

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/243658165>

Reactions of Hydroxyl Radicals with Several Hydrofluorocarbons: The Temperature Dependencies of the Rate Constants for $\text{CHF}_2\text{CF}_2\text{CH}_2\text{F}$ (HFC245ca), $\text{CF}_3\text{CHFCHF}_2$ (HFC236ea), $\text{CF}_3\text{CHFCF}_3$ (HFC...

ARTICLE in THE JOURNAL OF PHYSICAL CHEMISTRY · APRIL 1994

Impact Factor: 2.78 · DOI: 10.1021/j100067a017

CITATIONS

25

READS

18

5 AUTHORS, INCLUDING:



Robert Huie

National Institute of Standards and Technology

192 PUBLICATIONS 7,897 CITATIONS

SEE PROFILE



Michael J. Kurylo

Universities Space Research Association

184 PUBLICATIONS 6,232 CITATIONS

SEE PROFILE

Reactions of Hydroxyl Radicals with Several Hydrofluorocarbons: The Temperature Dependencies of the Rate Constants for CHF₂CF₂CH₂F (HFC-245ca), CF₃CHFCHF₂ (HFC-236ea), CF₃CHFCF₃ (HFC-227ea), and CF₃CH₂CH₂CF₃ (HFC-356ffa)

Zhengyu Zhang,[†] S. Padmaja,[‡] Rameshwar D. Saini,[§] Robert E. Huie,^{*} and Michael J. Kurylo

Chemical Kinetics and Thermodynamics Division, National Institute of Standards and Technology, Gaithersburg, Maryland 20899

Received: December 7, 1993; In Final Form: February 7, 1994[⊙]

Rate constants were determined for the gas-phase reactions of the hydroxyl radical with four hydrofluorocarbon compounds, CF₃CHFCF₃ (HFC-227ea), CF₃CHFCHF₂ (HFC-236ea), CHF₂CF₂CH₂F (HFC-245ca), and CF₃CH₂CH₂CF₃ (HFC-356ffa), using the flash photolysis resonance fluorescence technique over the temperature range 260–365 K. Arrhenius expressions were derived for the four OH reactions: $k(\text{CF}_3\text{CHFCF}_3) = 3.63 \times 10^{-13} \exp[(1613 \pm 135)/T]$, $k(\text{CF}_3\text{CHFCHF}_2) = 1.05 \times 10^{-12} \exp[(1434 \pm 161)/T]$, $k(\text{CHF}_2\text{CF}_2\text{CH}_2\text{F}) = 2.87 \times 10^{-12} \exp[(1661 \pm 170)/T]$, and $k(\text{CF}_3\text{CH}_2\text{CH}_2\text{CF}_3) = 2.94 \times 10^{-12} \exp[(1734 \pm 87)/T]$ cm³ molecule⁻¹ s⁻¹. Tropospheric lifetimes for the four compounds were estimated to be 43, 7.8, 6.5, and 8.2 years, respectively.

Introduction

A number of hydrofluorocarbons (HFCs) are under consideration as possible chlorofluorocarbon (CFC) alternatives since they contain neither Cl nor Br and, thus, should pose no threat to the stratospheric ozone layer. Nevertheless, their infrared absorbing properties raise concerns over such compounds as potential "greenhouse gases". Hence, their residence time in the atmosphere is a critical element in assessing their roles in radiative forcing and in calculating their global warming potentials (GWPs). The atmospheric lifetimes and tropospheric chemistry of such compounds are controlled primarily by their reactions with the tropospheric hydroxyl radical, OH. As part of our continuing effort to determine the atmospheric reactivities of proposed and currently used CFC alternatives, we have conducted experiments on the kinetics of the reactions of OH with CHF₂CF₂CH₂F (HFC-245ca), CF₃CHFCHF₂ (HFC-236ea), CF₃CHFCF₃ (HFC-227ea), and CF₃CH₂CH₂CF₃ (HFC-356ffa) using the flash photolysis resonance fluorescence technique over the temperature range 260–365 K. The rate constants thus determined have been fit to the Arrhenius equation, and the tropospheric lifetime (τ) of each compound was estimated relative to that for CH₃CCl₃ by using the OH rate constants at 277 K for CH₃CCl₃ and the HFC.

Experimental Section

Rate measurements were conducted using the flash photolysis resonance fluorescence technique. The apparatus, developed in this laboratory,^{1–3} was modified by redesigning the flash photolysis component. The original, specially fabricated nitrogen flash lamp and associated charging and triggering electronics were replaced by (1) a commercial Xe flash lamp with an arc length of 3.2 mm and a sapphire window, (2) a small high-voltage trigger module, and (3) a charging assembly consisting of a compact power supply, a 4 μ F/2 kV energy storage capacitor, and a 5 k Ω /25 W charging resistor. The optical components in the evacuated coupling between the flash lamp and the reaction cell were all fused silica and consisted of a collimating lens (0.5-in. diameter and 15-mm focal length), a converging lens (1-in. diameter and 50-mm focal

length), and several light baffles to minimize scattered light. With this arrangement, emission from the flash lamp produced a light spot of about 1-cm diameter at the center of the cell, as recorded on UV-sensitive paper. The Xe lamp can operate at a higher, and more easily tunable, repetition rate than the N₂ lamp with better flux reproducibility and thus has proved to be more efficient. OH radicals were typically generated by flash photolysis ($\lambda \geq 165$ nm) of 0.17 Torr of H₂O (1 Torr = 133.32 Pa = 9.66×10^{18} /T molecule cm⁻³) and monitored following the flash by their resonance fluorescence at 308 nm ($A^2\Sigma^+ \rightarrow X^2\Pi$, 0–0 band). The latter was excited by a cw microwave-powered OH resonance lamp (~ 1 Torr of He saturated with water vapor) and was monitored at right angles to both the flash and resonance lamps through an interference filter. The fluorescence decay, directly proportional to the OH concentration, was recorded on a PC-based multichannel scaler as a summation of multiple flash photolysis experiments. Synchronous triggering of both the flash lamp and the fluorescence recording electronics was effected by applying a trigger input to the flash lamp power supply and to the multichannel scaler from a common pulse generator.

Reaction mixtures of the HFC reactant, H₂O, and Ar were slowly flowed through a double-walled Pyrex reaction cell (100 cm³ in volume) at a total pressure of 35 Torr. The cell's temperature was controlled by passing methanol (for cooling) or glycol (for heating) between the walls of the cell. Reaction mixtures were generated and used in two different manners. First, they could be prepared manometrically in 5-L glass storage bulbs and flowed through the cell at a typical flow rate of 0.36 cm³ s⁻¹ STP. Alternatively, they could be prepared upstream of the cell by the confluence of separate flows of HFC, H₂O/Ar, and Ar at a typical total flow rate of 1.36 cm³ s⁻¹ STP. In all cases, the HFC concentration in the reaction cell was in great excess over that of OH (10^{10} – 10^{11} molecule cm⁻³) so that first-order kinetic behavior applied. The OH decay curves (Figure 1) were analyzed with a weighted linear least-squares routine [$\ln(\text{fluorescence signal})$ vs time] to derive the first-order decay rates k_{1st} . Several such determinations were made at each set of experimental conditions, and after a suitable delay period following the flash (see later discussion), the decays were all well represented by exponential fits. First-order decay rates, k_{1st} , were determined at several reactant partial pressures at each temperature, and the second-order rate constants were derived from weighted linear least-squares plots of k_{1st} vs reactant concentration (Figure 2).

Samples of HFC-227ea and -245ca were obtained from Allied Signal Corp. whereas those of HFC-236ea and -356ffa were

[†] Present address: Brookhaven National Laboratory, Bldg. 815, P.O. Box 5000, Upton, NY 11973-5000.

[‡] Present address: Louisiana State University, Department of Chemistry, Baton Rouge, LA 70803.

[§] Present address: Bhabha Atomic Research Centre, Chemistry Division, Trombay, Bombay, 400 085 India.

[⊙] Abstract published in *Advance ACS Abstracts*, March 15, 1994.

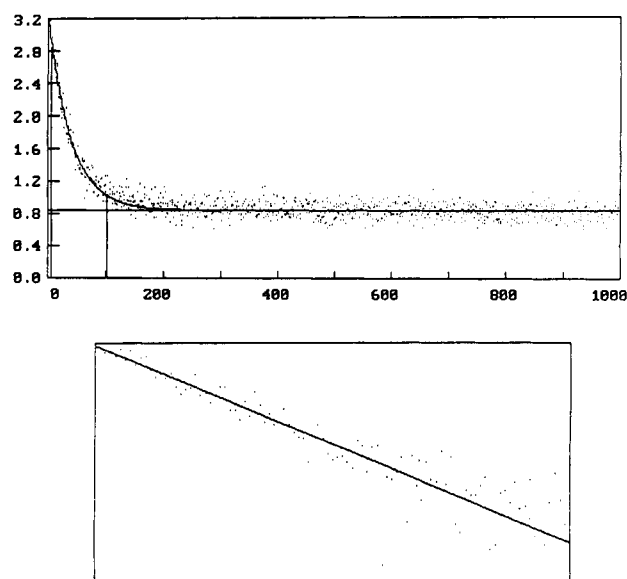


Figure 1. Upper panel shows the decay of OH resonance fluorescence from an average of 700 flashes with a $\text{CF}_3\text{CHFCF}_3$ (HFC-227ea) partial pressure of 3.39 Torr at a total pressure of 35 Torr and a temperature of 296 K. The x axis gives the channel number (channel width = 100 μs) and the y axis the number of counts per channel. Data within the marked range were used to derive the first-order decay rate: $252 \pm 19 \text{ s}^{-1}$. The lower panel is a semilogarithmic plot of the marked range in the upper panel.

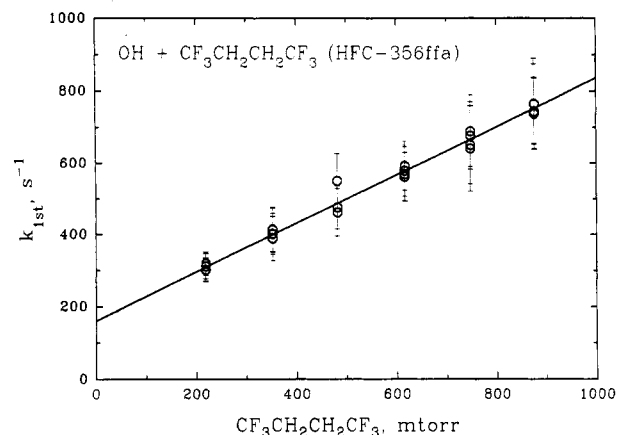


Figure 2. Plot of first-order OH decay rate (s^{-1}) vs partial pressure of $\text{CF}_3\text{CH}_2\text{CH}_2\text{CF}_3$ (HFC-356ffa) in mTorr at a total pressure of 35 Torr and a temperature of 365 K. The fit to this data yields $k = (2.55 \pm 0.12) \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

provided by the Environmental Protection Agency, Air and Energy Engineering Research Laboratory. The analysis provided with the HFC samples indicated that the sample of HFC-227ea contained less than 1 ppm of hexafluoropropene and that the sample of HFC-245ca contained no olefinic impurity and less than 30 ppm of other (presumably less reactive) impurities. The sample of HFC-356ffa had a stated purity of 99.99% and that of HFC-236ea 98.97%. Before use, the samples of HFC-227ea and -245ca were outgassed and those of HFC-236ea and -356ffa were further treated by two-stage vacuum fractional distillations. The argon diluent gas had a manufacturer's stated purity of $\geq 99.998\%$ and was used as supplied.

Results and Discussion

Rate constants determined for the OH + HFC reactions are tabulated in Table 1, and the derived Arrhenius parameters are summarized in Table 2 and plotted in Figure 3. All uncertainties given in Tables 1 and 2 and Figure 3 are two standard deviations derived from the statistical analyses and do not include an estimated additional uncertainty of $\sim 10\%$ for possible systematic errors. Since our measurements were performed over temperature

TABLE 1: Rate Constants for the Reactions of OH + HFC^a

compound	<i>T</i> (K)	<i>k</i> ($10^{15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)	flash energy, rate
$\text{CF}_3\text{CHFCF}_3$ (HFC-227ea)	270	0.926 ± 0.070	
	296	1.56 ± 0.11	
	296	1.60 ± 0.11	1.3 J
	313	1.82 ± 0.27	
	330	2.70 ± 0.15	
$\text{CF}_3\text{CHFCHF}_2$ (HFC-236ea)	365	4.64 ± 0.55	
	260	5.04 ± 0.76	1.3 J
	260	4.38 ± 0.83	
	270	5.22 ± 0.59	
	270	4.91 ± 0.54	2 Hz
	283	6.58 ± 0.87	
	301	7.67 ± 0.99	
	305	8.87 ± 1.26	
$\text{CHF}_2\text{CF}_2\text{CH}_2\text{F}$ (HFC-245ca)	330	13.9 ± 1.6	
	365	21.8 ± 2.3	
	260	5.35 ± 0.90	
	270	6.41 ± 1.10	0.6 J, 3 Hz
	270	5.48 ± 0.48	3.0 J
	270	6.27 ± 0.80	3.0 J, 5 Hz
	270	5.93 ± 0.65	3.0 J, 3 Hz
$\text{CF}_3\text{CH}_2\text{CH}_2\text{CF}_3$ (HFC-356ffa)	283	9.00 ± 1.14	
	301	12.9 ± 1.3	2.5 J
	330	18.1 ± 1.7	
	365	29.5 ± 3.5	
	260	4.31 ± 0.62	
	260	3.90 ± 0.50	1.3 J
	270	4.49 ± 0.51	
	270	4.28 ± 0.58	1.3 J
	283	6.51 ± 0.69	
	296	8.17 ± 1.04	
	330	15.5 ± 1.1	
	365	25.5 ± 1.2	

^a Except where separately noted, the flash energy is 2.6 J and the flash repetition frequency is 4 Hz.

ranges around room temperature, we have fitted the $k(T)$ data to the modified Arrhenius equation $\ln(k)$ vs $(1/T - 1/298)$, which yields E/R in the slope and $k(298 \text{ K})$ in the intercept. The preexponential factors, A were then calculated using the E/R and $k(298 \text{ K})$ values derived from these weighted linear least-squares fits. We elected to present the results in this manner (consistent with the procedure used by the NASA Panel for Data Evaluation⁴) because the statistical uncertainty in the derived A factor does not necessarily reflect the true spread of the experimental data obtained over a limited temperature range. Thus, the uncertainty is expressed in the derived $k(298 \text{ K})$ and E/R values.

Prior to the experimental work reported here being conducted, a series of tests were carried out to ensure that experimental conditions and data analysis procedures would be properly adjusted to accommodate the characteristics of the new Xe flash lamp, thereby minimizing contributions to the OH decays due to reactions other than those with the HFC. Such competing OH reactions could include those with photolysis or reaction products, either transient (produced during or immediately after each flash) or longer-lived (accumulated in multiframe experiments). Contributions to the OH fluorescence decays could be significant in some circumstances⁵ if flash energy and repetition frequency were too high and/or gas flow rate through the reaction cell too low.

Tests were performed with a number of $\text{CH}_3\text{Br}/\text{H}_2\text{O}/\text{Ar}$ mixtures to examine the effects of flash energy, flash repetition frequency, and gas flow rate on the derived first-order OH decay rates, k_{1st} . Since the reaction of OH with CH_3Br is quite slow and the subsequent OH + CH_2Br reaction very fast, this system provides a stringent test of the possible occurrence of interfering secondary radical-radical reactions.⁶ To check for the influence of flash energy, for example, each reaction mixture was used to obtain values of k_{1st} at flash energies ranging from 0.5 to 3.0 J. Such experiments resulted in a less than 10% increase in the observed first-order decay rate, indicating that any effect of OH reactions with transient primary and photolysis products was

TABLE 2: Arrhenius Parameters for the OH Reactions and Estimated Tropospheric Lifetimes of the HFCs Studied^a

compound (HFC)	$k(298\text{ K})$	$E/R \pm \Delta E/R$	A -factor	τ (tropospheric)
$\text{CF}_3\text{CHFCF}_3$ (227ea)	1.62 ± 0.03	1613 ± 135	0.363	40
$\text{CF}_3\text{CHFCHF}_2$ (236ea)	8.51 ± 0.26	1434 ± 161	1.05	7.2
$\text{CHF}_2\text{CF}_2\text{CH}_2\text{F}$ (245ca)	10.9 ± 0.3	1661 ± 170	2.87	6.3
$\text{CF}_3\text{CH}_2\text{CH}_2\text{CF}_3$ (356ffa)	8.75 ± 0.18	1734 ± 87	2.94	7.6

^a Units: $k(298\text{ K})$, $10^{-15}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$; E/R , K; A , $10^{-12}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$; τ , year.

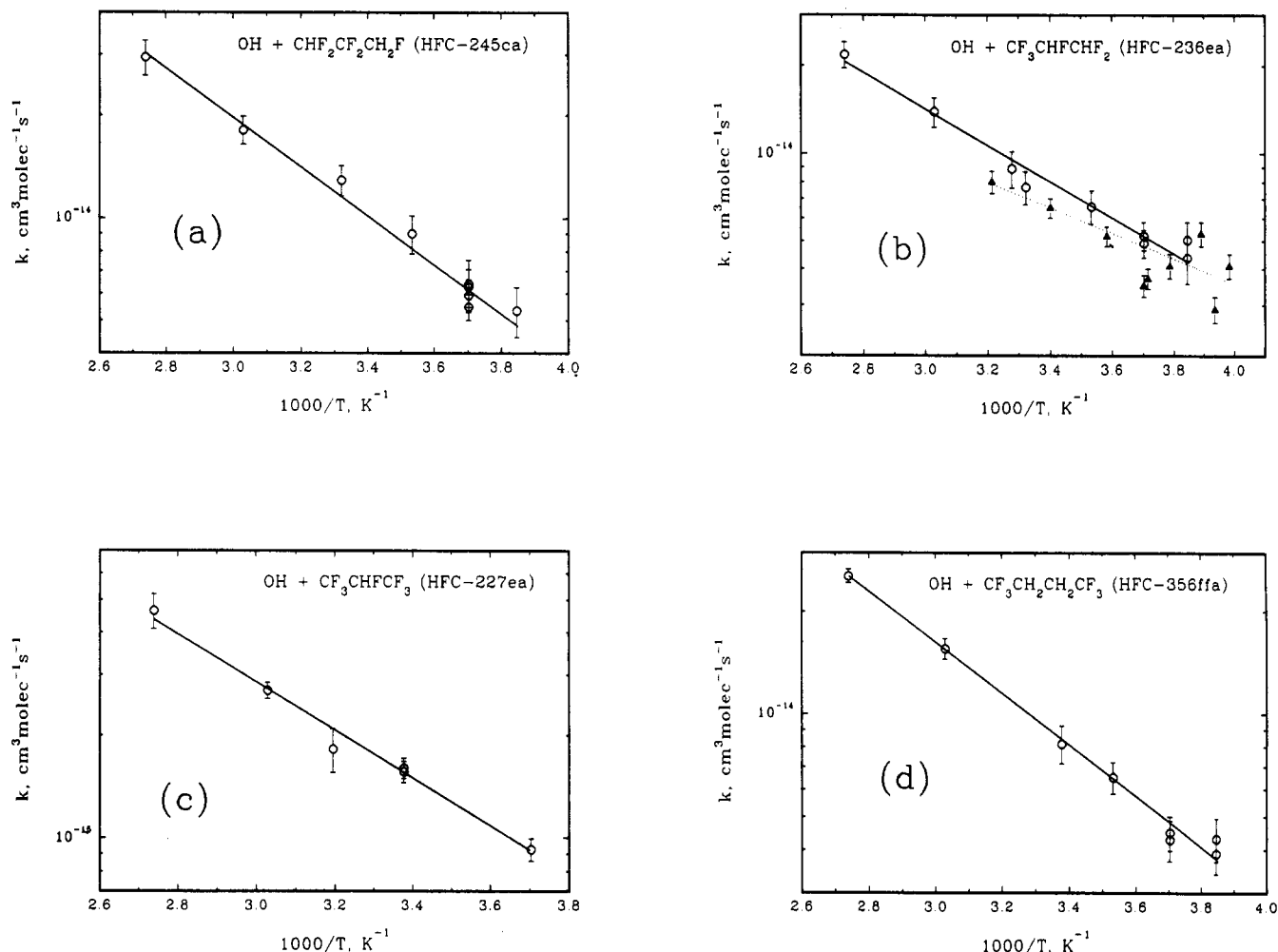


Figure 3. Arrhenius plots for the four title reactions. The solid lines and open circles indicate this work; the dotted line and filled triangles in part b indicate the work of Garland *et al.* (ref 9).

within the level of overall uncertainty of the measurements. In similar experiments, no change was discernible in k_{1st} when the reaction mixture flow rate was reduced from 3.33 to $0.36\text{ cm}^3\text{ s}^{-1}$, thus indicating that the decays were free from contributions from OH reacting with accumulated reaction or photolysis products.

To further verify the absence of significant contributions from competing reactions, rate constant determinations for the reaction of OH with $\text{CHF}_2\text{CF}_2\text{CH}_2\text{F}$ (HFC-245ca) were carried out at a number of different flash energy and flash repetition frequency levels. No statistically significant difference could be found among rate constants obtained at the same temperature (Table 1). Nor did the Arrhenius plot (Figure 3) exhibit noticeable curvature beyond uncertainty limits. The flash energy, flash repetition frequency, and gas flow rate were therefore set at 2.6 J, 4 Hz, and 0.36 (or $1.36\text{ cm}^3\text{ s}^{-1}$), respectively, in subsequent measurements for the three other compounds. Nevertheless, some experiments were conducted with reduced flash energy or repetition frequency for each compound at temperatures around 270 K. Again, effects of competing reactions turned out to be insignificant (Table 1).

As noted in the Experimental Section, first-order decay rates were derived from weighted linear least-squares analyses of $\ln(\text{OH fluorescence signal})$ vs reaction time. For a truly

exponential decay, the derived value for k_{1st} should be constant, regardless of which part of the decay curve is selected for use in the regression. However, larger values for k_{1st} were calculated when the selected analysis range extended from the origin of the decay curve, whereas it decreased to a nearly constant value as the starting point for analysis was displaced from the flash onset. This behavior is attributed to complications from scattered flash lamp radiation, short-lived flash-initiated fluorescence of the cell and optical materials, and possibly (to a lesser extent) contributions from radical-radical reactions at short times. The least-squares analyses of the decay curves were thus carried out by fitting different time spans to determine a "common" starting point for unbiased analysis. For all curves, this point was a few hundred microseconds after the common flash lamp and analysis electronics trigger. As shown in Figure 1, data points were collected well after the OH signal had dropped to background level, allowing for baseline determination from the average signal intensity over the last few hundred channels.

To our knowledge, there are no published or unpublished results for $\text{CHF}_2\text{CF}_2\text{CH}_2\text{F}$ (HFC-245ca) and $\text{CF}_3\text{CH}_2\text{CH}_2\text{CF}_3$ (HFC-356ffa) with which to compare the present work. For the reaction $\text{OH} + \text{CF}_3\text{CHFCF}_3$ (HFC-227ea), two recent studies have yielded results nearly identical with those reported here. Nelson *et al.*⁷

have determined the Arrhenius expression $k = (3.7 \pm 1.1) \times 10^{-13} \exp[-(1615 \pm 190)/T] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ from data between 294 and 369 K. Zellner *et al.*⁸ have also performed experiments at room temperature and above (298–463 K) from which they derive the expression $k = (3.8 \pm 0.8) \times 10^{-13} \exp[-(1596 \pm 77)/T] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. Hence, our data provide experimental validation of the extrapolation of the higher temperature data to the lower temperatures of atmospheric importance.

Garland *et al.*⁹ have recently reported studies of the reaction $\text{OH} + \text{CF}_3\text{CHFCHF}_2$ (HFC-236ea) for which they derive the Arrhenius expression $k = (2.0 \pm 0.9) \times 10^{-13} \exp[-(1000 \pm 200)/T] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. As seen in Figure 3, their data show considerable scatter at lower temperature but agree with the present work over the entire temperature range of overlap within the statistically derived error limits. Thus, the differences in the derived Arrhenius parameters are quite misleading.

An important use of these kinetic data is in the calculation of atmospheric lifetimes. While the exact lifetime is best calculated by using an atmospheric photochemical model and taking into account loss mechanisms other than gas-phase reaction with OH, an estimate of the tropospheric lifetime can be obtained by a comparison of the reactivity of a compound with that of methylchloroform (CH_3CCl_3).¹⁰ Such a calculation assumes that reaction with OH is the dominant tropospheric loss mechanism for both methylchloroform and the compound of interest and, hence, is useful only in a semiquantitative manner to compare the relative lifetimes of species whose atmospheric photochemistries are similar. The overall atmospheric lifetime is then calculated from the sum of the reciprocals of the tropospheric lifetime and the stratospheric lifetime (estimated from modeling calculations). Considering only tropospheric loss due to reaction with OH, the HFC tropospheric lifetime, $\tau(\text{HFC})$, can be approximated by

$$\tau(\text{HFC})/\tau(\text{CH}_3\text{CCl}_3) = k_{277\text{K}}(\text{CH}_3\text{CCl}_3)/k_{277\text{K}}(\text{HFC})$$

where $\tau(\text{CH}_3\text{CCl}_3)$ is the tropospheric lifetime of methylchloroform with respect to reaction with OH and $k_{277\text{K}}(\text{CH}_3\text{CCl}_3)$ and $k_{277\text{K}}(\text{HFC})$ are the rate constants for the reactions of OH with CH_3CCl_3 and the HFC (from this work), respectively, at 277 K. A value of $\tau(\text{CH}_3\text{CCl}_3)$ of approximately 6.6 years with respect to reaction with OH can be calculated by adjusting the total lifetime of 5.4 years^{11,12} for the estimated 85-year lifetime due to ocean loss and the 45-year lifetime calculated for stratospheric loss.^{12,13} Thus, with $k_{277\text{K}}(\text{CH}_3\text{CCl}_3)^{14} = 6.5 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ we have estimated the tropospheric lifetimes included in Table 1. As can be seen, the lifetimes calculated in this manner range from 6.0 to 40 years. This simple method has its greatest utility for compounds such as these, with OH rate constants similar to that for CH_3CCl_3 and lifetimes long enough to minimize the effects of seasonal variability in the tropospheric OH field and complications due to the interhemispheric variability observed for very short-lived compounds.

Finally, it is interesting to compare the Arrhenius parameters derived from the present data to see if they reveal any effects that can be associated with the extent and nature of the fluorine substitution. As for other C_2 - and C_3 -halogenated alkanes,⁴ the fluorine substitution increases the activation energy over that derived for the OH + alkane reactions. For the HFCs investigated here, there are little or no statistically significant differences among the E/R values. They are all quite similar to those for the fluorinated ethanes,⁴ with the small differences making the determination of any trends extremely difficult. The more significant differences among the derived A -factors, however, do permit some observations to be made regarding their relationships to the number and types of abstractable H-atoms.

When one considers that in nonhalogenated alkanes the average A -factor is approximately 1×10^{-12} (in units of $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$), it is quite apparent that F-atom substitution can markedly reduce this parameter. For example, the A -factor of 0.36×10^{-12} for HFC-227ea can be associated entirely with the single C–H

bond in the $-\text{CHF}-$ group. It appears that the presence of two CF_3 groups α to the $-\text{CHF}-$ have reduced the A -factor from its alkane value. A similar A -factor for the $-\text{CHF}-$ group is obtained from data for HFC-43-10mee.^{15,16} Subtraction of the value of the $-\text{CHF}-$ A -factor allows a value of 0.7×10^{-15} to be derived for the $-\text{CHF}_2$ group in HFC-236ea, slightly larger than that derived from HFC-125.⁴ Hence the negative influence of the $\text{CF}_3\text{CHF}-$ group in HFC-236ea is not as great as that of the $-\text{CF}_3$ group in HFC-125. With this value for the A -factor for $-\text{CHF}_2$, we can assign an A -factor per C–H bond of approximately 1.1×10^{-12} to the $-\text{CH}_2\text{F}$ group in HFC-245ca. While this value is similar to that for the C–H bonds in alkanes, it is considerably smaller than the average value of 1.8×10^{-12} in CH_3F . Hence, the CHF_2CF_2- group in HFC-245ca can be considered as having effectively reduced the A -factor associated with $-\text{CH}_2\text{F}$. Lastly, an A -factor of 0.74×10^{-12} per C–H bond can be calculated for the $-\text{CH}_2-$ groups in HFC-336ffa. Again, it appears that the $-\text{CF}_3$ α to each $-\text{CH}_2-$ lowers the A -factor of the latter. While these observations are semiquantitative, the growing body of precise kinetic data for such compounds should eventually permit a more quantitative appraisal of such effects in the near future.

Acknowledgment. This work was funded by the U.S. Environmental Protection Agency and the National Aeronautics and Space Administration. Although the manuscript has undergone an EPA policy review, it does not necessarily reflect the views of or infer an official endorsement by the agency. The authors thank Dr. H. Magid of Allied Chemicals for the analyzed samples of HFC-227ea and HFC-245ca and Dr. D. Smith of the U.S. Environmental Protection Agency for arranging the supply of the samples of HFC-236ea and HFC-356ffa. We also wish to express our gratitude to Dr. H. Nelson of the Naval Research Laboratory and Dr. R. Zellner of the University of Essen (Germany) for communicating the results from their laboratories prior to publication and to Dr. A. R. Ravishankara of the National Oceanic and Atmospheric Administration for providing information on the Xe flash lamp.

References and Notes

- (1) Kurylo, M. J.; Cornett, K. D.; Murphy, J. L. *J. Geophys. Res.* **1982**, *87*, 3081.
- (2) Wallington, T. J.; Neuman, D. M.; Kurylo, M. J. *Int. J. Chem. Kinet.* **1987**, *19*, 725.
- (3) Liu, R.; Huie, R. E.; Kurylo, M. J. *J. Phys. Chem.* **1990**, *94*, 3247.
- (4) DeMore, W. B.; Sander, S. P.; Golden, D. M.; Hampson, R. F.; Kurylo, M. J.; Howard, C. J.; Ravishankara, A. R.; Kolb, C. E.; Molina, M. J. *Chemical Kinetics and Photochemical Data for Use in Stratospheric Modeling*; Evaluation Number 10 of the NASA Panel for Data Evaluation, *JPL Publication 92-20*, August 15, 1992.
- (5) Zhang, Z.; Huie, R. E.; Kurylo, M. J. *J. Phys. Chem.* **1992**, *96*, 1533.
- (6) Zhang, Z.; Saini, R. D.; Kurylo, M. J.; Huie, R. E. *Geophys. Res. Lett.* **1992**, *19*, 2413.
- (7) Nelson, D. D., Jr.; Zahniser, M. S.; Kolb, C. E. *Geophys. Res. Lett.* **1993**, *20*, 197.
- (8) Zellner, R.; Bednarek, G.; Hoffmann, A.; Kohlmann, J. P.; Mörs, V.; Saathoff, H. *Ber. Bunsen-Ges. Phys. Chem.*, in press.
- (9) Garland, N. L.; Medhurst, L. J.; Nelson, H. H. Presented at the Third International Conference on Chemical Kinetics; Gaithersburg, MD; July, 1993.
- (10) Prather, M.; Spivakovsky, C. M. *J. Geophys. Res.* **1990**, *95*, 18723.
- (11) Prinn, R.; Cunnold, D.; Simmonds, P.; Alyea, F.; Boldi, R.; Crawford, A.; Fraser, P.; Gutzler, D.; Hartley, D.; Rosen, R.; Rasmussen, R. *J. Geophys. Res.* **1992**, *97*, 2445.
- (12) Prather, M. J. Presented at the NASA/NOAA/AFEAS Workshop on the Atmospheric Degradation of HCFCs and HFCs; Boulder, CO; November, 1993.
- (13) World Meteorological Organization (WMO) Global Ozone Research and Monitoring Project, Report No. 25, *Scientific Assessment of Ozone Depletion*; 1991.
- (14) Talukdar, R. K.; Mellouki, A.; Schmoltnner, A.-M.; Watson, T.; Montzka, S.; Ravishankara, A. R. *Science* **1992**, *257*, 227.
- (15) Zhang, Z.; Saini, R. D.; Kurylo, M. J.; Huie, R. E. *Chem. Phys. Lett.* **1992**, *200*, 230.
- (16) Schmoltnner, A. M.; Talukdar, R. K.; Warren, R. F.; Mellouki, A.; Goldfarb, L.; Gierczak, T.; McKeen, S. A.; Ravishankara, A. R. *J. Phys. Chem.* **1993**, *97*, 8976.