CH_2F	CH_2FCH_2F	CH_3CHF_2
210	**7.94 ± 0.17**	**3.68 ± 0.11**	**0.84 ± 0.031**
	3.35−22.4 (22)	*3.35−17.5 (10)*	*17.7−58.1 (13)*
220	**9.62 ± 0.087**	**4.19 ± 0.11**	**0.99 ± 0.017**
	1.59−21.7 (16)	*3.25−21.7 (16)*	*9.34−117.3 (45)*
230	**10.58 ± 0.20**	**4.61 ± 0.06**	**1.19 ± 0.019**
	3.02−20.2 (17)	*3.09−20.7 (21)*	*8.93−112.2 (24)*
250	**13.48 ± 0.32**	**5.77 ± 0.09**	**1.66 ± 0.021**
	2.86−17.5 (9)	*5.48−19.0 (9)*	*15.2−142.5 (31)*
272	**17.47 ± 0.237**	**7.66 ± 0.23**	**2.38 ± 0.036**
	1.29−8.82 (8)	*2.62−17.5 (8)*	*13.9−84.1 (21)*
298	**22.04 ± 0.334**	**9.92 ± 0.18**	**3.38 ± 0.047**
	1.70−12.0 (27)	*2.37−16.0 (23)*	*4.54−46.1 (30)*
330	**28.79 ± 0.515**	**13.58 ± 0.22**	**4.92 ± 0.074**
	0.83−14.5 (13)	*0.85−12.9 (13)*	*3.98−51.9 (33)*
370	**40.42 ± 0.948**	**19.56 ± 0.83**	**7.71 ± 0.099**
	0.38−2.59 (8)	*0.76−4.64 (9)*	*1.81−28.2 (32)*
420	**57.67 ± 1.10**	**29.61 ± 0.51**	**12.05 ± 0.19**
	0.32−2.59 (16)	*0.65−5.18 (16)*	*3.71−25.1 (18)*
480	**81.04 ± 1.35**	**45.03 ± 0.60**	**19.36 ± 0.26**
	0.34−2.27 (15)	*0.68−4.53 (16)*	*1.67−19.7 (14)*

[a] Values given in italics represent the fluoroethane concentration range, in units of 10^{14} molecules cm^{-3}. Values given in parentheses represent the number of concentrations used. Uncertainties for each value listed represent statistical levels of confidence of 95% and do not include an estimated uncertainty of 4% that is associated with possible systematic errors.

Given the measured amount of impurities and their reactivity toward OH, the detected impurities could not cause an error in the measured reaction rate constants of the subject compounds. Given that the presence of unsaturated olefinic impurities was our main concern, because of their extremely high reactivity toward OH, we purified the samples of HFC-161 and HFC-152a using photobromination.[16] No significant difference in the OH reactivity was obtained when original and purified samples were used. Thus, we are confident that the curvature observed when the data for all three reactions are presented as standard Arrhenius plots (discussed below) is not an artifact due to the reactions of OH with unsaturated impurities such as ethane ($CH_2{=}CH_2$) or vinyl fluoride ($CH_2{=}CHF$), which would be expected to become increasingly more important with decreasing temperature. Rather, as discussed below, such curvature appears to be associated with the actual mechanistic aspects of the reactions.

Results and Discussion

The rate constants obtained for the title reactions, along with information on the reactant concentration ranges utilized and the number of experimental determinations (number of measured decays rates) associated with the final rate constant values at each temperature, are presented in Table 1. Figure 1 shows examples of plots of the pseudo-first-order decay rates versus

TABLE 2: Comparison of Room-Temperature Rate Constants and Arrhenius Parameters Derived from Studies of the OH Reactions with HFC-161, HFC-152, and HFC-152a[a]

temp range, K	k_{HFC}(298 K), 10^{-13} cm^3 molecule^{-1} s^{-1}	A, 10^{-12} cm^3 molecule^{-1} s^{-1}	$E/R \pm \Delta E/R$, K	ref (technique)
		CH_3-CH_2F (HFC-161)		
297	2.32 ± 0.37			4 (FP−RA)
243−373	2.12 ± 0.07	2.00	670 ± 92	10 (LP-LIF)
285−364	1.64 ± 0.04	10.1	1228 ± 72	9 (relative CH_3CH_3)
298−480	2.12 ± 0.12^b	6.78	1033 ± 74	this work
210−298	2.19 ± 0.07^b	2.42	716 ± 36	this work
		CH_2F-CH_2F (HFC-152)		
298	1.12 ± 0.12			12 (FP−RA)
311−393	0.903 ± 0.015	3.89	1120 ± 33	20 (relative CH_3CHF_2)^c
287−409	0.976 ± 0.030	3.60	1075 ± 58	20 (relative cyclopropane)
293−397	0.931 ± 0.022	3.16	1050 ± 47	20 (relative CH_3CH_3)
298−480	0.943 ± 0.077^b	5.11	1190 ± 106	this work
210−298	0.957 ± 0.060^b	1.02	706 ± 70	this work
		CH_3-CHF_2 (HFC-152a)		
296	0.31 ± 0.07			1 (DF-LMR)
293	0.35 ± 0.05			2 (FP−RA)
293−417	0.50 ± 0.03	3.0	1216 ± 99	3 (DF−RF)
297	0.37 ± 0.037			4 (FP−RA)
220−423	0.41 ± 0.05	1.22	1009 ± 170	6 (DF−RF)
224−300	0.388 ± 0.012	1.19	1018 ± 46	7 (FP-LIF)
293−422	0.348 ± 0.026	2.72	1299 ± 97	7 (DF-LMR)
212−293	0.331 ± 0.05	0.583	857 ± 170	7 (DF-LMR)
295−388	0.45 ± 0.09	1.8	1098 ± 380	8 (PR−RA)
298−358	0.305 ± 0.013	1.59	1178 ± 135	9 (relative CH_4)
298−358	0.311 ± 0.11	2.46	1300 ± 114	9 (relative CH_3CCl_3)^c
298−480	0.324 ± 0.022^b	3.24	1372 ± 89	this work
210−298	0.329 ± 0.017^b	0.936	998 ± 56	this work

[a] Results of our fit to the data set presented in the original paper. Indicated uncertainties are two standard errors and do not include any possible systematic error or any uncertainty associated with the rate constant of the reference reaction. [b] The deviation of the measured value of k(298 K) from a three-parameter modified Arrhenius dependence is <1%. This higher uncertainty obtained from a two-parameter Arrhenius fit is due to curvature of the Arrhenius plot. [c] Recalculated using the current recommendations for the rate constants of the reference reactions.[18]

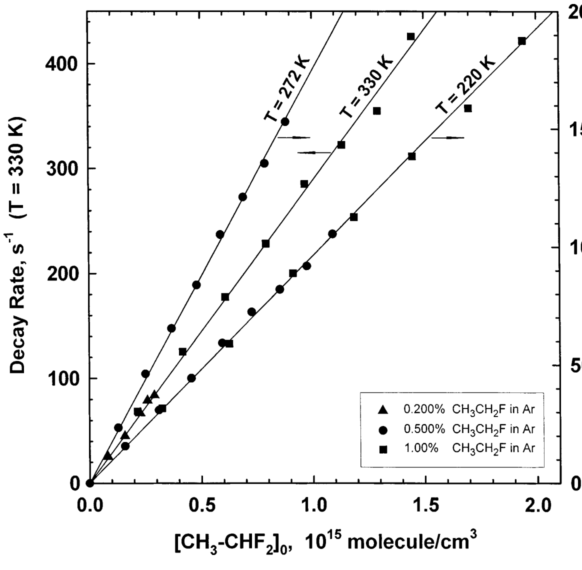

Figure 1. Pseudo-first-order OH decay rate versus CH_3CH_2F concentration from experiments at 220, 272, and 330 K using the indicated reactant mixtures.

fluorinated ethane (HFC-161) concentration at different temperatures. The rate-constant data are plotted in Arrhenius form in Figures 2−4, along with other available data from the literature for each reaction. The 95% confidence intervals (obtained from the statistical fits) for our data at each temperature are masked by the size of the symbols. These figures clearly illustrate the Arrhenius curvature over the temperature range of our study. This matter is discussed below for each reaction, and rate-constant recommendations are presented for the purposes of atmospheric modeling. In Table 2, we have summarized the information that can be obtained from the experimental data available in the literature. The table shows results of our fit to the data sets presented in the original papers. Keeping in mind the needs of atmospheric modeling and the obvious curvature of the Arrhenius plots obtained in the present work for all three reactions, we subdivided those data into "below room temperature" and "above room temperature" subsets. They are also grouped according to experimental techniques. Uncertainties shown for the rate constants at room temperature (k_i(298 K)) and E/R are simply two standard errors from our fit to the original data over the indicated temperature interval and do not include any possible systematic errors or uncertainties associated with the rate constants of the reference reactions (when data were obtained by a relative rate technique). The uncertainties are those from original papers when only room-temperature measurements are available. Note that the uncertainties obtained from the fit to our data reflect the curvature of the Arrhenius plots that is statistically significant, even over these restricted temperature intervals. This is the reason uncertainties in k(298 K) obtained from a two-parameter Arrhenius fit to our data and presented in Table 2 are as high as 3%−8%, whereas the deviation of measured values of k(298 K) from a three-parameter Arrhenius fit is <1% for all three reactions. From Table 2, one can see that the E/R values derived from below-room-temperature results are systematically lower than those obtained from above-room-temperature results.

OH + CH_3CH_2F (HFC-161). As can be seen in Figure 2, there is excellent agreement in the room-temperature rate constants obtained in the present work and in the studies of Nip et al.[4] and Schmoltner et al.[10] There is also good agreement between the results of our study and those of Schmoltner et al. over the common temperature range covered by both studies.

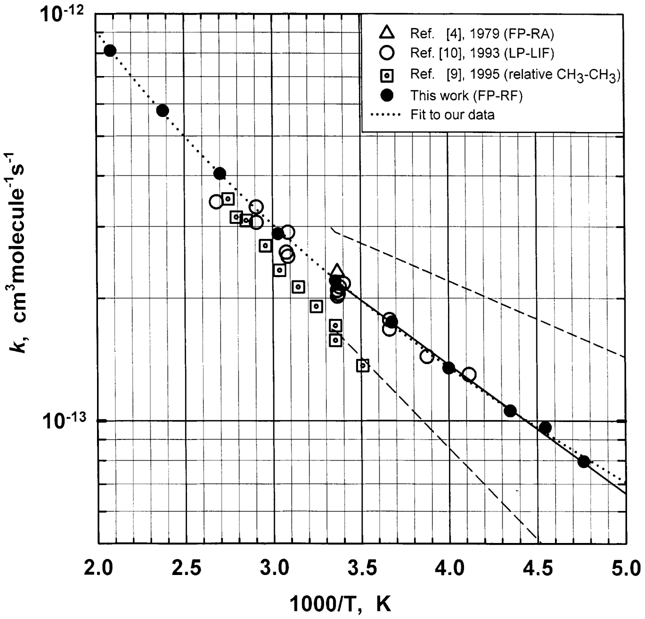

Figure 2. Arrhenius plot for the reaction of OH with HFC-161. The dotted line is the three-parameter modified Arrhenius fit to our data. The solid line is the rate constant recommended for the NASA/JPL evaluation ($T < 300$ K); the dashed lines represent the approximate 95% confidence limits on the recommended rate expression.

However, the smaller temperature range of the latter study, coupled with a larger data scatter than that observed in the present work, prevented the unequivocal identification of Arrhenius curvature by these authors. The results obtained in the relative rate study of Hsu and DeMore[9] are significantly different from those of all the absolute rate studies, with respect to both the rate constant at room temperature (which is ca. 25% lower) and the temperature dependence (which is markedly greater). The reasons for these differences are speculative at best. The reaction is fast enough so that the main possible complication of an absolute technique, the presence of highly reactive micro-impurities, should not be a serious problem here. Indeed, $CH_2{=}CH_2$ (which has a rate constant of ca. 9×10^{-12} cm^3 molecule^{-1} s^{-1} for its reaction with OH)[11] is the most likely reactive impurity in a sample of CH_3CH_2F. To explain the difference between the results of the absolute and relative measurements (ca. 6×10^{-14} cm^3 molecule^{-1} s^{-1} at both room temperature and 250 K, which is the lowest temperature used by Schmoltner et al.,[10] and ca. 5×10^{-14} cm^3 molecule^{-1} s^{-1} at 210 K, the lowest temperature of the present study), the samples should contain as much as ca. 0.6%−0.7% of ethene. Our GC-MS analysis indicated <0.01% ethane in both our samples of HFC-161. The rate constants obtained at $T = 210$ K when two different samples of HFC-161 were used coincide within the combined uncertainties. In addition, purification of our sample using a photobromination procedure[16] also revealed no significant amount of unsaturated impurities. Therefore, the above-mentioned disagreement is probably due to other experimental problems. Furthermore, as we will see, a consistent picture is presented by the absolute rate studies and the relative rate studies for all three fluoroethanes, with the exception of this single set of relative rate results.

It seems likely that the reaction between OH and HFC-161 has two channels with different activation energies, corresponding to abstraction of an H atom from either CH_3 or CH_2F. These two channels are the most likely cause of the Arrhenius curvature observed over the extended temperature range of the present work, although tunneling at lower temperatures may also contribute. Singleton et al.[17] determined that 85% ± 3% of the abstraction by OH is from the CH_2F group at room temperature. Hence, the observed curvature is quite possibly due to the increasing importance of H atom abstraction from the unsubstituted methyl group (CH_3) with increasing temperature and the value of $E/R = 730$ K derived from the results at $T < 300$ K (discussed below) is primarily associated with abstraction from the CH_2F group.

Because of the rate-constant temperature dependence, representation of our results over the complete temperature range that was probed requires more than a simple two-parameter Arrhenius expression. Thus, the data are well described by the following three-parameter modified Arrhenius expression:

$$k_{CH_3CH_2F}(T) = 3.14 \times 10^{-13}(T/298)^{2.45} \times \exp\{-103/T\} \quad \mathrm{cm^3\ molecule^{-1}\ s^{-1}}$$

This expression gives rate constants that are within 3% of the values measured in the present work and reported in Table 1. Nevertheless, at $T < 300$ K, a simple Arrhenius expression does an excellent job of representing the complete experimental database.

For the purposes of atmospheric modeling, we have formulated rate-constant recommendations for the title reactions for inclusion in the NASA/JPL 2003 data evaluation.[18] For HFC-161, the recommended value of $k_{CH_3CH_2F}(298\ \mathrm{K})$ is an average of the values determined in the present work and in the studies of Nip et al.[4] and Schmoltner et al.[10] The recommended value of E/R is derived from a fit to the data from these three studies at or below room temperature, and the Arrhenius factor A was then calculated. Thus, we obtain

$$k_{CH_3CH_2F}(T < 300\ \mathrm{K}) = 2.55 \times 10^{-12} \times \exp\{-730/T\} \quad \mathrm{cm^3\ molecule^{-1}\ s^{-1}}$$

The values for the uncertainty parameters, f(298 K) and g, are then assigned to permit the calculation of the overall rate-constant uncertainty factor at any temperature <300 K.[19]

$$f(T) = f(298\ \mathrm{K})\ \exp\left\{g\left|\frac{1}{T} - \frac{1}{298}\right|\right\}$$

The 1σ deviation values for these parameters were chosen to bracket (at the 2σ, or 95% confidence, level) the reasonable range of rate-constant uncertainty for modeling purposes. This involved visually inspecting the 95% confidence limits derived from these parameters, together with the complete experimental database, for consistency. Thus, for this reaction, we have assigned 1σ values of $f(298\ \mathrm{K}) = 1.1$ and of $g = 100$ K. The recommended (below-room-temperature) Arrhenius expression and 95% confidence limits are shown by the solid and dashed lines, respectively, in Figure 2.

OH + CH_2FCH_2F (HFC-152). As can be seen in Figure 3, the present work provides the only rate-constant data for this reaction below room temperature. In fact, until the completion of the present investigation and a concurrently conducted relative rate study,[20] the only experimental rate-constant information was from a single room-temperature study.[12] For this reaction, distinct curvature is evident in the Arrhenius plot, despite the fact that the molecule is apparently symmetric (i.e., H atom abstraction occurs only from a CH_2F group). Such curvature might be explained by significant tunneling at lower temperatures and/or the existence of reactant conformers (the populations and reactivity of which differ with temperature).

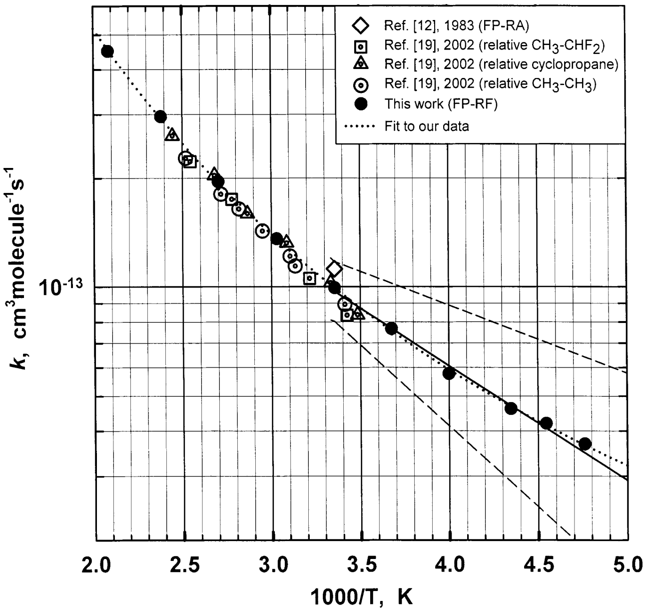

Figure 3. Arrhenius plot for the reaction of OH with HFC-152. The dotted line is the three-parameter modified Arrhenius fit to our data. The solid line is the rate constant recommended for the NASA/JPL evaluation ($T < 300$ K); the dashed lines represent the approximate 95% confidence limits on the recommended rate expression.

Reasonable agreement exists among the room-temperature rate constants obtained from the two absolute rate investigations and the relative rate investigation (three studies using CH_3CHF_2, cyclopropane, and ethane as reference reactants). The above-room-temperature data from the present work are in excellent agreement with the three relative rate data sets.[20]

As in the case of HFC-161, representation of our results over the complete temperature range probed requires at least a three-parameter modified Arrhenius fit:

$$k_{CH_2FCH_2F}(T) = 4.33 \times 10^{-14}(T/298)^{3.85} \times \exp\{+247/T\} \quad \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$$

However, at $T < 300$ K, a simple Arrhenius expression once again does a very good job of representing the complete experimental database and has been used to formulate a recommendation for the 2003 NASA/JPL data evaluation. The recommended value for k(298 K) is an average of the values from the present work, Martin and Paraskevopoulos,[12] and DeMore et al.[20] (recalculated using our recommendation for the rate constant of the reference reaction, $k_{CH_3CHF_2}(T > 300\text{ K})$; see below). The value for E/R is from a fit to our data at and below room temperature, and the Arrhenius factor A was then calculated.

$$k_{CH_2FCH_2F}(T < 300\text{ K}) = 1.12 \times 10^{-12} \times \exp\{-730/T\} \quad \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$$

Values for both f(298 K) and g were assigned as described for the HFC-161 reaction.[19] This resulted in $f(298\text{ K}) = 1.1$ and $g = 150$ K. The recommended (below-room-temperature) Arrhenius expression and associated 95% confidence limits are shown by the solid and dashed lines, respectively, in Figure 3.

It is interesting to note that this value for E/R is identical to that derived (at $T < 300$ K) for HFC-161. Thus, the low-temperature reactivity would appear to be associated primarily with an abstraction process almost identical to that in HFC-161. The factor-of-2.2-lower value of k(298 K) may be due to a steric influence of one CH_2F group on the other.

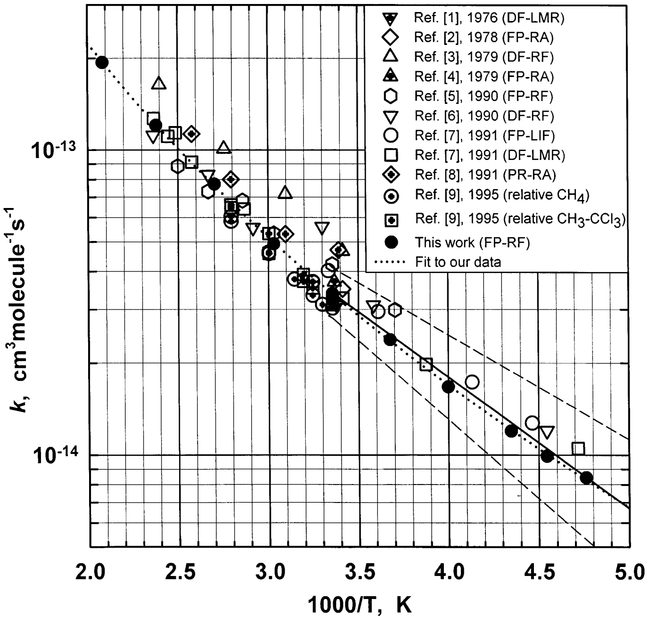

Figure 4. Arrhenius plot for the reaction of OH with HFC-152a. The dotted line is the three-parameter modified Arrhenius fit to our data. The solid line is the rate constant recommended for the NASA/JPL evaluation ($T < 300$ K); the dashed lines represent the approximate 95% confidence limits on the recommended rate expression.

OH + CH_3CHF_2 (HFC-152a). As can be seen in Figure 4, there is a more extensive database for this reaction than for the other two fluoroethanes studied in this work. Careful inspection of the data shows that there are systematic differences in the temperature dependencies determined in the absolute studies (particularly below room temperature) and relative rate studies (conducted at and above room temperature). Curvature in the Arrhenius plot is also evident, although not as pronounced as that for either HFC-161 or HFC-152. This curvature (as first suggested by the data of Gierczak et al.[7]) has been more clearly demonstrated in the present work and seems to explain the earlier cited differences in Arrhenius parameters derived from the relative and absolute rate data. This curvature is likely due to the presence of two different H atom abstraction reaction channels (from CH_3 and CHF_2), although tunneling at low temperatures may also contribute. The slightly lower curvature for this reaction than that for the reactions of HFC-161 and HFC-152 is probably due to the temperature dependencies for the two probable reaction channels being more similar in magnitude.

As with HFC-161 and HFC-152, excellent representation of our results over the complete temperature range probed is accomplished using a three-parameter modified Arrhenius expression:

$$k_{CH_3CHF_2}(T) = 7.72 \times 10^{-14}(T/298)^{3.02} \times \exp\{-247/T\} \quad \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$$

This expression gives rate constants that are within 2% of the values measured in the present work and reported in Table 1. For the purposes of atmospheric modeling, we recommend the following Arrhenius expression for inclusion in the NASA/JPL

2003 data evaluation:

$$k_{CH_3CHF_2}(T < 300\ K) = 0.94 \times 10^{-12} \times \exp\{-990/T\} \quad cm^3\ molecule^{-1}\ s^{-1}$$

The recommended value for k(298 K) is an average of the values from the present work, Howard and Evenson,[1] Handwerk and Zellner,[3] Nip et al.,[4] Gierczak et al.[7] (two different absolute determinations), and Hsu and DeMore[9] (two relative rate determinations, which have been recalculated on the basis of the current recommendations for the rate constants of the OH + CH_4 and OH + CH_3CCl_3 reference reactions). The recommended value for E/R is derived from a fit to the data ($T \leq$ 300 K) of Gierczak et al.[7] and the present work. The results from Clyne and Holt,[3] Brown et al.,[6] and Nielsen[8] are significantly different from the other studies and may have been affected by reactant impurities. The earlier results from our laboratory (Liu et al.[5]) may suffer from similar impurity effects and are considered to be superseded by the present study. None of these studies were used in deriving the recommended parameters. Values for both f(298 K) and g were assigned as described for the HFC-161 reaction.[19] This resulted in f(298 K) = 1.1 and g = 100 K. The recommended (below-room-temperature) Arrhenius expression and associated 95% confidence limits are shown by the solid and dashed lines, respectively, in Figure 4. Given that the rate-constant temperature dependence obtained at $T < 300$ K ($E/R = 990$ K) can be associated primarily with H atom abstraction from CHF_2, this finding is consistent with the lower value of $E/R = 730$ K associated with H atom abstraction from CH_2F, obtained in the analyses of the HFC-161 and HFC-152 reactions.

Clearly, in light of the observed Arrhenius curvature, the above-described procedure for deriving our recommendation for k at $T < 300$ K does not yield an expression suitable for use in recalculating rate constants from relative rate studies in which the OH + CH_3CHF_2 reaction was the reference and in which the experiment was conducted at $T > 300$ K. Such use would yield rate constant values that are systematically different from those determined relative to other reactions or determined by absolute techniques. To recalculate relative rate data, one should use an Arrhenius expression for the reference reaction derived from data over the appropriate temperature range. A fit to the absolute rate data of Gierczak et al.[7] and the present work between room temperature and 400 K yields the Arrhenius expression

$$k^{abs}_{CH_3CHF_2}(T \geq 300\ K) = 2.36 \times 10^{-12} \times \exp\{-1255/T\} \quad cm^3\ molecule^{-1}\ s^{-1}$$

This relation is in good agreement with the expression derived solely from the relative rate data of Hsu and DeMore:[9]

$$k^{rel}_{CH_3CHF_2}(T \geq 300\ K) = 2.1 \times 10^{-12} \times \exp\{-1265/T\} \quad cm^3\ molecule^{-1}\ s^{-1}$$

Thus, the following expression derived from the above-described room-temperature E/R value and the recommended k(298 K) value can be used to renormalize relative rate data and was, in fact, used to recalculate the results of DeMore et al.[20] for HFC-152 that were obtained relative to HFC-152a.

$$k_{CH_3CHF_2}(T > 300\ K) = 2.33 \times 10^{-12} \times \exp\{-1260/T\} \quad cm^3\ molecule^{-1}\ s^{-1}$$

However, this expression should not be used at $T < 298$ K, because erroneous values for OH + CH_3CHF_2 reaction rate constants would be obtained.

In conclusion, it appears that the high-precision results from the present work, obtained over a temperature range that encompasses all the earlier absolute and relative reaction rate investigations, explain the higher activation energies derived from the relative rate studies for HFC-152 and HFC-152a. Thus, they provide a more reliable basis for comparing absolute studies with other relative rate studies that have employed these fluoroethanes as reference reactants.

Possible Mechanistic Interpretations of the Curvature of the Arrhenius Plots. A nonlinearity of the Arrhenius dependence (ln{$k(T)$} vs $1/T$) is often observed at high temperatures when various internal molecular motions (vibrations, rotations) become active (i.e., their non-ground levels become thermally populated). The vast majority of the OH abstraction reactions at moderate and low temperatures ($T < 400-500$ K) are generally assumed to follow a “normal” linear Arrhenius dependence. The combination of the wide temperature range covered in the present study and the precision of the data allows clear demonstration of a curvature in the Arrhenius dependence at $T = 210-480$ K, which is often masked by a scattering of data obtained and a narrower temperature interval of study. We are confident that the observed curvatures cannot be attributed to the presence of reactive impurities; thus, we can utilize the precision of the data to perform a few calculational exercises.

It is reasonable to speculate that the Arrhenius curvature for the CH_3CH_2F and CH_3CHF_2 reactions is due to abstraction of an H atom from two different reactive sites: methyl and fluorinated methyl. Assuming a linear Arrhenius dependence for each reaction channel, we can fit a sum of two Arrhenius expressions to the data obtained for these reactions. In the case of CH_3CH_2F, such a fit gives

$$k_{CH_3CH_2F} = 23.9 \times 10^{-12} \exp\{-(1960 \pm 330)/T\} + 1.51 \times 10^{-12} \exp\{-(620 \pm 130)/T\} \quad cm^3\ molecule^{-1}\ s^{-1}$$

(where the uncertainties in E/R are two standard errors from the fit). Recalling that Singleton et al.[17] reported values of 15% ± 3% and 85% ± 3% for the contributions of H atom abstraction from the methyl and fluoromethyl groups, respectively, at room temperature, we can assign the higher and lower activation energies, respectively, to these same two abstraction channels. Remarkably, at $T = 298$ K, our double Arrhenius fit gives the same branching ratio, although, given the uncertainties in the fit and in the Singleton at al. study, such agreement is fortuitous. We should note that, because of the possible contribution of tunneling to the rate constants at low temperature, the E/R value for the second summand in our fit must be considered to be a lower limit to the actual energy barrier for H atom abstraction from the CH_2F group. Furthermore, one can observe that the A factor and E/R of the first summand appear quite reasonable for the OH reaction with a methyl group. For example, a fit to the highest temperature (577−705 K) data of Tully et al.,[21] which is the most comprehensive study of the reaction between OH and CH_3CH_3 above room temperature, gives $k_{CH_3CH_3} \approx 4.1 \times 10^{-11} \exp\{-1740/T\}$ cm^3 $molecule^{-1}$ s^{-1}.

The same double Arrhenius fit to our data for the CH_3CHF_2 reaction results in

$$k_{CH_3CHF_2} = 7.75 \times 10^{-12} \exp\{-(1954 \pm 300)/T\} + 0.30 \times 10^{-12} \exp\{-(774 \pm 146)/T\} \quad cm^3\ molecule^{-1}\ s^{-1}$$

TABLE 3: Estimation of OH Radical Reactivity toward Methyl and Fluoromethyl Groups in Ethane and Fluoroethanes at Room Temperature[a]

molecule ($CH_3-CH_{3-n}F_n$)	rate constant for CH_nF_{3-n}, 10^{-14} cm^3 molecule^{-1} s^{-1}	source	rate constant for CH_nF_{3-n} (per H atom), 10^{-14} cm^3 molecule^{-1} s^{-1}	source
CH_3-CH_3	$k_0(CH_3) = 12.0$	$k(C_2H_6)/2$	$k_0^{CH}(CH_3) = 4.0$	$k(C_2H_6)/6$
CH_3-CH_2F	$k_1(CH_3) = 3.3$	$k(C_2H_5F) \times 0.15$ [ref 17]	$k_1^{CH}(CH_3) = 1.1$ $k_1^{CH}(CH_2F) = 9.35$	$k(C_2H_5F) \times 0.15 \times (^1/_3)$ [ref 17] $k(C_2H_5F) \times 0.85 \times (^1/_2)$ [ref 17]
CH_2F-CH_2F	$k_1(CH_2F) = 5.0$	$k(CH_2F-CH_2F) \times (^1/_2)$	$k_1^{CH}(CH_2F) = 2.5$	$k(CH_2F-CH_2F) \times (^1/_4)$
CH_3-CHF_2	$k_2(CH_3) = 0.89$	$k_1(CH_3)/3.7$	$k_0(CHF_2) = 2.51$	$k(CH_3-CHF_2) - k_2(CH_3)$
CH_2F-CHF_2	$k_2(CH_2F) = 1.35$ $k_2(CH_2F) = 1.36$	$k_1^1(CH_2F) \times 2/3.7$ $k_2(CH_3) \times (^1/_3) \times 2.3 \times 2$	$k_1(CHF_2) = 0.69$	$k_0(CHF_2)/3.7$
	an estimation gives $k(CH_2F-CHF_2) \approx 2.0 \times 10^{-14}$ versus the measured $k(CH_2F-CHF_2) \approx 1.7 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} [ref 18]			
CHF_2-CHF_2	$k_2(CHF_2) = 0.18$	$k_2(CH_2F) \times (^1/_2)/3.7$	$k_2(CHF_2) = 0.19$	$k_1(CHF_2)/3.7$
	an estimation gives $k(CHF_2-CHF_2) \approx 3.7 \times 10^{-15}$ versus the measured $k(CHF_2-CHF_2) \approx 6.1 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} [ref 18]			
CH_3-CF_3	$k_3(CH_3) = 0.24$	$k_2(CH_3)/3.7$	$k_0(CF_3) = 0$	*assumed*
	an estimation gives $k(CH_3-CF_3) \approx 2.4 \times 10^{-15}$ versus the measured $k(CH_3-CF_3) \approx 1.3 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} [ref 18]			

[a] A subscript beside the rate constant symbol *k* denotes the number of F atoms in the adjacent (fluoro)methyl group, whereas the superscript "CH" indicates that the rate constant is per H atom in the group. The italicized values denote results from our calculations discussed in the text, to differentiate them from values that are based on the experimental results.

From this expression, we can calculate branching ratios at $T = 298$ K of 33% and 67% for H atom abstractions from the CH_3 and CHF_2 groups, respectively, indicating a larger relative contribution of abstraction from the methyl group in this reaction. Note that the *E/R* parameter of the first summand, which is associated with the rate constant of the reaction between OH and the methyl group, remains essentially unchanged from that derived previously for the reaction between OH and CH_3CH_2F. Interestingly, we note that the *E/R* value for the reaction between OH and CH_3CF_3[18] is also ~2000 K. Thus, changes in the values of the above-mentioned rate constants appear to be mainly associated with changes in the *A* factors, not in the *E*/*R* values. Additionally, as noted for CH_3CH_2F, because of the possible contribution of tunneling to the rate constants at low temperature, the *E/R* value for the second summand in our fit must be considered to be a lower limit to the actual energy barrier for H atom abstraction from the CHF_2 group.

The somewhat satisfying interpretation provided for CH_3CH_2F and CH_3CHF_2 does not apply as conveniently to the results obtained for the reaction of CH_2FCH_2F, because there is no obvious mechanistic reason for two different reaction channels for this seemingly symmetrical molecule. Nevertheless, this same fitting procedure can be used to obtain

$$k_{CH_2FCH_2F} = 13.6 \times 10^{-12} \exp\{-1777/T\} + 0.29 \times 10^{-12} \exp\{-450/T\} \quad \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$$

One can speculate on the possibility of two different reaction pathways involving the reaction intermediate conformers that are associated with, for example, cis and trans rotational isomers of the reactant. Again, tunneling can contribute to the observed curvature of the Arrhenius plot.

Possible Influence of Fluorine Atom Substitution on Hydrogen Atom Abstraction from the Substituted or Adjacent Methyl Groups. The reactivities of the three fluoroethanes studied in this work offer an opportunity to examine the effects of fluorine substitution on H atom abstraction from a methyl radical in which the substitution occurs and from one adjacent to a methyl radical in which it occurs. We have attempted to summarize these observations in Table 3. Our first set of calculations is based on the OH rate constants measured for ethane (ref 18) and for fluoroethane and 1,2-difluoroethane (this work), combined with the branching ratio[17] measured for the reaction between OH and CH_3CH_2F. The second column in this table shows the overall rate constant for OH attack on the methyl group (whose structure is given in parentheses) in the molecule shown in the first column, with a brief explanation given in the third column. The subscript (0, 1, or 2) beside the *k* indicates the number of F atoms in the adjacent methyl group. The fourth column gives the rate constant for OH attack on the methyl group given in the parentheses on a per-H-atom basis (indicated by the superscript CH). The subscripts beside the *k* symbols again indicate the degree of fluorination of the adjacent methyl radical; a brief explanation is given in the fifth column.

Comparing (on a per-H-atom basis) the rate constants for a CH_3 group in ethane with those for a CH_3 group in ethyl fluoride, we find that the reactivity of CH_3 is decreased by a factor of ca. 3.7, because of the first fluorination of the adjacent methyl group. On the other hand, comparing (on a per-H-atom basis) the rate constants for a CH_3 group in ethane with those for the CH_2F group in ethyl fluoride, we observe that the first fluorination in the reacting methyl group increases the reactivity by a factor of ca. 2.3. Next, we find, through examination of the reactivity of OH toward 1,2-difluoroethane (CH_2FCH_2F) (this work), that the rate constant (on a per-H-atom basis) for the CH_2F group in CH_2FCH_2F is smaller than that for the CH_2F group in CH_3CH_2F by the same factor (ca. 3.7), because of fluorination of the adjacent methyl group.

As an application of these factors, we use them to estimate the reactivity of the CH_3 group in CH_3CHF_2. We do this by assuming that the rate constant for CH_3 in CH_3CHF_2 is a factor of 3.7 lower than that for CH_3 in CH_3CH_2F. Then, on the basis of the total reactivity of 1,1-difluoroethane (CH_3CHF_2) (this work), we can calculate the reactivity of CHF_2 group as a residual. Interestingly, on a per-H-atom basis, the CHF_2 reactivity in CH_3CHF_2 is a factor of 3.7 slower than the reactivity of CH_2F in CH_3CH_2F. This would suggest that the addition of a second F atom reduces the reactivity of the already-fluorinated methyl group by a factor of 3.7 (on a per-H-atom basis), regardless of the site of the second fluorination. We can use this calculation to estimate the branching ratio at $T = 298$ K for the reaction of OH with CH_3CHF_2. These calculations predict that ~26% of the reaction occurs via abstraction from the CH_3 end of the molecule, with the remaining 74% occurring at the CHF_2 end.

Next, we can examine how well these factors do in an estimation of the overall rate constant for the reaction of OH with 1,1,2-trifluoroethane (CHF_2CH_2F). We can do this using CH_3CHF_2 and CH_2FCH_2F as starting molecules, and the results are shown in Table 3. First, we can estimate the reactivity of the CH_2F group in CHF_2CH_2F as being a factor of 3.7 lower than that for the same group in CH_2FCH_2F. We can also estimate the reactivity of the CH_2F group as being a factor of 2.3 greater (on a per-H-atom basis) than the reactivity of the CH_3 group in CH_3CHF_2. Either way, as seen in Table 3, we obtain the same result. We can then estimate the reactivity of the CHF_2 group in CHF_2CH_2F as being a factor of 3.7 lower than that for the same group in CH_3CHF_2. Combining the reactivities of these two groups yields a rate constant value of 2.0×10^{-14} cm^3 molecule^{-1} s^{-1} at $T = 298$ K, which is in reasonable agreement with the measured value of 1.7×10^{-14} cm^3 molecule^{-1} s^{-1}. This level of agreement lends some confidence to the branching ratios obtained from the reactivity estimates for the two fluorinated methyl groups; i.e., approximately one-third of the reaction occurs at the CHF_2 end of the molecule and approximately two-thirds of the reaction occurs at the CH_2F end.

Two other estimation examples are also shown in Table 3 for CHF_2CHF_2 and CH_3CF_3. In the first case, the factors obtained previously underestimate the measured rate constant by ~40%. In the second case, the estimated value is almost 85% greater than the measured value. A series of ab initio calculations performed for the more heavily fluorinated compounds or for those containing a CF_3 group could provide some further insight into the reactivity trends.

Atmospheric Implications. The atmospheric lifetimes of these three fluoroethanes can be estimated on the basis of the rate constants obtained in the present work. Reactions with hydroxyl radicals in the troposphere dictate their atmospheric lifetimes; therefore, a simple scaling procedure can be used to calculate them. This 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[22]

$$\tau_i^{OH} = \frac{k_{MC}(272)}{k_i(272)} \tau_{MC}^{OH}$$

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 ($\tau_{MC}^{OH} = 5.9$ years), and k_i(272 K) and k_{MC}(272 K) are the rate constants for the reactions of OH with these chemicals at $T = 272$ K ($k_{MC}(272\ K) = 6.0 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1}).[18] The value of $\tau_{MC}^{OH} = 5.9$ years was obtained following the procedure used by Prinn et al.[23] 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 fluoroethanes of this study yields the estimated atmospheric lifetimes of ca. 2.4 months, 5.5 months, and 1.4 years for CH_3CH_2F, CH_2FCH_2F, and CH_3CHF_2, respectively. As can be seen, the lifetimes derived here are somewhat shorter than the characteristic time of mixing processes in the troposphere and, hence, are only estimates of the true lifetimes. The correct residence time of the compounds in the atmosphere will depend on the emission location and season, in addition to local atmospheric conditions. Some results of detailed atmospheric modeling for short-lived chemicals can be found in recent publications.[24−26] Nevertheless, the presented estimations give reasonable average values of the lifetimes and provide useful scaling among such compounds.

Acknowledgment. This work was supported by the Upper Atmosphere Research Program of the National Aeronautics and Space Administration. The authors thank William B. DeMore for providing experimental results on the OH + CH_2FCH_2F reaction prior to publication.

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