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Environmental assessment of CFC alternatives Rate constants for the reactions of OH radicals with fluorinated compounds

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Abstract

The rate constants for the reactions of OH radicals with $CF_3OCHFCF_3$, and CF_3CHFCF_3 have been measured over the temperature range 250–430 K. Kinetic measurements have been carried out using the flash photolysis, and laser photolysis methods combined, respectively, with the laser induced fluorescence technique. The influence of impurities in the samples has been investigated by using gas chromatography. No sizable effect of impurities was found on the measured rate constants of these fluorinated compounds, if the purified samples were used in the measurements. The following Arrhenius expressions were determined: $k(CF_3OCHFCF_3) = (4.39 \pm 1.38) \times 10^{-13} \exp[-(1780 \pm 100)/T]$ cm^3 molecule^{-1} s^{-1}, and $k(CF_3CHFCF_3) = (6.19 \pm 2.07) \times 10^{-13} \exp[-(1830 \pm 100)/T]$ cm^3 molecule^{-1} s^{-1}.

Keywords: Environmental evaluation; CFC alternatives; OH radical; Fluorinated compound; Rate constant

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1. Introduction

Since chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs) cause the depletion of the stratospheric ozone layer as well as the global warming, a number of replacement compounds such as hydrofluorocarbons (HFCs) have been investigated for industrial applications. Recently, partially fluorinated ethers (HFEs) have been closed up as new candidates for CFC alternatives [1]. Since HFEs and 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 atom are expected to be oxidized by OH radicals in the troposphere [2], the atmospheric lifetime is determined primary by the reaction rate of these molecules against OH radicals. Thus, the study of the reactivity against OH radicals is crucial for the environmental evaluation of CFC alternatives.

Since the reactivity of some HFEs and HFCs are fairly small, the reactive impurities contained in the sample may seriously affect the rate constant determination using absolute rate method. It is crucial to carry out the kinetic measurements for samples of extremely high purity. In fact, there have been some cases where too large values of rate constants were reported possibly due to reactive impurities contained in the samples. It is necessary to examine the sample purity and its influence on the measurement very carefully, if the absolute rate method is used in the kinetic measurements.

Accurate measurement of the reaction rate constants for a wide variety of molecules is required for the environmental assessment as well as the development of the method for predicting the OH reaction rate constants by theoretical and empirical approaches. Although there is a substantial database for rate constants for HFCs, there is little

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information on the OH reaction rate constants for HFEs. In this paper, we report the results of kinetic measurements for the reactions of OH radicals with $CF_3OCHFCF_3$ and CF_3CHFCF_3 at 250–430 K. Effects of impurities on the measured rate constants have been carefully investigated through the sample purification with gas chromatography.

2. Results and discussion

2.1. Effects of impurities

According to the gas chromatographic analysis, the purities of samples have been found to be 99.9, 99.74, and 99.6%, respectively, for $CF_3OCHFCF_3$ (No. 1), $CF_3OCHFCF_3$ (No. 2), and CF_3CHFCF_3. The individual impurities were not identified. At the beginning, in order to make a rough estimation of the impurity effect, the OH reaction rate constants of these samples have been measured by using the FP, and LP 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 not 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 two different methods agree to each other within the estimated uncertainties. However, from the purity of the samples, the contribution of reactive impurities on the measured rate constants are estimated to be about 7, 20, and 9 times as large as the measured values themselves for $CF_3OCHFCF_3$ (No. 1), $CF_3OCHFCF_3$ (No. 2), and CF_3CHFCF_3, if the OH reaction rate constants of impurities are assumed to be as large as 1×10^{-11} cm^3 molecule^{-1} s^{-1} (the worst case conceivable).

In order to examine the effects of reactive impurities on the measured rate constants, the samples of $CF_3OCHFCF_3$ (No. 2) and CF_3CHFCF_3 were subjected to the purification by gas chromatography. The validity of the sample purification by gas chromatography has been demonstrated in detail previously [3]. As an example, in the case of $CF_3CH_2OCF_2CHF_2$, it has been found that the measured rate constants of purified sample are about 29% smaller on the average than those of the original sample [3]. Furthermore, the measured rate constant for the purified sample is in excellent agreement with our recent result obtained using relative rate method [4].

The OH reaction rate constants of $CF_3OCHFCF_3$ and CF_3CHFCF_3 for the purified samples are summarized in Table 1. The concentrations of the impurities contained in the purified samples are approximately 1/26 and 1/130 of the original amounts for $CF_3OCHFCF_3$ (No. 2) and CF_3CHFCF_3, respectively. On the average, the measured rate constants of purified samples are about 0.84 and 0.27 times of the original samples of $CF_3OCHFCF_3$ (No. 2) and CF_3CHFCF_3, 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 $CF_3OCHFCF_3$ and CF_3CHFCF_3 of 8.1×10^{-14} and 8.6×10^{-13} cm^3 molecule^{-1} s^{-1}, respectively. For the purified samples, 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 are estimated to be about 92 and 24% of the observed values for $CF_3OCHFCF_3$ and CF_3CHFCF_3, respectively. On the other hand, if the OH rate constants of remaining impurities in $CF_3OCHFCF_3$ and CF_3CHFCF_3 are as large as 8.1×10^{-14} and 8.6×10^{-13} cm^3 molecule^{-1} s^{-1}, respectively, their remaining influence on the measured rate constants can be no larger than 0.7 and 2.1% of the observed values for $CF_3OCHFCF_3$ and CF_3CHFCF_3, respectively.

Table 1
Observed values of OH reaction rate constants of $CF_3OCHFCF_3$ and CF_3CHFCF_3 at 298 K

Fluorinated compound	k ($\times 10^{15}$ cm^3 molecule^{-1} s^{-1})[a]	Technique[b]	Purity (%)
$CF_3OCHFCF_3$			
Original No. 1	1.40 ± 0.10	FP	99.9
	1.41 ± 0.11	LP	
Original No. 2	1.24 ± 0.06	FP	99.74
	1.35 ± 0.07	LP	
Purified sample	1.05 ± 0.07	FP	99.99
	1.12 ± 0.08	LP	
CF_3CHFCF_3			
Original	4.46 ± 0.21	FP	99.6
	4.89 ± 0.26	LP	
Purified sample	1.23 ± 0.08	FP	99.997
	1.26 ± 0.09	LP	

[a] The quoted errors represent 95% confidence level from linear least squares analysis and not include systematic errors.

[b] FP, flash photolysis; LP, laser photolysis.

2.2. Measurements of rate constants

The procedures for the kinetic measurements as well as the data analysis have been described in detail in our previous report [5]. Briefly, observed LIF signal intensities from OH radicals have been monitored and 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 from each decay plots. 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.

The purified samples of $CF_3OCHFCF_3$ and CF_3CHFCF_3 were used in this work. Fig. 1 shows a typical example of pseudo-first-order OH decay plot obtained with the FP method for various $CF_3OCHFCF_3$ concentrations. Since these plots show linear relationship with small scatters, the value of k_{obs} is derived from the slopes of the each decay

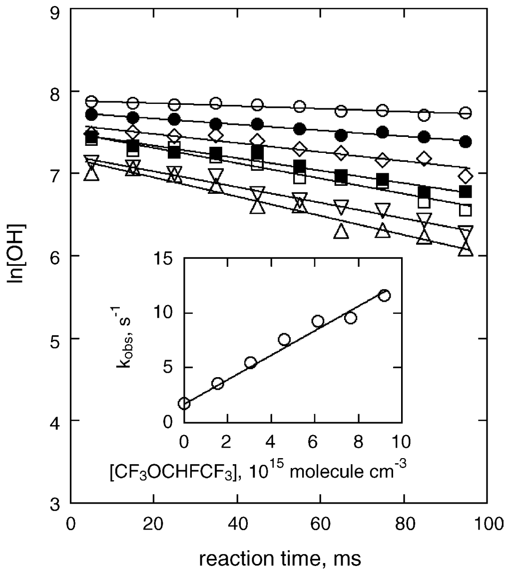

Fig. 1. Pseudo-first-order decay of OH for various $CF_3OCHFCF_3$ concentrations. FP-LIF method, p = 100 Torr, T = 298 K. [$CF_3OCHFCF_3$] in 10^{15} molecule cm^{-3}. (○) 0; (●) 1.53; (◇) 3.06; (■) 4.60; (□) 6.12; (▽) 7.66; (△) 9.16. The inset shows the plot of the observed pseudo-first-order rate constant k_{obs} against $CF_3OCHFCF_3$ concentration.

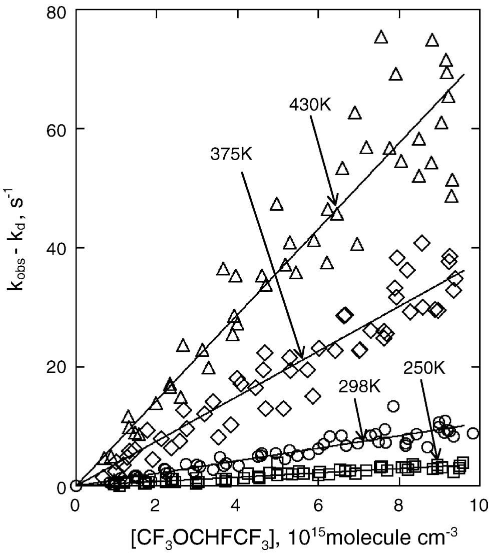

Fig. 2. Plot of the pseudo-first-order rate constants corrected for wall loss, $k_{obs} - k_d$, against $CF_3OCHFCF_3$ concentration. FP-LIF method. (□) 250 K; (○) 298 K; (◇) 375 K; (△) 430 K.

plot. In the inset of Fig. 1, the observed pseudo-first-order rate constants are plotted against $CF_3OCHFCF_3$ concentration. These points are distributed along a straight line, and the absolute value of the bimolecular rate constant for the reaction of OH with $CF_3OCHFCF_3$ is derived from the slope of the observed data.

In order to minimize the systematic errors, the experiments were repeated at intervals ranging from several days to a few months under a variety of experimental conditions. In the case of FP and LP methods, the intercept of k_{obs} for zero reactant (k_d) is mainly due to the diffusion of OH radicals from the viewing zone, and partially due to the reaction of OH radicals with impurities contained in the gas mixture. Thus, the values of k_d depend upon the experimental conditions such as total pressure, carrier gas, and so forth. From the values of k_{obs} such as plotted in the inset of Fig. 1, the background value (k_d) is subtracted, and the resulting values ($k_{obs} - k_d$) are plotted against concentration as shown in Fig. 2 for various temperatures. The plots show linear relationships with relatively small scatters. Therefore, it is concluded that the present rate constants derived from the least squares fits to the observed data are not dependent on any of the experimental factors.

The OH reaction rate constants of $CF_3OCHFCF_3$ and CF_3CHFCF_3 over the temperature range 250–430 K for the different methods are listed in Tables 2 and 3, respectively. The experimental conditions for individual measurements are also listed in these tables. The experiment was repeated six times or more (usually 60–80 measurements of OH decay) at a temperature for each experimental method. In Tables 2 and 3, the concentration range of fluorinated compounds (sixth column) represents the minimum and maximum concentrations during repetitive experiments. In

Table 2
Experimental conditions and the observed values of OH reaction rate constant of $CF_3OCHFCF_3$

Temperature (K)	Technique[a]	k ($\times 10^{15}$ cm^3 molecule^{-1} s^{-1})[b]	$\bar{t}$ range[c] (s)	Pressure range (Torr)	[$CF_3OCHFCF_3$] range ($\times 10^{-15}$ molecule cm^{-3})	No. of experiments
250	FP	0.370 ± 0.031	0.37–0.50	60–100	0.94–9.58	6
	LP	0.372 ± 0.039	0.34–0.50	60–100	0.84–9.33	6
273	FP	0.636 ± 0.037	0.36–0.46	60–100	0.87–9.40	6
298	FP	1.05 ± 0.07	0.31–0.43	20–100	0.82–9.83	7
	LP	1.12 ± 0.08	0.36–0.61	60–200	1.03–9.76	7
331	FP	1.77 ± 0.10	0.34–0.50	40–80	0.82–9.64	8
375	FP	3.80 ± 0.24	0.34–0.51	20–80	0.66–9.38	6
430	FP	7.15 ± 0.52	0.35–0.46	20–80	0.69–9.31	6
	LP	7.61 ± 0.41	0.35–0.47	40–80	0.85–9.17	6

[a] FP, flash photolysis; LP, laser photolysis.

[b] The quoted errors represent 95% confidence level from linear least squares analysis and not include systematic errors.

[c] Residence time.

Table 3
Experimental conditions and the observed values of OH reaction rate constant of CF_3CHFCF_3

Temperature (K)	Technique[a]	k ($\times 10^{15}$ cm^3 molecule^{-1} s^{-1})[b]	$\bar{t}$ range[c] (s)	Pressure range (Torr)	[CF_3CHFCF_3] range ($\times 10^{-15}$ molecule cm^{-3})	No. of experiments
250	FP	0.424 ± 0.037	0.37–0.50	40–100	0.89–9.47	8
	LP	0.473 ± 0.041	0.36–0.50	40–100	0.86–9.49	8
273	FP	0.737 ± 0.065	0.35–0.46	40–100	0.75–9.34	6
298	FP	1.23 ± 0.08	0.31–0.48	40–100	0.85–9.62	6
	LP	1.26 ± 0.09	0.35–0.61	60–100	0.90–9.45	6
331	FP	2.33 ± 0.12	0.30–0.42	20–60	0.82–9.51	8
375	FP	4.70 ± 0.22	0.34–0.51	20–80	0.74–9.42	6
430	FP	9.02 ± 0.29	0.34–0.45	20–80	0.95–9.44	6
	LP	9.58 ± 0.36	0.33–0.42	20–80	0.92–9.54	6

[a] FP, flash photolysis; LP, laser photolysis.

[b] The quoted errors represent 95% confidence level from linear least squares analysis and not include systematic errors.

[c] Residence time.

all cases, the OH decay shows exponential behavior, and the scatter of the points for individual decay plots are much the same as the ones shown in Fig. 1. Also, the linearity and scatter of the plotted points for individual experiments are much the same as the ones shown in the inset of Fig. 1. Figs. 3 and 4 show the Arrhenius plots for the OH reactions for $CF_3OCHFCF_3$ and CF_3CHFCF_3. As is apparent in Figs. 3 and 4, the differences among the results obtained by the two methods are small. Since the activation energy of reactive compounds is small, the Arrhenius plots will show curvature, if the sample contained detectable amount of reactive impurities. However, as is apparent in Figs. 3 and 4, the Arrhenius plots give linear relationships in the temperature range examined. Thus, it is concluded that the effects of any remaining impurities contained in the fluorinated samples are negligibly small for the purified samples. The Arrhenius rate parameters for the OH reactions of fluorinated compounds have been calculated from unit weighted non-linear least square fit to the data shown in Figs. 3 and 4. The results are listed in Table 4.

2.3. Comparison with literature data

The OH rate constant of $CF_3OCHFCF_3$ has been studied by Li et al. [6] at 298 K by using the discharge flow combined with the resonance fluorescence method to monitor the OH concentration. The value reported by Li et al. is plotted in Fig. 3 together with the present result. The

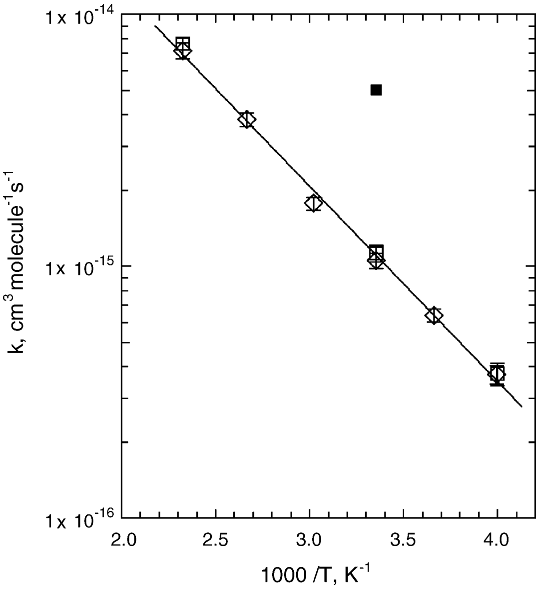

Fig. 3. Arrhenius plots of the OH reaction rate coefficients of $CF_3OCHFCF_3$. (◇) FP-LIF; (□) LP-LIF. The solid lines represent the result of the non-linear least squares fit to this work. The error bars of this work represent 95% confidence level from linear least squares analysis and not include systematic errors. (■) Li et al. [6].

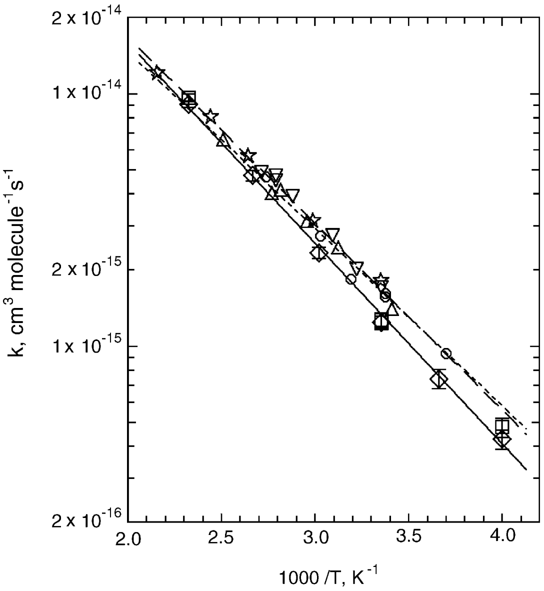

Fig. 4. Arrhenius plots of the OH reaction rate coefficients of CF_3CHFCF_3. (◇) FP-LIF; (□) LP-LIF. The solid lines represent the result of the non-linear least squares fit to this work. The error bars of this work represent 95% confidence level from linear least squares analysis and not include systematic errors. (○) Zhang et al. [10]; (☆) Zellner et al. [11]; (▽) Hsu and DeMore [12], dotted line; (△) and Nelson et al. [9], dashed line, JPL 97-4 [13].

Table 4
Arrhenius rate parameters for the reactions of OH with $CF_3OCHFCF_3$ and CF_3CHFCF_3

Fluorinated compound	A ($\times 10^{13}$ cm^3 molecule^{-1} s^{-1})	E/R (K)	$k_{298\ K}$ ($\times 10^{15}$ cm^3 molecule^{-1} s^{-1})	Purity (%)	τ (year)
$CF_3OCHFCF_3$	4.39 ± 1.38	1780 ± 100	1.11 ± 0.07	99.99	58
CF_3CHFCF_3	6.19 ± 2.07	1830 ± 100	1.34 ± 0.08	99.997	49

The quoted errors represent 95% confidence level from non-linear least squares analysis and not include systematic errors. The fluorinated compounds used in the measurements were purified by using gas chromatograph.

room temperature rate constant reported by Li et al. [6] ($(4.98 \pm 1.64) \times 10^{-12}$) is about 4.5 times as large as the present value. As was mentioned in Section 2.1, the reactive impurities contained in the samples give serious errors to the measured value. One of likely reason for the large values of Li et al. is the presence of reactive impurities in their sample. The purity of $CF_3OCHFCF_3$ used in the study of Li et al. was stated as 99.99%. If it is the case and if the OH rate constant of impurities are as large as 1×10^{-11}, the contribution of the impurities to the rate constant may become 1×10^{-15}. Thus, the estimated contribution of reactive impurities on the measured rate constant of Li et al. [6] is only 20%.

In a previous study, we have measured the OH rate constants of $CF_3OCF{=}CF_2$ using the same technique as the one adopted here as well as another two LP methods over the temperature range 250–430 K [7]. Li et al. [8] have also measured the rate constant of OH with $CF_3OCF{=}CF_2$ by using discharge flow coupled with resonance fluorescence method over the temperature range 253–348 K. Although the rate constant at 298 K reported by Li et al. [8] agree to our value [7] within the estimated uncertainties, their Arrhenius expression ($(6.41 \pm 0.82) \times 10^{-11} \exp[(-868 \pm 40)/T]$) is quite different from ours ($1.01 \pm 0.04 \times 10^{-12} \exp[(320 \pm 10)/T]$). As was noticed by the authors themselves [8], the Arrhenius A-factor is substantially higher than the usual value for the OH reaction, and the positive temperature dependence for this reaction is not understandable. Thus, another possibility for the discrepancy of the result of Li et al. seems to be the systematic errors in their measurements.

The OH reaction rate constant of CF_3CHFCF_3 has been reported by four research groups. Nelson et al. [9] have measured the reaction rate constant by using the discharge flow combined with the laser induced fluorescence technique over the temperature range 294–369 K. Zhang et al. [10] have measured the rate constant by using the flash photolysis combined with the resonance fluorescence method over the temperature range 270–365 K. Zellner et al. [11] have measured the rate constant by using the laser photolysis combined with the resonance fluorescence method over the temperature range 298–463 K. In their study, OH radicals were generated by excimer laser photolysis of HNO_3 at $\lambda = 193$ nm. Hsu and DeMore [12] have measured the rate constant by using the relative rate technique over the temperature range 296–367 K. CH_4 and CH_3CHF_2 were used as the reference compounds. These four results are shown in Fig. 4 together with the present result. Fig. 4 also shows the recommended value by DeMore et al. [13]. In Fig. 4, the results of Hsu and DeMore have been reevaluated using the recommended rate constants of CH_4 and CH_3CHF_2 [13].

The rate constants reported by Hsu and DeMore [12] are about 20% larger on the average than that of ours, but the estimated uncertainties of the two results overlap each other. In principle, the relative rate technique used in the study of Hsu and DeMore [12] is not affected by the reactive impurities. Thus, if our results are not affected by the reactive impurities, it is quite reasonable that the temperature dependency of our results agrees well to those of Hsu and DeMore.

Although the present value agrees well to Nelson et al. [9], Zhang et al. [10], and Zellner et al. [11] within about 10% at 430 K, the results of these three groups are 20–35% larger than that of ours at 298 K. This deviation of temperature dependency leads to a difference in the activation energy; the values of E/R reported by three groups are 12–13% smaller than that of ours. These three groups have measured OH rate constants by using the absolute rate technique. As was mentioned in Section 2.1, in the case of the absolute rate technique, the presence of reactive impurities causes serious errors on the measured rate constants. One of likely reason for the discrepancy is the presence of reactive impurities in their sample. The unsaturated compounds in the sample used by Nelson et al. [9] are stated as 22 ppm (3,3,3-trifluoropropene is 18 ppm, and another heavily halogenated olefin is 4 ppm). Zhang et al. [10] have mentioned that their sample contained less than 1 ppm of hexafluoropropene. The OH rate constant of 3,3,3-trifluoropropene ($CH_2{=}CHCF_3$) and hexafluoropropene ($CF_2{=}CFCF_3$) at 298 K have been reported as 1.52×10^{-12} [14] and 2.12×10^{-12} cm^3 molecule^{-1} s^{-1} [7], respectively. If the OH rate constants of unsaturated compounds are as large as 2×10^{-12} cm^3 molecule^{-1} s^{-1}, the contributions of the impurities on the measured rate constant of Nelson et al. [9] and Zhang et al. [10] are less than few percentages. Thus, if it is the case the contribution of the impurities on the measured rate constant is negligibly small. Zellner et al. [11] have not mentioned the purity of their sample.

Another reason for the difference of the temperature dependency between our result and other three groups is the difference of the measured temperature range, especially absence of the data at lower temperature in other groups. The rate constant of Zhang et al. [10] at lowest temperature (270 K) is about 30% larger than that of ours, but other values agree to ours within about 25%. Also, the rate constant of Zellner et al. [11] at 298 K (lowest temperature in their data) is about 35% larger than that of ours, but other values agree to ours within about 20%. The temperature dependency of Nelson et al. [9] is 12% smaller than that of ours, but their results agree to ours within about 25% in their temperature range examined. At any rate, the present result agrees to those of other three groups within the estimated uncertainties, except for some data.

2.4. Tropospheric lifetime of fluorinated compounds

The lifetime (τ) for removal by tropospheric OH can be estimated by using the following simple scaling procedure [15]:

$$\tau = \frac{k_{\mathrm{MC,272\,K}}}{k_{\mathrm{272\,K}}} \times \tau_{\mathrm{MC}}$$

where τ_{MC} is the tropospheric lifetime of CH_3CCl_3 (MC) due to reactions with OH radicals in the troposphere only (6 years) [16], and $k_{\mathrm{MC,272\,K}}$ the rate constants for the reactions of OH with MC at 272 K (6.0×10^{-15} cm^3 molecule^{-1} s^{-1} [13]). $k_{\mathrm{272\,K}}$ is the rate constants for the reactions of OH with fluorinated compound at 272 K. The values of rate constants at 272 K are calculated from the Arrhenius rate parameters shown in Table 4. The calculated lifetimes of $CF_3OCHFCF_3$ and CF_3CHFCF_3 are listed in Table 4.

3. Conclusions

We have studied the kinetic measurements for reactions of OH radicals with $CF_3OCHFCF_3$ and CF_3CHFCF_3 at 250–430 K using the absolute rate technique. OH radicals have been generated by using the flash photolysis and laser photolysis methods. The measurements have been carried out under the first-order condition, and the OH radical concentration has been measured by using the laser induced fluorescence technique. The influence of reactive impurities contained in the fluorinated compounds has been examined by means of sample purification using gas chromatography. No sizable effect of impurities was found on the measured rate constants of these two fluorinated compounds when the purified samples were used in the kinetic measurements. The Arrhenius rate parameters were determined from the kinetic data obtained as $k(CF_3OCHFCF_3) = (4.39 \pm 1.38) \times 10^{-13} \exp[-(1780 \pm 100)/T]$ cm^3 molecule^{-1} s^{-1}, and $k(CF_3CHFCF_3) = (6.19 \pm 2.07) \times 10^{-13} \exp[-(1830 \pm 100)/T]$ cm^3 molecule^{-1} s^{-1}. Using the OH reaction rate constant of CH_3CCl_3 at 272 K (6.0×10^{-15} cm^3 molecule^{-1} s^{-1}) and the tropospheric lifetime of CH_3CCl_3 (6 years), the tropospheric lifetimes of $CF_3OCHFCF_3$ and CF_3CHFCF_3 due to reactions with OH radicals were estimated as 58 and 49 years, respectively.

4. Experimental

The kinetic measurements have been carried out using absolute rate method. The experimental apparatus and procedure for the kinetic measurements have been described in detail elsewhere [5], and only a brief summary will be given here.

OH radicals are generated by the flash photolysis (FP) and laser photolysis (LP) methods. In the case of FP method, H_2O was directly photolyzed with pulsed light from a Xe flash lamp ($\lambda \geqq 180$ nm, quartz cut-off) in the presence of a large excess of argon bath gas. In the case of LP method, OH radicals are produced by the reaction, $O(^1D) + H_2O \rightarrow 2OH$, where $O(^1D)$ atoms are generated by photo-dissociation of N_2O with ArF excimer laser ($\lambda = 193$ nm). In all cases, the measurements have been carried out under the first-order condition, and the OH radical concentration has been monitored by using the laser induced fluorescence (LIF) technique. The excitation light for the LIF method was from a frequency doubled tunable dye laser (pumped by 2nd harmonic of Nd:YAG laser, 10 Hz), and the wavelength was tuned at about 308 nm. The photo-multiplier tube was used to monitor the fluorescence signal from the OH radicals. The signals were accumulated by a multi-channel scaler/averager, and stored in a microcomputer for further data processing.

The flow rate of each gas was measured and controlled by calibrated mass flow controllers. A capacitance manometer was used to measure the total gas pressure of the reactor. The temperature of the reactor was maintained either by electric heater, or by circulating fluid to the outer jacket of the reactor from a thermostatted bath, and was monitored with a CA thermocouple (Type K). During the experiments, the temperature across the reaction volume was maintained better than ±2 K over the temperature range examined. In order to ensure that the experimental data are free from any daily fluctuation errors, the experiments have been repeated at intervals from several days to several months under a variety of experimental conditions.

The fluorinated samples were analyzed by using a gas chromatograph equipped with FID detector, where the integrated intensity of the main peak against the total area was taken as the sample purity. The lowest value obtained by using different columns was taken as the sample purity.

For $CF_3OCHFCF_3$ (Research Institute of Innovative Technology for the Earth, RITE), two samples (Nos. 1 and 2) were used in the present study. The purities of $CF_3OCHFCF_3$ were found to be 99.9 and 99.74%, respectively, for Nos. 1 and 2. The purity of CF_3CHFCF_3 (PCR) was found to be 99.6%. $CF_3OCHFCF_3$ (No. 2) and CF_3CHFCF_3 were purified by using gas chromatography. The apparatus and procedure for the purification of samples have been described in detail previously [3]. Briefly, the sample gas was charged in an evacuated sampling tube, and then supplied to stainless steel column packed with Silicone DC 702. Nitrogen was used as the carrier gas. The middle fraction of the main peak was collected through a four-way switching cock into a trap cooled with liquid nitrogen.

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