J. Phys. Chem. A **2000,** *104,* 1165−1170

Rate Constants for the Reactions of OH Radicals with $CH_3OCF_2CHF_2$, $CHF_2OCH_2CF_2CHF_2$, $CHF_2OCH_2CF_2CF_3$, and $CF_3CH_2OCF_2CHF_2$ over the Temperature Range 250−430 K

Kazuaki Tokuhashi,*,† Akifumi Takahashi,† Masahiro Kaise,† Shigeo Kondo,† Akira Sekiya,†
Shiro Yamashita,‡ and Haruaki Ito‡

National Institute of Materials and Chemical Research, 1-1 Higashi, Tsukuba, Ibaraki 305-8565, Japan, and Research Institute of Innovative Technology for the Earth, Hongo Wakai Bldg., 2-40-17, Hongo, Bunkyo-ku, Tokyo 113-0033, Japan

Received: April 29, 1999; In Final Form: November 30, 1999

The OH reaction rate constants have been measured for $CH_3OCF_2CHF_2$, $CHF_2OCH_2CF_2CHF_2$, $CHF_2OCH_2CF_2CF_3$, and $CF_3CH_2OCF_2CHF_2$ over the temperature range 250−430 K. Kinetic measurements have been carried out using the flash photolysis, laser photolysis, and discharge flow methods, combined respectively with the laser-induced fluorescence technique to monitor the OH radical concentrations. The influence of impurities contained in the samples of fluorinated ethers has been investigated by means of sample purification using gas chromatography. No sizable effect of impurities was found on the measured rate constants of these fluorinated ethers, if the purified samples were used in the kinetic measurements. The Arrhenius rate constants have been determined from the respective kinetic data as $k(CH_3OCF_2CHF_{2)} = 2.60 \times 10^{-12} \exp[-(1420 \pm 170)/T]$, $k(CHF_2OCH_2CF_2CHF_2) = 2.49 \times 10^{-12} \exp[-(1500 \pm 170)/T]$, $k(CHF_2OCH_2CF_2CF_3) = 2.14 \times 10^{-12} \exp[-(1580 \pm 170)/T]$, and $k(CF_3CH_2OCF_2CHF_2) = 1.49 \times 10^{-12} \exp[-(1520 \pm 170)/T]$ cm^3 molecule^{-1} s^{-1}, where the quoted errors represent the 95% confidence level and included systematic errors. Uncertainty factors at 298 K (with the formulation of the NASA panel for data evaluation[14]) for these fluorinated ethers were 1.1.

Introduction

Since fully halogenated chlorofluorocarbons (CFCs) cause the depletion of the stratospheric ozone layer as well as the global warming, a number of replacement compounds such as hydrofluorocarbons (HFCs), hydrochlorofluorocarbons (HCFCs), and partially fluorinated ethers, have been investigated for industrial applications. In particular, partially fluorinated ethers are now candidates as new CFC alternatives.[1] Since partially fluorinated ethers as well as HFCs do not contain Cl atoms, they do not contribute to the ozone depletion, but may potentially cause the global warming effect. The global warming potential is estimated from the atmospheric lifetime of these molecules and the infrared absorption intensity. Since saturated organic compounds containing hydrogen atoms are expected to be oxidized by OH radicals in the troposphere,[2] the atmospheric lifetime is determined primarily by the reaction rate of these molecules against OH radicals. Thus, the study of the reactivity against OH radicals is crucial for the evaluation of the atmospheric lifetime of these molecules.

To obtain the environmental assessment of chemical substances, accurate measurement of the OH reaction rate constant is required as well as the development of the method for predicting their values by theoretical and empirical approaches. The problem here is that the reactive impurities contained in the sample may seriously affect the rate constant determination, because the reactivity of some fluorinated ethers as well as HFCs and HCFCs are fairly small. It is necessary to carry out the kinetic measurements for the samples with high enough purity. In fact, there have been some cases where too large values of rate constants were reported possibly due to interference from reactive impurities. It is essential to examine the sample purity and its influence on the obtained values very carefully. Although there are a numerous data of OH reaction rate constants for HFCs and HCFCs, there is little information on fluorinated ethers. In this paper, we report the results of the kinetic measurements for the OH reaction rate constants of $CH_3OCF_2CHF_2$, $CHF_2OCH_2CF_2CHF_2$, $CHF_2OCH_2CF_2CF_3$, and $CF_3CH_2OCF_2CHF_2$ over the temperature range 250−430 K. Effects of impurities on the measured rate constants have been carefully investigated by the sample purification with gas chromatography.

Experimental Section

The kinetic measurements have been carried out over the temperature range 250−430 K by using the flash photolysis (FP), laser photolysis (LP), and discharge flow (DF) methods. The concentration of OH radicals has been monitored by using the laser-induced fluorescence (LIF) technique. The experimental apparatus and procedure for the kinetic measurements have been described in detail previously,[3] and only a brief summary will be given here.

The Pyrex glass reactor with an inner diameter of 25 mm (about 40 cm long) is used for the LP and FP experiments. In the case of the FP method, H_2O was directly photolyzed with pulsed light of the Xe flash lamp (EG & G, FX-193U, 600−

---

* Corresponding author. Address: Department of Physical Chemistry, National Institute of Materials and Chemical Research, 1-1 Higashi, Tsukuba, Ibaraki 305-8565, Japan, E-Mail: tokuhashi@nimc.go.jp.

† National Institute of Materials and Chemical Research.

‡ Research Institute of Innovative Technology for the Earth.

10.1021/jp991421+ CCC: \$19.00

1300 V and 2 μF, 0.36−1.69 J pulse^{-1}, typically 0.64 J pulse^{-1}, pulse width is 10−20 μs, $\lambda \geq 180$ nm, quartz cutoff) in the presence of a large excess of argon bath gas. In the case of the LP method, OH radicals are produced by the reaction $O(^1D) + H_2O \rightarrow 2OH$, in the presence of a large excess of helium bath gas, where $O(^1D)$ atoms are generated by photodissociation of N_2O with ArF excimer laser (around 2−5 mJ cm^{-2} pulse^{-1}). To prevent accumulation of photoflagments and/or reaction products, all photolysis experiments were carried out under slow flow conditions. The repetition rate of the FP lamp and excimer laser was 10 Hz.

For the DF method, Pyrex flow tubes (20 mm in inner diameter, about 700 and 900 mm long) with a movable double sliding injector have been used. Helium was used as the primary carrier gas. OH radicals are produced by the reaction, $H + NO_2 \rightarrow OH + NO$, which follows the microwave discharge of Ar gas containing a trace amount of hydrogen. Both the flow tube and the sliding injector are coated with Teflon to minimize the wall loss of OH radicals. In the case of the DF method, a small correction factor (around 1%) is applied to each pseudo-first-order rate constant to account for the axial diffusion effect.[4] The $H + NO_2$ reaction produces some vibrationally excited OH radicals.[5] However, in our typical experimental condition (P = 6 Torr, U = 5 m s^{-1}, Helium carrier gas), the distance required for 99% quenching of excited OH is calculated to be about 5.4 cm by using the relation reported by Howard.[6] Thus, the effects of vibrationally excited OH generated by the $H + NO_2$ reaction are negligible. In the case of the DF method, the initial concentration of OH radicals is estimated from the flow rate of hydrogen. For both LP and FP methods, the initial concentrations of OH radicals is estimated from comparison of the fluorescence intensities with the DF method.[3] In all cases, the initial concentration of OH radicals is always kept less than 10^{11} molecules cm^{-3}.

The excitation light for the LIF method is from a frequency-doubled tunable dye laser (pumped by the second harmonic of 10 Hz Nd:YAG laser), and the wavelength is tuned at about 308 nm. The fluorescence signal from the OH radicals was monitored at about 308 nm, and the scattered light of the excitation light (and photolysis light source for LP and FP methods) was reduced by a monochromator. A photomultiplier tube was used to monitor the fluorescence signals. The signals were accumulated by a multichannel scaler/averager or averaged by a digital storage oscilloscope.

The flow rate of each gas was measured and controlled by calibrated mass flow controllers. The total gas pressure of the reactor was monitored by using a capacitance manometer and was kept constant by an electrically controlled exhaust throttle valve. The temperature of the reactor was maintained either by an electric heater or by circulating fluid through the outer jacket of the reactor from a thermostated bath. It was measured with a CA thermocouple. During the experiments, the temperature across the reaction volume was maintained better than ±2 K over the temperature range examined. To ensure that the experimental data are free from unexpected daily fluctuation of experimental conditions and experimental setup, the experiments were repeated at intervals from several days to several months under a variety of experimental conditions.

The sample purity was analyzed by using gas chromatography with an FID detector, where the integrated intensity of the main peak against the total area was taken as the purity. The lowest value obtained by using different columns was taken as the sample purity. The results of the analysis are 99.82, 99.9, 99.65, and 99.75%, respectively, for $CH_3OCF_2CHF_2$, $CHF_2OCH_2CF_2CHF_2$, $CHF_2OCH_2CF_2CF_3$, and $CF_3CH_2OCF_2CHF_2$. These samples were purified by gas chromatography.

TABLE 1: Observed OH Reaction Rate Constants of $CH_3OCF_2CHF_2$, $CHF_2OCH_2CF_2CHF_2$, $CHF_2OCH_2CF_2CF_3$, and $CF_3CH_2OCF_2CHF_2$ at 298 K

fluorinated ether	$10^{14}k$,[a] cm^3 molecule^{-1} s^{-1}	technique[b]	purity, %
$CH_3OCF_2CHF_2$	2.97 ± 0.35	FP	99.82
	3.00 ± 0.36	LP	99.82
	2.74 ± 0.29	DF	99.82
	2.10 ± 0.25	FP	99.99[c]
	2.25 ± 0.26	LP	99.99[c]
	2.27 ± 0.25	DF	99.99[c]
$CHF_2OCH_2CF_2CHF_2$	1.73 ± 0.21	FP	99.9
	1.74 ± 0.19	LP	99.9
	1.96 ± 0.24	DF	99.9
	1.45 ± 0.16	FP	99.997[c]
	1.56 ± 0.17	LP	99.997[c]
	1.68 ± 0.22	DF	99.997[c]
$CHF_2OCH_2CF_2CF_3$	1.17 ± 0.14	FP	99.65
	1.33 ± 0.17	LP	99.65
	1.23 ± 0.14	DF	99.65
	0.975 ± 0.103	FP	99.9976[c]
	1.02 ± 0.13	LP	99.9976[c]
	1.02 ± 0.11	DF	99.9976[c]
$CF_3CH_2OCF_2CHF_2$	1.17 ± 0.13	FP	99.75
	1.28 ± 0.15	LP	99.75
	1.33 ± 0.16	DF	99.75
	0.854 ± 0.101	FP	99.996 [c]
	0.921 ± 0.107	LP	99.996 [c]
	0.926 ± 0.117	DF	99.994 [c]

[a] The quoted errors represent the 95% confidence level from linear least-squares analysis and included systematic errors. [b] FP, flash photolysis; LP, laser photolysis; DF, discharge flow. [c] Purified sample by using gas chromatography.

In the purification process, the sample gas or vapor was charged in an evacuated sampling tube (inner volume of about 15−25 cm^3) and introduced to a stainless steel column (7.4−9.6 mm i.d., about 4−8m long) packed with Silicone DC 702 (Shimadzu). Nitrogen was used as the carrier gas. The middle fraction of the main peak was collected into a trap cooled with liquid nitrogen. This procedure was automatically repeated hundreds of times in order to collect the purified sample. To obtain a sufficient amount of sample for the measurements of the temperature dependency of the OH reaction rate by using several techniques, it is necessary to make the purification process continuously for a period of one month or more. The yield of purified sample is approximately one-quarter of the original sample. The results of the analysis for purified samples are 99.99, 99.997, 99.9976, and 99.994%, respectively, for $CH_3OCF_2CHF_2$, $CHF_2OCH_2CF_2CHF_2$, $CHF_2OCH_2CF_2CF_3$, and $CF_3CH_2OCF_2CHF_2$. The rate constants were determined for both the original and purified samples using all three techniques.

Results and Discussion

Effects of Impurities. According to the gas chromatographic analysis, the original sample purities have been found to be 99.82, 99.9, 99.65, and 99.75%, respectively, for $CH_3OCF_2CHF_2$, $CHF_2OCH_2CF_2CHF_2$, $CHF_2OCH_2CF_2CF_3$, and $CF_3CH_2OCF_2CHF_2$. The individual impurities were not identified. At the beginning, to make a rough estimation of the impurity effect, the OH reaction rate constants of these samples have been measured by using the FP, LP, and DF methods at 298 K. The results are summarized in Table 1. Here, the error limits are at the 95% confidence level derived from the linear least-squares fit to the plot of first-order rate constant versus reactant concentration and included systematic errors. The systematic errors in our experiments are estimated to be less than ±10%. As is apparent in Table 1, the measured rate constants by the three different methods agree with each other within the estimated uncertainties. To test for the presence and effects of reactive impurities, experiments were conducted by all three techniques for both the original and purified samples.

In a previous study[7] such a purification procedure has been shown to yield purified samples whose rate constants were in good agreement with established literature values even when the starting samples were highly impure. The OH reaction rate constants measured in the present study by using the purified samples of fluorinated ethers are summarized in Table 1. The measured rate constants of purified samples are about 24, 14, 19, and 29% smaller on the average than those of the original samples of $CH_3OCF_2CHF_2$, $CHF_2OCH_2CF_2CHF_2$, $CHF_2OCH_2CF_2CF_3$, and $CF_3CH_2OCF_2CHF_2$, respectively. If the sum total of impurities removed in each sample were responsible for the decreases in the observed rate constants, this would correspond to OH rate constants for the impurities in $CH_3OCF_2CHF_2$, $CHF_2OCH_2CF_2CHF_2$, $CHF_2OCH_2CF_2CF_3$, and $CF_3CH_2OCF_2CHF_2$ of 4.1, 2.6, 0.70, and 1.5 ($\times 10^{-12}$ cm^3 molecule^{-1} s^{-1}), respectively. For the purified samples, even if the OH rate constants of remaining impurities are as large as 1×10^{-11} cm^3 molecule^{-1} s^{-1}, their remaining influence on the measured rate constants can be no larger than 4.5, 1.9, 2.4, and 6.7% of the observed values for $CH_3OCF_2CHF_2$, $CHF_2OCH_2CF_2CHF_2$, $CHF_2OCH_2CF_2CF_3$, and $CF_3CH_2OCF_2CHF_2$, respectively. Thus, it is concluded that the effects of any remaining impurities is negligibly small for the purified samples.

Measurements of Rate Constants. The procedure for the kinetic measurements has been described in detail in our previous report.[3] Briefly, the observed LIF signal intensities from OH radicals have been plotted against reaction time for a certain sample concentration, and the pseudo-first-order rate constant (k_{obs}) has been derived from the slope of the straight line by the least-squares method. Then, the values of k_{obs} obtained for various sample concentrations have been plotted against the sample concentration, and the bimolecular rate constant has been derived from the slope by the linear least-squares fit to the observed data. To ensure that the experimental data are free from unexpected daily fluctuation of experimental conditions and experimental setup, the experiments were repeated at intervals ranging from several days to a few months under a variety of experimental conditions. The intercept of k_{obs} at zero reactant (k_d for FP and LP methods, and k_w for DF method) in the plot of k_{obs} versus concentration depends on the experimental conditions. However, in the case of the FP method, the values of k_d were smaller than about 20 s^{-1}. On the other hand, in the case of LP method, the values of k_d were smaller than about 20 s^{-1} for 250−298 K and 100 s^{-1} for 430 K. In the case of the DF method, the values of k_w were smaller than about 10 s^{-1}. From the values of k_{obs}, the background value (k_d or k_w) is subtracted, and the resulting values of ($k_{obs} - k_d$, or $k_{obs} - k_w$) are plotted against concentration. Figure 1 shows a typical example of the plot of $k_{obs} - k_d$ versus $CH_3OCF_2CHF_2$ concentration for various temperatures measured using the FP method. The plots show linear relationships with relatively small scatters. Therefore, it is concluded that the present rate constants derived from the least-squares fits are not dependent on any of the experimental factors.

The measurement of temperature dependency of the rate constants has been carried out for the purified samples. The OH reaction rate constants of $CH_3OCF_2CHF_2$, $CHF_2OCH_2CF_2CHF_2$, $CHF_2OCH_2CF_2CF_3$, and $CF_3CH_2OCF_2CHF_2$ over the temperature range 250−430 K measured with different methods are listed in Tables 2−5, respectively. The experimental conditions of individual measurements are also listed in these tables. The experiments were usually repeated six times (40−50 measurements of OH decay) at a temperature for each experimental method. In general, the degree of linearity and scatter of the $k_{obs} - k_d$ (or $k_{obs} - k_w$) versus reactant concentration plot is similar to the ones shown in Figure 1. In Tables 2−5, the concentration range of fluorinated ether (sixth column) represents the minimum and maximum concentrations during repetitive experiments. In all cases, the OH decay shows exponential behavior, and the linearity and scatter of the plotted points for individual experiments are much the same as the ones shown in Figure 1. Figure 2 shows the Arrhenius plots for the OH reaction rate constants, where the error bars of the data points represent the 95% confidence level derived from the linear least-squares fit to the plot of $k_{obs} - k_d$ (for FP and LP methods) and $k_{obs} - k_w$ (for DF method) versus reactant concentration. The estimated systematic errors are included here. As is apparent in Figure 2, the Arrhenius plots give linear relationships in the temperature range examined. The differences among the results obtained with the three different methods are small. Also, the systematic errors contained in the values derived with the individual techniques seem to be negligibly small in the experimental conditions employed here. The resulting Arrhenius rate parameters for the OH reactions are summarized in Table 6.

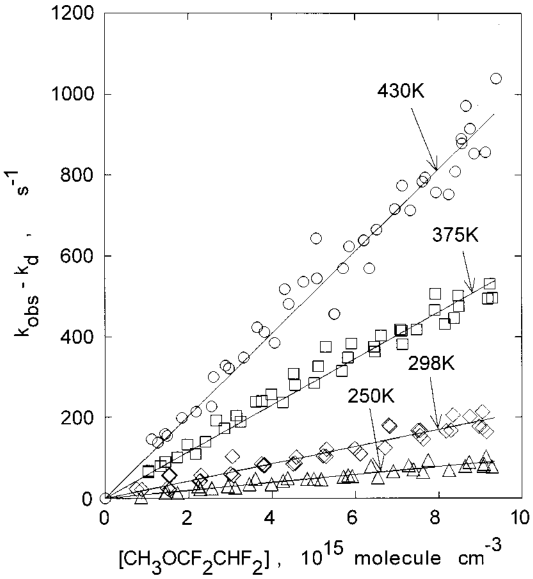

Figure 1. Plot of the pseudo-first-order rate constants corrected for background value, $k_{obs} - k_d$, against $CH_3OCF_2CHF_2$ concentration (FP-LIF method): (△) 250 K; (◇) 298 K; (□) 375 K; (○) 430 K.

Comparison with Literature Data. In Table 7, the OH reaction rate constants at room temperature of the four compounds are listed together with some other relevant molecules. The present values are those calculated from the Arrhenius rate parameters shown in Table 6. For $CH_3OCF_2CHF_2$ and $CF_3CH_2OCF_2CHF_2$, Heathfield et al.[8] have measured the OH rate constants at 298 K using the pulse radiolysis technique combined with the absorption method to monitor the OH concentration. As is shown in Table 7, their results are about 9 and 10 times as large as the present values for $CH_3OCF_2CHF_2$ and $CF_3CH_2OCF_2CHF_2$, respectively. In a previous study, we have measured the OH rate constants of $CH_3CH_2OCF_2CHF_2$ and CH_3OCF_2CHFCl using the same technique as the one adopted here over the temperature range 250−430 K.[9] The OH reaction rate

TABLE 2: Experimental Conditions and the Observed Values of OH Reaction Rate Constant of $CH_3OCF_2CHF_2$

temp, K	technique[a]	$10^{14}k$,[b] cm^3 $molecule^{-1}$ s^{-1}	$\tilde{t}$ or U range,[c] s or m s^{-1}	press. range, Torr	$10^{15}[CH_3OCF_2CHF_2]$ range, molecule cm^{-3}	no. of expts
250	FP	0.966 ± 0.115	0.31−0.49	20−40	0.85−9.28	6
	LP	0.998 ± 0.107	0.37−0.46	20−60	1.32−9.40	6
273	FP	1.35 ± 0.15	0.31−0.38	20−40	0.78−9.26	6
	LP	1.48 ± 0.16	0.33−0.39	20−40	1.07−9.38	6
298	FP	2.10 ± 0.25	0.32−0.38	20−40	0.75−9.15	6
	LP	2.25 ± 0.26	0.29−0.35	20−40	1.21−9.24	6
	DF	2.27 ± 0.25	5.0−7.5	5−6	0.19−1.92	5
331	FP	3.23 ± 0.36	0.31−0.40	20−40	0.91−9.22	6
375	FP	5.66 ± 0.60	0.29−0.38	20−40	1.03−9.29	6
430	FP	10.1 ± 1.1	0.30−0.37	20−40	1.11−9.39	6
	LP	10.5 ± 1.1	0.34−0.40	20−40	0.84−9.38	6

[a] FP, flash photolysis; LP, laser photolysis; DF, discharge flow. [b] The quoted errors represent the 95% confidence level from linear least-squares analysis and included systematic errors. [c] $\bar{t}$, residence time for FP and LP methods; U, linear flow velocity for DF method.

TABLE 3: Experimental Conditions and the Observed Values of OH Reaction Rate Constant of $CHF_2OCH_2CF_2CHF_2$

temp, K	technique[a]	$10^{14}k$,[b] cm^3 $molecule^{-1}$ s^{-1}	$\bar{t}$ or U range,[c] s or m s^{-1}	press. range, Torr	$10^{15}[CHF_2OCH_2CF_2CHF_2]$ range, molecule cm^{-3}	no. of expts
250	FP	0.682 ± 0.075	0.31−0.48	20−40	0.80−9.31	6
	LP	0.677 ± 0.072	0.36−0.44	40−60	0.86−9.42	7
273	FP	0.932 ± 0.110	0.30−0.38	10−40	0.74−9.11	6
	LP	1.04 ± 0.11	0.35−0.43	40−60	0.69−9.10	6
298	FP	1.45 ± 0.16	0.29−0.40	20−40	0.73−8.91	5
	LP	1.56 ± 0.17	0.30−0.37	20−40	1.18−9.11	6
	DF	1.68 ± 0.22	5.6−7.2	5−6	0.13−1.89	6
331	FP	2.50 ± 0.26	0.31−0.40	20−40	0.91−9.16	6
375	FP	4.53 ± 0.48	0.30−0.37	20−40	0.89−9.88	6
430	FP	8.11 ± 0.84	0.31−0.40	20−40	0.76−9.31	6
	LP	7.87 ± 0.81	0.34−0.40	20−40	1.06−9.23	6

[a] FP, flash photolysis; LP, laser photolysis; DF, discharge flow. [b] The quoted errors represent the 95% confidence level from linear least-squares analysis and included systematic errors. [c] $\bar{t}$, residence time for FP and LP methods; U, linear flow velocity for DF method.

TABLE 4: Experimental Conditions and the Observed Values of OH Reaction Rate Constant of $CHF_2OCH_2CF_2CF_3$

temp, K	technique[a]	$10^{14}k$,[b] cm^3 $molecule^{-1}$ s^{-1}	$\bar{t}$ or U range,[c] s or m s^{-1}	press. range, Torr	$10^{15}[CHF_2OCH_2CF_2CF_3]$ range, molecule cm^{-3}	no. of expts
250	FP	0.385 ± 0.042	0.38−0.49	20−60	0.85−9.71	6
	LP	0.413 ± 0.045	0.41−0.57	40−80	0.87−9.53	7
273	FP	0.636 ± 0.073	0.30−0.41	10−40	0.76−9.39	9
	LP	0.659 ± 0.071	0.35−0.41	40−60	1.18−9.51	6
298	FP	0.975 ± 0.103	0.33−0.42	20−60	0.69−9.41	6
	LP	1.02 ± 0.13	0.32−0.39	40−60	0.86−9.27	6
	DF	1.02 ± 0.11	5.0−7.1	5−6	0.15−1.86	5
331	FP	1.69 ± 0.18	0.35−0.40	20−40	0.74−9.09	6
375	FP	3.06 ± 0.33	0.30−0.40	20−40	0.74−9.43	6
430	FP	5.68 ± 0.58	0.30−0.40	20−40	0.61−7.35	6
	LP	5.61 ± 0.62	0.35−0.40	20−40	1.04−9.19	6

[a] FP, flash photolysis; LP, laser photolysis; DF, discharge flow. [b] The quoted errors represent the 95% confidence level from linear least-squares analysis and included systematic errors. [c] $\bar{t}$, residence time for FP and LP methods; U, linear flow velocity for DF method.

constants at 298 K were $(2.24 \pm 0.07) \times 10^{-13}$ and $(3.76 \pm 0.13) \times 10^{-14}$ cm^3 $molecule^{-1}$ s^{-1} for the former and the latter, respectively. Heathfield et al.[8] have also measured the OH reaction rate constants of these compounds at 298 K. As is apparent in Table 7, their values are about 2.0 and 4.4 times as large as our values[9] for $CH_3CH_2OCF_2CHF_2$ and CH_3OCF_2CHFCl, respectively. The purities of the samples used by Heathfield et al. are stated as better than 99% (the samples were supplied by ICI).[8] If it is the case and if the OH rate constants of impurities are as large as 1×10^{-11} (the worst case conceivable), the contribution of the impurities to the rate constant may approach 1×10^{-13}. It cannot be denied that the large values reported by Heathfield et al. are due to the presence of reactive impurities in their samples. As for $CF_3CH_2OCF_2CHF_2$ reported by Heathfield et al.[8] and $CHF_2OCH_2CF_3$ recommended by DeMore et al.,[14] there is no reason that the former should be about 8 times as large as the latter. Furthermore, as for CH_3OCF_2CHFCl and $CH_3OCF_2CHF_2$ reported by Heathfield et al.,[8] it seems that there is no reason that the reactivity of the former should be about 20% lower than that of the latter. Therefore, the results of Heathfield et al. seem to be doubtful. At any rate, the superior sample purity as well as the very small scatters of measured rate constants obtained through repetitive experiments under various experimental conditions and different methods may suggest that the present values are more reliable.

Estimation of Rate Constants by the SAR Method. Atkinson and co-workers[10−12] have proposed a method of predicting the OH reaction rate constants for a variety of compounds based on the structure activity relationship (SAR). It is of interest to examine whether this method can reproduce the reaction rate constants obtained in the present study. The predicted values of the OH reaction rate constants are also listed in Table 7. Here, since there is no substituent factor available for the $-OCH_2CF_2-$ group, this factor has been assumed to be equal to that for $-OCH_2CF_3$ to estimate the reaction rate

TABLE 5: Experimental Conditions and the Observed Values of OH Reaction Rate Constant of $CF_3CH_2OCF_2CHF_2$

temp, K	technique[a]	$10^{14}k$,[b] cm^3 molecule^{-1} s^{-1}	$\bar{\imath}$ or U range,[c] s or m s^{-1}	press. range, Torr	$10^{15}[CF_3CH_2OCF_2CHF_2]$ range, molecule cm^{-3}	no. of expts
250	FP	0.340 ± 0.042	0.35−0.45	20−40	0.80−9.26	6
	LP	0.362 ± 0.043	0.37−0.44	40−60	0.96−9.30	6
273	LP	0.591 ± 0.067	0.36−0.43	20−60	0.75−9.84	6
298	FP	0.854 ± 0.101	0.34−0.44	20−40	0.88−9.43	6
	LP	0.921 ± 0.107	0.37−0.43	20−60	0.83−9.36	6
	DF	0.926 ± 0.117	5.0−7.4	5−6	0.19−1.89	5
331	FP	1.39 ± 0.15	0.31−0.39	20−40	1.16−9.57	6
375	FP	2.47 ± 0.27	0.30−0.40	20−40	0.72−9.15	6
430	FP	4.63 ± 0.48	0.31−0.40	20−40	0.52−9.25	7
	LP	4.63 ± 0.49	0.34−0.40	20−40	0.90−9.57	6

[a] FP, flash photolysis; LP, laser photolysis; DF, discharge flow. [b] The quoted errors represent the 95% confidence level from linear least-squares analysis and included systematic errors. [c] $\bar{\imath}$, residence time for FP and LP methods; U, linear flow velocity for DF method.

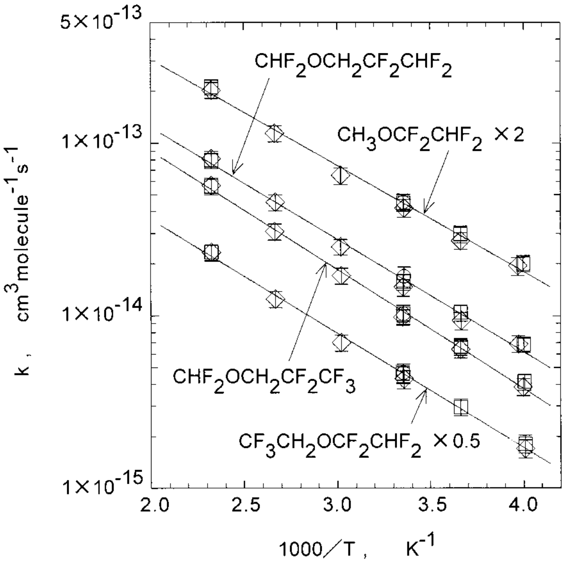

Figure 2. Arrhenius plots of the OH reaction rate coefficients of $CH_3OCF_2CHF_2$, $CHF_2OCH_2CF_2CHF_2$, $CHF_2OCH_2CF_2CF_3$, and $CF_3CH_2OCF_2CHF_2$. The solid lines represent the result of the least-squares fit to the data: (◇) FP-LIF; (□) LP-LIF; (○) DF-LIF. The error bars represent the 95% confidence level and included systematic errors.

TABLE 6: Arrhenius Rate Parameters for the OH Reaction Rate Constants of $CH_3OCF_2CHF_2$, $CHF_2OCH_2CF_2CHF_2$, $CHF_2OCH_2CF_2CF_3$, and $CF_3CH_2OCF_2CHF_2$ over the Temperature Range 250−430 K

sample	$10^{12}A$, cm^3 molecule^{-1} s^{-1}	E/R,[a] K	f(298)[b]	purity, %
$CH_3OCF_2CHF_2$	2.60	1420 ± 170	1.1	99.99
$CHF_2OCH_2CF_2CHF_2$	2.49	1500 ± 170	1.1	99.997
$CHF_2OCH_2CF_2CF_3$	2.14	1580 ± 170	1.1	99.9976
$CF_3CH_2OCF_2CHF_2$	1.49	1520 ± 170	1.1	99.994

[a] The quoted errors represent the 95% confidence level from linear least-squares analysis and included systematic errors. [b] Uncertainty factor at 298 K with the formulation of the NASA panel for data evaluation.[14]

TABLE 7: OH Reaction Rate Constants of Partially Halogenated Compounds at 298 K

compound	$10^{14}k_{298}$,[a] cm^3 molecule^{-1} s^{-1}	reference
$CH_3OCF_2CHF_2$	2.24 ± 0.25	this work
	20.4 ± 3.3	8
	2.34[b]	12
$CHF_2OCH_2CF_2CHF_2$	1.62 ± 0.18	this work
	1.07 [b]	12
$CHF_2OCH_2CF_2CF_3$	1.05 ± 0.11	this work
	1.04[b]	12
$CF_3CH_2OCF_2CHF_2$	0.916 ± 0.100	this work
	9.35 ± 0.22	8
	1.16[b]	12
$CHF_2OCH_2CF_3$	1.2	14
CH_3OCF_3	1.2	14
$CH_3OCF_2CF_3$	1.21 ± 0.09	13
$CH_3OCF_2CF_2CF_3$	1.18 ± 0.05	13
$CH_3CH_2OCF_2CHF_2$	22.4 ± 0.7	9
	43.3 ± 6.9	8
CH_3OCF_2CHFCl	3.76 ± 0.13	9
	16.5 ± 3.2	8
CF_3CH_2OH	10.0 ± 0.4	3
$CF_3CF_2CH_2OH$	10.2 ± 0.4	3

[a] The error limits are those quoted by the authors. Present values are the 95% confidence level and included systematic errors. [b] Estimated by using SAR.

constants of $CHF_2OCH_2CF_2CHF_2$ and $CHF_2OCH_2CF_2CF_3$. The ratios between the predicted and experimental rate constants, k_{est}/k_{exp}, are 1.04, 0.66, 0.99, and 1.27, respectively, for $CH_3OCF_2CHF_2$, $CHF_2OCH_2CF_2CHF_2$, $CHF_2OCH_2CF_2CF_3$, and $CF_3CH_2OCF_2CHF_2$. All of them lie within a factor of 2.

In our previous study,[13] the 298 K value of $CH_3OCF_2CF_3$ was predicted to be 2.31×10^{-14} cm^3 molecule^{-1} s^{-1} from the original value of the group rate constant ($k_{prim} = 1.36 \times 10^{-13}$) and a substituent factor ($F(-OCF_2-) = 0.17$) from the SAR method.[12] The ratio, k_{est}/k_{exp}, was 1.91, which was not very good. Then, in our previous study, we have attempted to improve the substituent factor of $F(-OCF_2-)$ as 0.088, based on the results of $CH_3OCF_2CF_3$ and $CH_3OCF_2CF_2CF_3$. The ratios, k_{est}/k_{exp}, are obtained as 0.55 and 0.67 for $CH_3OCF_2CHF_2$ and $CF_3CH_2OCF_2CHF_2$, respectively, if the modified substituent factor is used for the estimation. Unfortunately, as for the new experimental data, the prediction by using the modified substituent factor gives a lower accuracy than using the original value. Then, we have further attempted to improve the substituent factor by using new experimental data as well as previous results.[13] From the 298 K values of $CH_3OCF_2CHF_2$, $CF_3CH_2OCF_2CHF_2$, $CH_3OCF_2CF_3$, and $CH_3OCF_2CF_2CF_3$, the substituent factor of the $-OCF_2-$ group, $F(-OCF_2-)$, is obtained as 0.11. The ratios, k_{est}/k_{exp}, are 0.68, 0.83, 1.24, and 1.27 for these four fluorinated ethers, respectively.

In the case of $CHF_2OCH_2CF_2CHF_2$ and $CHF_2OCH_2CF_2CF_3$, the substituent factor for the $-OCH_2CF_2-$ group has been assumed to be equal to that for the $-OCH_2CF_3$ group ($F(-OCH_2CF_3) = 0.44$). Then, we have attempted to improve the substituent factor, $F(-OCH_2CF_2-)$ by using the present experimental results. From the 298 K values of $CHF_2OCH_2CF_2CHF_2$ and $CHF_2OCH_2CF_2CF_3$, the substituent factor of $F(-OCH_2CF_2-)$ is obtained as 0.58. The ratios, k_{est}/k_{exp}, are 0.81 and 1.22 for these two fluorinated ethers, respectively.

Comparison of the OH Rate Constants with Those of Analogous Compounds. The SAR method can be applied to a wide range of reactions. However, this method cannot always reproduce the experimental rate constants with enough accuracy. For example, the ratios between the predicted and experimental rate constants, k_{est}/k_{exp}, for CF_3CH_2OH[3] and CHF_2OCF_2CHFCl[9] are 3.7and 0.35, respectively. Therefore, it is important to predict the reactivity by other methods as well.

The molecule of $CH_3OCF_2CHF_2$ has two different reactive sites; one is the CH_3- group attached to $-OCF_2CHF_2$ and the other is $-CF_2CHF_2$ attached to CH_3O-. It is expected that the reactivity of $CH_3OCF_2CHF_2$ is obtained from the summation of the reactivities of CH_3OCF_3 and CF_3CHF_2, if the reactivity of active sites attached to both sides of $-OCF_2-$ is proportional to the reactivity attached to $-OCF_3$ and CF_3-. In the case of the hydrocarbon ethers, it is widely known that the reactivity of C$-$H is enhanced by the ether linkage. For example, the reactivity of CH_3OCH_3 is by about 10 times or more as large as that of CH_3CH_3. However, in the case of halogenated ethers, the error of the estimated rate constant by using the above method is smaller than about a factor of 2.[9]

The OH rate constant of $CH_3OCF_2CHF_2$ may be estimated by summing up the corresponding values for CH_3OCF_3 and CF_3CHF_2 (HFC-125). The OH reaction rate constants of CH_3OCF_3 and CF_3CHF_2 at 298 K have been recommended as 1.2×10^{-14} and 1.9×10^{-15} cm^3 molecule^{-1} s^{-1}, respectively.[14] Summing up the contributions from them, the OH rate constant of $CH_3OCF_2CHF_2$ can be estimated as 1.39×10^{-14} cm^3 molecule^{-1} s^{-1}. Similarly, the rate constant of $CHF_2OCH_2CF_2CHF_2$ is estimated as 1.39×10^{-14} cm^3 molecule $^{-1}$ s^{-1} from the data of $CHF_2OCH_2CF_3$ (1.2×10^{-14} [14]) and CF_3CHF_2. The ratio between the estimated and experimental rate constants, k_{est}/k_{exp}, is 0.62 for $CH_3OCF_2CHF_2$ and 0.86 for $CHF_2OCH_2CF_2CHF_2$. The present results as well as our previous study[9] show that this method always give an underestimation, though within a factor of 2. Thus, the present method can be conveniently used for estimating the lower limit of the reaction rate constants. These results suggest that the reactivity of the $-CHF_2$ group attached to $-CF_2-$ is a few times smaller than the CH_3- group attached to $-OCF_2-$, and the CHF_2OCH_2- group attached to $-CF_2-$.

The 298 K value of $CHF_2OCH_2CF_2CF_3$, $(1.05 \pm 0.04) \times 10^{-14}$, is in good agreement with that of $CHF_2OCH_2CF_3$ (1.2×10^{-14} [14]), the ratio between the two being about 0.88. This shows that the difference between the substituent effects of $-CF_3$ and $-CF_2CF_3$ groups is small. In our previous studies, similar results have been obtained for $CH_3OCF_2CF_3$ ($(1.21 \pm 0.09) \times 10^{-14}$) and $CH_3OCF_2CF_2CF_3$ ($(1.18 \pm 0.05) \times 10^{-14}$)[13] and also for CF_3CH_2OH ($(1.00 \pm 0.04) \times 10^{-13}$) and $CF_3CF_2CH_2OH$ ($(1.02 \pm 0.04) \times 10^{-13}$).[3]

As for $CF_3CH_2OCF_2CHF_2$, the lower reactivity of this molecule relative to that of $CF_3CH_2OCHF_2$ ($CHF_2OCH_2CF_3$, 1.2×10^{-14} [14]) is quite reasonable, because the reactivities of $-CH_2-$ and $-CHF_2$ attached to $-OCF_2-$ are smaller than in the case where they are directly attached to the O atom. As was discussed in the above, the reactivity of $-CHF_2$ attached to $-OCF_2$- is roughly equal to that of CF_3CHF_2. Thus, it seems that the reactivity of $-CH_2$- group attached to both CF_3- and $-OCF_2$- is a few times as large as that of $-CHF_2$ group attached to $-OCF_2$-.

In conclusion, as for the fluorinated ethers measured in this study, the predicted values of the OH reaction rate constants from comparison with molecules of similar structures agree reasonably well with the observed values. Since the method of predicting the OH rate constants with enough accuracy has not been established yet, it is profitable to estimate the reaction rate constants by using various methods. For this purpose, the method mentioned here can be conveniently used, when the reaction rate constants of compounds having similar structures are available.

Tropospheric Lifetime of Fluorinated Ethers. The lifetime (τ_{HFE}) for removal by tropospheric OH can be estimated by using the following simple scaling procedure:

$$\tau_{HFE} = k_{MC}(277\ \mathrm{K})/k_{HFE}(277\ \mathrm{K})\tau_{MC}$$

where τ_{MC} is the tropospheric lifetime of methylchloroform (CH_3CCl_3) due to reactions with OH radicals in the troposphere only and k_{MC}(277 K) is the rate constant for the reactions of OH with methylchloroform at 277 K (6.7×10^{-15} cm^3 molecule^{-1} s^{-1}) by using the preferred value of $k_{MC} = 1.8 \times 10^{-12} \exp[-(1550 \pm 150)/T]$ cm^3 molecule^{-1} s^{-1}.[14] k_{HFE}(277 K) is the rate constant for the reactions of OH with fluorinated ether at 277 K. The tropospheric lifetime of methylchloroform (τ_{MC}) was recommended to be 6.6 years[2] from the total lifetime of 5.4 years corrected for an estimated ocean removal lifetime of 85 years and a stratospheric removal lifetime of 40 years. The estimated tropospheric lifetimes of $CH_3OCF_2CHF_2$, $CHF_2OCH_2CF_2CHF_2$, $CHF_2OCH_2CF_2CF_3$, and $CF_3CH_2OCF_2CHF_2$ are 2.8, 4.0, 6.3, and 7.1 years, respectively.

Acknowledgment. The present investigation has been performed with the support of the New Energy and Industrial Technology Development Organization.

References and Notes

(1) Sekiya, A.; Misaki, S. *CHEMTECH* **1996**, *26*, 44.

(2) Scientific Assessment of Ozone Depletion: 1994; UNEP/WMO, Global Ozone Research and Monitoring Project, Report No. 37.

(3) Tokuhashi, K.; Nagai, H.; Takahashi, A.; Kaise, M.; Kondo, S.; Sekiya, A.; Takahashi, M.; Gotoh, Y.; Suga, A. *J. Phys. Chem. A* **1999**, *103*, 2664.

(4) Kaufman, F. *J. Prog. React. Kinet.* **1961**, *1*, 1.

(5) Brophy, J. H.; Silver, J. A.; Kinsey, J. L. *J. Chem. Phys.* **1975**, *62*, 3820.

(6) Howard, C. J. *J. Chem. Phys.* **1976**, *65*, 4771.

(7) Tokuhashi, K.; Takahashi, A.; Kaise, M.; Kondo, S. *Int. J. Chem. Kinet.*, submitted for publication.

(8) Heathfield, A. E.; Anastasi, C.; Pagsberg, P.; McCulloch, A. *Atmos. Environ.* **1998**, *32*, 711.

(9) Tokuhashi, K.; Takahashi, A.; Kaise, M.; Kondo, S. *J. Geophys. Res.* **1999**, *D15*, 18681.

(10) Atkinson, R. *Chem. Rev.* **1986**, *86*, 69.

(11) Atkinson, R. *Int. J. Chem. Kinet.* **1987**, *19*, 799.

(12) Kwok, E. S. C.; Atkinson, R. *Atmos. Environ.* **1995**, *29*, 1685.

(13) Tokuhashi, K.; Takahashi, A.; Kaise, M.; Kondo, S.; Sekiya, A.; Yamashita, S.; Ito, H. *Int. J. Chem. Kinet.* **1999**, *31*, 846.

(14) 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 12, JPL Publication 97-4; Jet Propulsion Laboratory: California Institute of Technology, Pasadena, CA, 1997.