

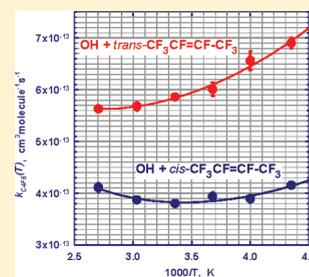
Rate Constants for the Reactions between OH and Perfluorinated Alkenes

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ABSTRACT: The rate constants for the reactions of OH radicals with fully fluorinated alkenes containing different numbers of $-\text{CF}_3$ groups next to olefinic carbon, $\text{CF}_2=\text{CF}_2$, $\text{CF}_2=\text{CFCF}_3$, $\text{CF}_3\text{CF}=\text{CFCF}_3$, and $(\text{CF}_3)_2\text{C}=\text{CFC}_2\text{F}_5$, were measured between 230 and 480 K using the flash photolysis resonance fluorescence technique to give the following expressions: $k_{\text{C}_2\text{F}_4}(250\text{--}480\text{ K}) = 1.32 \times 10^{-12} \times (T/298\text{ K})^{0.9} \times \exp(+600\text{ K}/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, $k_{\text{C}_3\text{F}_6}(230\text{--}480\text{ K}) = 9.75 \times 10^{-14} \times (T/298\text{ K})^{1.94} \times \exp(+922\text{ K}/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, $k_{\text{trans-C}_4\text{F}_8}(230\text{--}370\text{ K}) = 7.50 \times 10^{-14} \times (T/298\text{ K})^{1.68} \times \exp(+612\text{ K}/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, $k_{\text{cis-C}_4\text{F}_8}(230\text{--}370\text{ K}) = 2.99 \times 10^{-14} \times (T/298\text{ K})^{2.61} \times \exp(+760\text{ K}/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, and $k_{\text{C}_6\text{F}_{12}}(250\text{--}480\text{ K}) = 2.17 \times 10^{-15} \times (T/298\text{ K})^{3.90} \times \exp(+1044\text{ K}/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

The kinetics of the OH reaction in an industrial sample of octofluoro-2-propene (a mixture of the *cis*- and *trans*-isomers of $\text{CF}_3\text{CF}=\text{CFCF}_3$) was studied to determine the “effective” reaction rate constant for the typically industrial mixture: $k_{\text{C}_4\text{F}_8}(230\text{--}480\text{ K}) = 7.89 \times 10^{-14} \times (T/298\text{ K})^{1.71} \times \exp(+557\text{ K}/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. On the basis of these results, the atmospheric lifetimes were estimated to be 1.2, 5.3, 21, 34, and 182 days for $\text{CF}_2=\text{CF}_2$, $\text{CF}_3\text{CF}=\text{CF}_2$, *trans*- $\text{CF}_3\text{CF}=\text{CFCF}_3$, *cis*- $\text{CF}_3\text{CF}=\text{CFCF}_3$, and $(\text{CF}_3)_2\text{C}=\text{CFC}_2\text{F}_5$, respectively. The general pattern of halolalkene reactivity toward OH is discussed.



INTRODUCTION

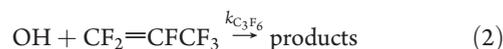
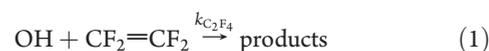
The international phase-out of the production and use of ozone-destroying chemicals under the Montreal Protocol on Substances that Deplete the Ozone Layer and its subsequent Amendments and Adjustments has stimulated considerable research on the atmospheric properties of potential chemical substitutes.¹ Chlorine-free, partially fluorinated hydrocarbons (hydrofluorocarbons or HFCs) have been among the leading ozone-friendly substitutes for chlorofluorocarbons (CFCs) originally targeted under the Montreal Protocol. However, more recently, rising concern about the potential impact of various industrial halocarbons on the Earth's climate has stimulated further search for chemicals that satisfy various industrial needs while having little impact on both stratospheric ozone and climate.^{2,3}

In general, fluorination of hydrocarbons decreases their reactivity toward tropospheric OH, thus increasing their residence time in the atmosphere to a few decades and even hundreds of years. Fully fluorinated alkanes do not react with OH, and their atmospheric lifetimes are estimated to be as long as thousands of years. The number of IR active C–F bonds also increases with fluorination, raising concerns about the climate forcing impacts of the use of highly fluorinated alkanes as industrial compounds. Fluorinated ethers have been suggested as potentially more environmentally friendly fluorinated compounds. However, the ether linkage, –O–, which increases the reactivity of hydrocarbons toward OH, does not have the same effect on the reactivity of heavily fluorinated alkanes of industrial interest.

Unsaturated fluorinated compounds are thus being considered as another class of alternatives. The presence of a carbon–carbon double bond is expected to render these

substances highly reactive toward the hydroxyl radical, OH, resulting in extremely short tropospheric lifetimes, thereby limiting their persistence in the atmosphere and their direct impact as greenhouse gases. Fluorinated alkenes are widely used in chemical industry as starting materials in syntheses of various halogenated compounds and in fluoropolymer production. They are also considered as potential replacements for industrial CFCs, fire suppressing, cleaning, and etching agents.

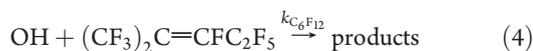
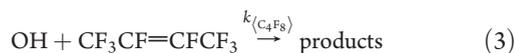
The reactivity toward OH radicals is an important property of a compound that often dictates its residence time in the atmosphere. The available kinetic literature confirms the higher reactivity of halogenated alkenes toward OH, although their reactivity trends have not been studied as well as those of fluorinated alkanes. In an earlier study, we found that the electron-withdrawing trifluoro methyl group ($-\text{CF}_3$) adjacent to olefinic carbon could substantially reduce the rate constant of the OH addition to the double bond.⁴ The current study was performed to check the difference between the effects of F and $-\text{CF}_3$ substitutions in fully fluorinated alkenes. We thus studied four reactions over the temperature range of atmospheric interest:



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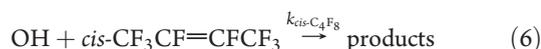
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The first three have been studied previously. The $\text{CF}_2=\text{CF}_2$ and $\text{CF}_2=\text{CFCF}_3$ reactions were studied both below and above room temperature.^{4–11} There are two recent studies of the $\text{CF}_3\text{CF}=\text{CFCF}_3$ reaction at room temperature,^{12,13} and no data are available for the reaction of $(\text{CF}_3)_2\text{C}=\text{CFC}_2\text{F}_5$.

Note that $\text{CF}_3\text{CF}=\text{CFCF}_3$ exists as two stereoisomers. Young et al.¹² and Cometto et al.¹³ used a relative rate method and, therefore, measured the change of $\text{CF}_3\text{CF}=\text{CFCF}_3$ concentration in their experiments by using FTIR and GC detection techniques, respectively. However, they were unable to provide information on the relative reactivity of the two isomers. We utilize measurements of OH concentration decay rates in a reactant-containing mixture and, therefore, cannot distinguish among OH reactions with different components of an isomeric mixture. Thus, we measured both the “total” rate constant for the reaction between OH and a mixture of stereoisomers in a typical industrial $\text{CF}_3\text{CF}=\text{CFCF}_3$ sample, $k_{(\text{C}_4\text{F}_8)}(T)$, as well as the OH reactions with the individual GC-separated stereoisomers of $\text{CF}_3\text{CF}=\text{CFCF}_3$ between 230 and 370 K.



EXPERIMENTAL SECTION¹⁴

Detailed descriptions of the apparatus and the experimental method used to measure the OH reaction rate constants are given in previous papers.^{4,15,16} Therefore, only a brief description is given here. The principal component of the flash photolysis-resonance fluorescence (FPRF) apparatus is a Pyrex reactor (of approximately 100 cm³ internal volume) thermostatted with water or methanol circulated through its outer jacket. Reactions were studied in argon carrier gas (99.9995% purity) at total pressures of 4.00 and 13.33 kPa (30.0 and 100.0 Torr). Flows of dry argon, argon bubbled through water thermostatted at 276 K, and perfluoroalkene mixtures (containing 0.02–1% of the reactant diluted with argon) were premixed and flowed through the reactor at a total flow rate between 0.6 and 1.4 cm³ 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 H₂O/argon mixture, and reactant/inert gas mixtures were maintained and measured by calibrated Tylan mass flow controllers. Hydroxyl radicals were produced by the pulsed photolysis (1–4 Hz repetition rate) of H₂O (introduced via the 276 K argon/H₂O bubbler) by a xenon flash lamp focused into the reactor. The radicals were then monitored by their resonance fluorescence near 308 nm, excited by a microwave-discharge resonance lamp (330 Pa or 2.5 Torr of a ca. 2% mixture of H₂O in UHP helium) focused into the reactor center. The resonance fluorescence signal was recorded on a computer-based multichannel scaler (channel width 100 μs)

as a summation of 1000–5000 consecutive flashes. The radical decay signal at each reactant concentration was analyzed as described by Orkin et al.¹⁶ to obtain the first-order decay rate coefficient due to the reaction under study. At each temperature, the rate constant was then determined from the slope of the plot of all of the decay rates obtained at that temperature versus perfluoroalkene concentration. A detailed analysis of the systematic (instrumental) uncertainty associated with maintaining and measuring the pressure, gas flow rates, and temperature and with preparation of reacting mixtures in the storage bulbs has been conducted.¹⁷ It is estimated to be ca. 4% for these experiments.

To check for any chemical complications, the following test experiments were performed. The flash energy was changed by a factor of 4 to change the initial OH concentration and, therefore, to examine the possible effect of stable and labile product accumulation. The measurements were performed at total pressures of 4.00 kPa (30 Torr) and 13.33 kPa (100 Torr) to check for the possible pressure dependence of the OH addition reactions under study. The measurements were performed with both the original and GC-purified samples (except the experiments with tetrafluoroethene) to check for the possible influence of reactive impurities in the original samples. No statistically significant changes of the measured reaction rate constant were observed in any of these experiments.

All samples, except tetrafluoroethene, were obtained from SynQuest Laboratories, Inc., and were used after several freeze/pump/thaw cycles or after purification using a preparative scale gas chromatograph. Hexafluoropropene, $\text{CF}_2=\text{CFCF}_3$, had a stated purity of 98.8% with the identified impurities being C_3F_8 (0.31%) and CO_2 (0.28%). Octofluoro-2-butene, $\text{CF}_3\text{CF}=\text{CFCF}_3$, was of 98.4% purity with approximately equal amounts of other halogenated butene impurities (2-chloroheptafluoro-2-butene, heptafluoro-2-butene, and hexafluoro-2-butene). Perfluoro-2-methyl-2-pentene, $(\text{CF}_3)_2\text{C}=\text{CFC}_2\text{F}_5$, was of 99% purity with perfluoro-4-methyl-2-pentene being the main impurity. There was no difference observed in the measured OH reaction rate constants when the original and GC-purified samples were used. Tetrafluoroethene, $\text{CF}_2=\text{CF}_2$ (Union Carbide Corp.), was ~98% purity stabilized with ~1% of α -pinene with hexafluorocyclopropane (1%) and CO_2 (0.2%) as the main impurities. The OH reaction rate constant of α -pinene at room temperature is 5.3×10^{-11} cm³ molecule⁻¹ s⁻¹,¹⁸ which exceeds the measured reaction rate constant of the target compound, C_2F_4 . To avoid an overestimation of the measured rate constant due to OH reaction with this chemical stabilizer, a sample of C_2F_4 was purified by passing through a -100 °C cold trap to decrease the α -pinene concentration from ca. 1% to below 0.03% (determined by UV absorption analysis near 220 nm).⁴

The original sample of octofluoro-2-butene, $\text{CF}_3\text{CF}=\text{CFCF}_3$, was a mixture of two stereoisomers containing 71.5% of *trans*-isomer and 28.5% of *cis*-isomer (NMR analysis provided by SynQuest Laboratories, Inc.). Our GC analysis using a thermal-conductivity detector gave approximately the same numbers after a correction for the slightly different sensitivity to these isomers. Samples of *cis*- C_4F_8 and *trans*- C_4F_8 were obtained from this original sample using a preparative scale gas chromatograph. GC analysis of the separated isomers resulted in no detectable residual *cis*-isomer impurity in the *trans*- $\text{CF}_3\text{CF}=\text{CFCF}_3$ sample and about 1% of *trans*-isomer impurity in the *cis*- $\text{CF}_3\text{CF}=\text{CFCF}_3$ sample.

Table 1. Rate Constants Measured for the Reactions of OH with Perfluorinated Alkenes

temperature, K	$k_i(T),^a 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (perfluoroalkene concentration range, $10^{13} \text{ molecule/cm}^3$)					
	$\text{CF}_2=\text{CF}_2$	$\text{CF}_2=\text{CFCF}_3$	$\text{CF}_3\text{CF}=\text{CFCF}_3^b$	<i>cis</i> - $\text{CF}_3\text{CF}=\text{CFCF}_3$	<i>trans</i> - $\text{CF}_3\text{CF}=\text{CFCF}_3$	$(\text{CF}_3)_2\text{C}=\text{CFCF}_3$
230		32.3 ± 1.6 (1.6–9.2)	5.69 ± 0.08 (4.8–54.6)	4.15 ± 0.05 (8.0–52.1)	6.90 ± 0.10 (8.0–41.3)	
250		28.2 ± 0.7 (2.0–8.0)	5.45 ± 0.12 (8.1–53.0)	3.89 ± 0.08 (7.4–38.0)	6.56 ± 0.18 (7.4–32.5)	0.705 ± 0.03 (37–211)
272		24.1 ± 1.2 (1.3–7.1)	5.25 ± 0.05 (7.4–42.2)	3.94 ± 0.09 (6.7–34.9)	6.01 ± 0.13 (6.8–34.9)	0.715 ± 0.012 (34–194)
298		21.6 ± 0.7 (1.7–13.2)	5.05 ± 0.09 (2.6–44.4)	3.80 ± 0.04 (3.4–61.7)	5.86 ± 0.06 (3.4–61.7)	0.712 ± 0.02 (31–177)
330		18.7 ± 0.7 (3.1–17.5)	5.01 ± 0.13 (6.1–40.1)	3.88 ± 0.06 (6.1–45.4)	5.68 ± 0.08 (5.6–55.7)	0.779 ± 0.036 (28–160)
370	80 ± 3 (0.55–3.15)	18.3 ± 0.5 (2.7–15.6)	5.14 ± 0.08 (5.5–31.0)	4.11 ± 0.09 (2.8–40.5)	5.63 ± 0.06 (5.0–49.7)	0.832 ± 0.023 (25–143)
420		17.4 ± 0.6 (2.7–15.6)	5.36 ± 0.12 (4.8–27.3)			0.991 ± 0.024 (22–126)
480	70.9 ± 2 (0.42–2.42)	16.5 ± 0.7 (2.1–12.0)	5.67 ± 0.14 (4.2–23.9)			1.23 ± 0.05 (19–110)

^aThe uncertainties are two standard errors from the least-squares fit of a straight line to the measured OH decay rates versus the reactant concentrations. A systematic uncertainty, estimated to be $\sim 4\%$, must be added to the listed uncertainties to yield the 95% confidence limits for the rate constants. ^bA mixture of *trans*- $\text{CF}_3\text{CF}=\text{CFCF}_3$ (71.5%) and *cis*- $\text{CF}_3\text{CF}=\text{CFCF}_3$ (28.5%).

RESULTS AND DISCUSSION

Rate constants measured for the reactions of hydroxyl radicals with the five perfluorinated alkenes at different temperatures are listed in Table 1 and illustrated in Figures 1–4 along with the data available from the literature. In the table and the figures, we show the “statistical” uncertainties of our data, which were derived at each temperature as two standard errors from the linear fit of the dependence of [OH] decay rates on reactant concentrations. The systematic uncertainty of the measurements, discussed earlier and estimated to be ca. 4%, must be added to the statistical uncertainties to yield the total 95% confidence limits of the derived rate constants. The literature data are shown with their reported uncertainties only when it is essential for understanding the significance of the data discrepancy.

$\text{CF}_2=\text{CF}_2$. Figure 1 illustrates all of the available data for this reaction. The reaction has been previously studied at room temperature^{4,5} and between 250 and 370 K.⁶ Both of our previous measurements at room temperature^{4,6} resulted in the same $k_{\text{CF}_2\text{F}_4}$ (298 K). Acerboni et al.⁵ measured the reaction by a relative rate technique with two different reference reactions. While their reported average value of the rate constant exceeds our results by $\sim 13\%$, the quoted uncertainty is much larger than the disagreement. Moreover, the disagreement is only $\sim 9\%$ when their measured rate constant ratios are combined with current recommendations for the OH reaction rate constants of reference compounds, propene¹⁸ and cyclohexane.¹⁹ This recalculated result is shown in Figure 1.

In the present work, we performed only higher temperature measurements of this reaction at 370 and 480 K. The measured $k_{\text{CF}_2\text{F}_4}$ (370 K) coincides (within 1%) with our previous result,⁴ and $k_{\text{CF}_2\text{F}_4}$ (480 K) extends the available temperature range to better capture the temperature dependence of this reaction rate constant. The combined fit to the higher temperature data from this study and those obtained between 250 and 370 K in our previous study⁴ yields the following expression between 250 and 480 K:

$$k_{\text{CF}_2\text{F}_4}(250 - 480 \text{ K}) = 1.32 \times 10^{-12} \times (T/298 \text{ K})^{0.9} \times \exp(+600 \text{ K}/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad (7)$$

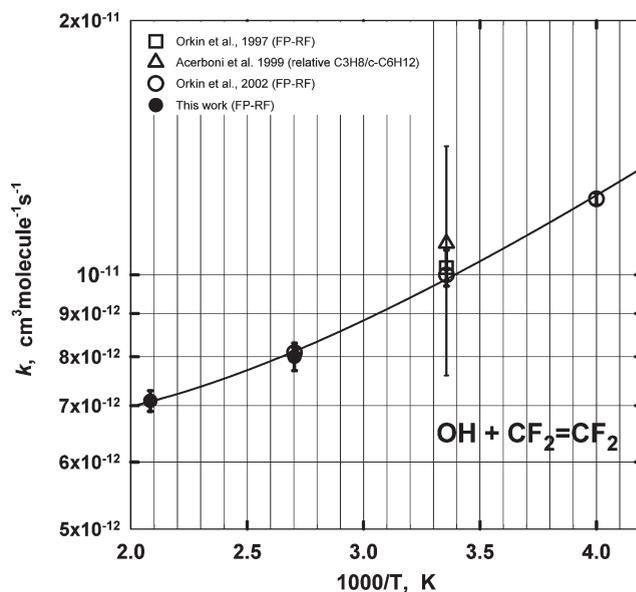


Figure 1. Results of the rate constant measurements for the reaction between OH and tetrafluoroethene, $\text{CF}_2=\text{CF}_2$: (□) Orkin et al.,⁴ (△) Acerboni et al.,⁵ recalculated by using recent recommendations for the rate constants of reference reactions,^{18,19} (○) Orkin et al.,⁶ and (●) this study. The line shows a three-parameter fit to the data from this study and from ref. 6.

While this three-parameter fit has no chemical significance, it captures the slight curvature in the Arrhenius plot that is evident for this reaction. This behavior is illustrated more strongly for the other perfluorinated alkenes reported on below.

$\text{CF}_2=\text{CFCF}_3$. This is the most studied reaction of the perfluoroalkenes. Figure 2 shows all of the available results of measurements of this reaction below 500 K. The temperature dependence of the rate constant has been previously studied by absolute techniques above room temperature⁷ and over the temperature ranges extended down to 250 K.^{8,4,9} Results of these studies are in good agreement (within 10%) over the common temperature ranges of measurements. There is an indication of curvature in the Arrhenius plot for this reaction when the data from all studies are compared. Room-temperature rate constants measured in two relative rate studies^{10,11} are slightly larger than the results of absolute measurements. We extended the temperature interval to measure the rate

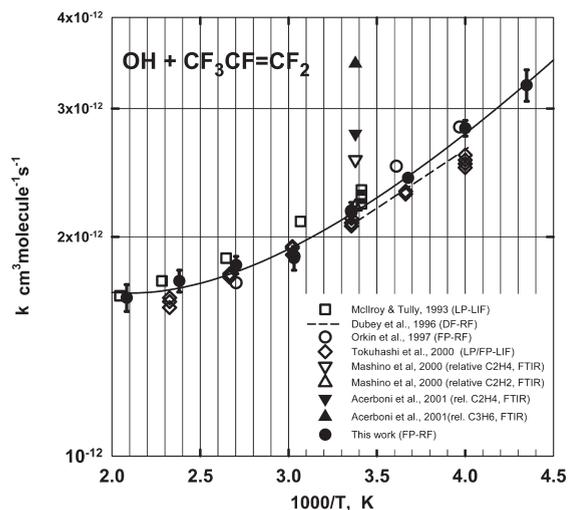


Figure 2. Results of the rate constant measurements for the reaction between OH and hexafluoropropene, $\text{CF}_3\text{CF}=\text{CF}_2$: (\square) McLlroy and Tully,⁷ (— —) Dubey et al.,⁸ (\circ) Orkin et al.,⁴ (\diamond) Tokuhashi et al.,⁹ (\triangle , ∇) Mashino et al.,¹¹ (\blacktriangle , \blacktriangledown) Acerboni et al.,¹⁰ and (\bullet) this study. The line shows a three-parameter fit to the data from this study.

constant between 230 and 480 K in the single study. As shown in Figure 2, our results are in good agreement with earlier data and clearly manifest a curvature of the Arrhenius plot. A three-parameter fit to our data results in the following expression:

$$k_{\text{C}_3\text{F}_6}(230 - 480 \text{ K}) = 9.75 \times 10^{-14} \times (T/298 \text{ K})^{1.94} \times \exp(+922 \text{ K}/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad (8)$$

and is shown in Figure 2 as a solid line. It is similar to the temperature dependence (7) obtained for $k_{\text{C}_2\text{F}_4}(T)$, although the curvature is more pronounced.

$\text{CF}_3\text{CF}=\text{CFCF}_3$. There are two room-temperature studies of the OH reaction with an industrial mixture of $\text{CF}_3\text{CF}=\text{CFCF}_3$, which were performed using a relative rate technique.^{12,13} Figure 3 shows all of the available data for this reaction. The results obtained by Young et al.¹² using the reference compounds C_2H_2 and C_2H_4 are shown as open triangles. The authors reported the combined result for this reaction rate constant to be $k_{\langle\text{C}_4\text{F}_8\rangle}(296 \text{ K}) = (4.82 \pm 1.15) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. The quoted uncertainty is mainly due to the difference between these two determinations and also accounts for the scattering of the experimental data. Cometto et al.¹³ report $k_{\langle\text{C}_4\text{F}_8\rangle}(298 \text{ K}) = (3.7 \pm 0.2) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, which is shown as “ \diamond ”. The authors also used two different reference compounds ($\text{C}_2\text{H}_5\text{Cl}$ and C_2H_6) to obtain indistinguishable results. The quoted uncertainty reflects only data scattering. Results of our measurements between 230 and 480 K are shown with “ \circ ” and agree with the results from Young et al.¹² within their reported uncertainties. The rate constant recently reported by Cometto et al.¹³ is ca. 30% smaller. Our data clearly indicate curvature of the Arrhenius plot, and a three-parameter fit yields:

$$k_{\langle\text{C}_4\text{F}_8\rangle}(230 - 480 \text{ K}) = 7.89 \times 10^{-14} \times (T/298 \text{ K})^{1.71} \times \exp(+557 \text{ K}/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad (9)$$

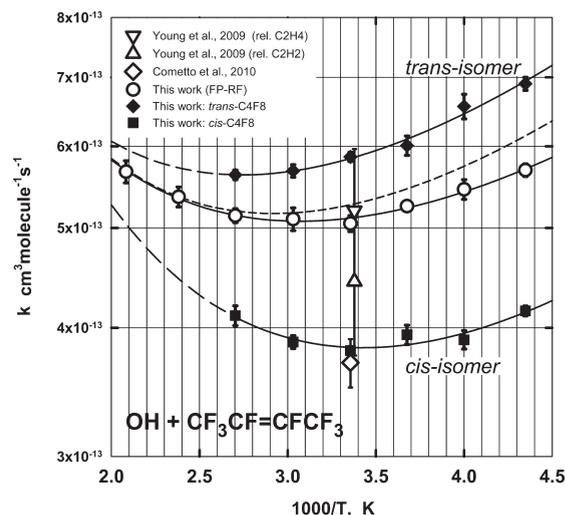


Figure 3. Results of the rate constant measurements for the reaction between OH and octafluoro-2-butene, $\text{CF}_3\text{CF}=\text{CFCF}_3$. Mixture of isomers: (\triangle , ∇) Young et al.,¹² (\diamond) Cometto et al.,¹³ (\circ) this study, (\blacklozenge) *trans*- $\text{CF}_3\text{CF}=\text{CFCF}_3$, this work, (\blacksquare) *cis*- $\text{CF}_3\text{CF}=\text{CFCF}_3$, this work. Solid lines show three-parameter fits to the corresponding data sets; long-dashed lines show their extrapolations to higher temperatures. The short-dashed line shows $k_{\Sigma}(T) = 0.715 \times k_{\text{trans-C}_4\text{F}_8}(T) + 0.285 \times k_{\text{cis-C}_4\text{F}_8}(T)$ (see the discussion in the text).

The curvature of this temperature dependence is even more pronounced than that of $k_{\text{C}_3\text{F}_6}(T)$, and it goes through a minimum near room temperature.

***trans*- $\text{CF}_3\text{CF}=\text{CFCF}_3$ and *cis*- $\text{CF}_3\text{CF}=\text{CFCF}_3$.** The “rate constant” reported above, $k_{\langle\text{C}_4\text{F}_8\rangle}(T)$, was measured for a mixture of the two existing stereoisomers of octafluoro-2-butene, $\text{CF}_3\text{CF}=\text{CFCF}_3$. However, these stereoisomers can have different individual reactivities with respect to OH addition. Therefore, we prepared the samples of the individual stereoisomers by GC separation from the original sample that was used to measure $k_{\langle\text{C}_4\text{F}_8\rangle}(T)$ and studied the isomer reactivity between 230 and 370 K.

The rate constant for the reaction of *trans*- $\text{CF}_3\text{CF}=\text{CFCF}_3$, $k_{\text{trans-C}_4\text{F}_8}(T)$ (shown in Figure 3 as “ \blacklozenge ”), noticeably increases with decreasing temperature. Its Arrhenius plot exhibits a noticeable curvature and can be represented as

$$k_{\text{trans-C}_4\text{F}_8}(230 - 370 \text{ K}) = 7.50 \times 10^{-14} \times (T/298 \text{ K})^{1.68} \times \exp(+612 \text{ K}/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad (10)$$

This temperature dependence is shown in Figure 3 as a solid line going through the $k_{\text{trans-C}_4\text{F}_8}(T)$ data points. Its extrapolation above 370 K is shown as a long-dashed line and is used in a later analysis.

The results of our measurements of the rate constant for the reaction of *cis*- $\text{CF}_3\text{CF}=\text{CFCF}_3$ are shown as “ \blacksquare ” in Figure 3. In contrast to the *trans*-isomer, $k_{\text{cis-C}_4\text{F}_8}(T)$ does not exhibit a pronounced temperature dependence between 230 and 370 K. Although measured $k_{\text{cis-C}_4\text{F}_8}(T)$ varies by less than 10%, a curvature of the Arrhenius is statistically significant. A three-parameter fit to these data is shown in Figure 3 as the solid line through the “ \blacksquare ” data points and can be represented as

$$k_{\text{cis-C}_4\text{F}_8}(230 - 370 \text{ K}) = 2.99 \times 10^{-14} \times (T/298 \text{ K})^{2.61} \times \exp(+760 \text{ K}/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad (11)$$

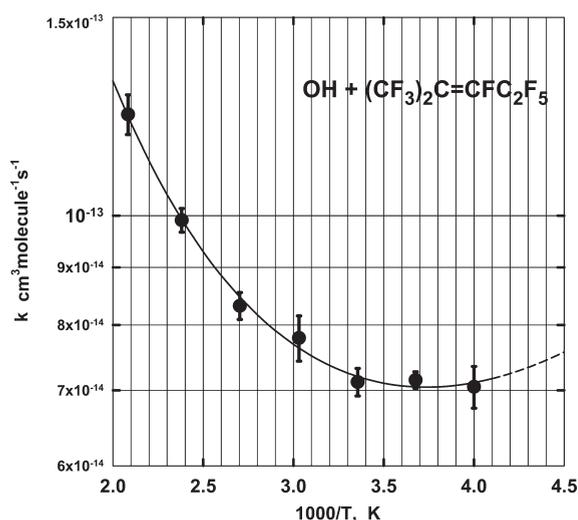


Figure 4. Results of the rate constant measurements for the reaction between OH and perfluoro-2-methyl-2-pentene, $(\text{CF}_3)_2\text{C}=\text{CFC}_2\text{F}_5$, obtained in this study. The line shows a three-parameter fit to the data.

The extrapolation of this dependence above 370 K is also shown with a long-dashed line.

Finally, we can compare the kinetic results obtained for individual stereoisomers with those obtained for the original mixture containing 71.5% of *trans*-isomer and \sim 28.5% of *cis*-isomer. The short-dashed line drawn through the entire temperature range in Figure 3 represents a sum of rate constants determined for individual stereoisomers using their fractional abundances in the original mixture, that is:

$$k_{\Sigma}(T) = 0.715 \times k_{\text{trans-C}_4\text{F}_8}(T) + 0.285 \times k_{\text{cis-C}_4\text{F}_8}(T) \quad (12)$$

where $k_{\text{trans-C}_4\text{F}_8}(T)$ and $k_{\text{cis-C}_4\text{F}_8}(T)$ are represented by eqs 10 and 11, respectively. One can see that $k_{\Sigma}(T)$ shown in Figure 3 as the short-dashed line generally reproduces the temperature trend of the measured $k_{(\text{C}_2\text{F}_5)}$ (T).

$(\text{CF}_3)_2\text{C}=\text{CFC}_2\text{F}_5$. The results of our measurements between 250 and 480 K are shown in Figure 4. The rate constant has the negative temperature dependence over the entire range of measurements, and the Arrhenius plot has clearly resolved curvature. The three-parameter fit to our data yields the following expression between 250 and 480 K:

$$k_{\text{C}_6\text{F}_{12}}(250 - 480 \text{ K}) = 2.17 \times 10^{-15} \times (T/298 \text{ K})^{3.90} \times \exp(+1044 \text{ K}/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad (13)$$

To the best of our knowledge, there are no other data available for this reaction.

Discussion of Kinetics. We have found that the rate constant of the OH addition to the double bond drastically decreases with each $-\text{CF}_3$ added to the olefinic carbon. Unfortunately, we could not obtain a couple of perfluorinated alkenes to complete this $-\text{CF}_3$ substitution series: $(\text{CF}_3)_2\text{C}=\text{CFCF}_3$ and $(\text{CF}_3)_2\text{C}=\text{C}(\text{CF}_3)_2$. Therefore, $(\text{CF}_3)_2\text{C}=\text{CFC}_2\text{F}_5$ was chosen as the available substitute for $(\text{CF}_3)_2\text{C}=\text{CFCF}_3$ in this series. On the basis of the available kinetic data, we expected the effect of $-\text{C}_2\text{F}_5$ substitution to be similar to that of $-\text{CF}_3$. Indeed, the reactivities of $\text{CH}_2=\text{CH}-\text{CF}_3$ and $\text{CH}_2=\text{CH}-\text{C}_2\text{F}_5$ toward OH are indistinguishable,^{4,20} the same being true for the

Table 2. Hydroxyl Radical Reactivity toward Fluorinated Alkenes

molecule	$k(298) \times 10^{12}$, $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	reference
$\text{CH}_2=\text{CH}_2$	9.0	29
$\text{CH}_2=\text{CHF}$	5.2	30
$\text{CH}_2=\text{CF}_2$	2.8	30
$\text{CF}_2=\text{CF}_2$	10.	6
$\text{CH}_2=\text{CH}-\text{CH}_3$	30.	29
$\text{CH}_2=\text{CH}-\text{CH}_2\text{F}$	16.5	31
$\text{CH}_2=\text{CH}-\text{CF}_3$	1.5	4
$\text{CH}_2=\text{CH}-\text{C}_2\text{F}_5^a$	1.4	20
$\text{CH}_2=\text{CF}-\text{CF}_3$	1.1	17,32
$\text{CHF}=\text{CF}-\text{CF}_3$, <i>trans</i> -	2.2	22
$\text{CHF}=\text{CF}-\text{CF}_3$, <i>cis</i> -	1.3	22,32
$\text{CHF}=\text{CH}-\text{CF}_3$, <i>trans</i> -	0.7	17
$\text{CF}_2=\text{CF}-\text{CF}_3$	2.2	this work
$\text{CF}_2=\text{CF}-\text{C}_2\text{F}_5$	1.9	12
$\text{CF}_3-\text{CF}=\text{CF}-\text{CF}_3$, <i>trans</i> -	0.58	this work
$\text{CF}_3-\text{CF}=\text{CF}-\text{CF}_3$, <i>cis</i> -	0.38	this work
perfluorocyclopentene	0.10	21
perfluorocyclobutene	0.086	21
$(\text{CF}_3)_2-\text{C}=\text{CF}-\text{C}_2\text{F}_5$	0.072	this work

^aThe room-temperature rate constant was found to be the same for all reactions of OH with a series of fluorinated alkenes, $\text{CH}_2=\text{CH}-\text{C}_x\text{F}_{2x+1}$ ($x = 1, 2, 4, 6$, and 8).

reactivity of $\text{CF}_2=\text{CF}-\text{CF}_3$ and $\text{CF}_2=\text{CF}-\text{C}_2\text{F}_5$.¹² As we assumed, the OH addition to the double bond became even slower when the third fluorinated replacement, $-\text{C}_2\text{F}_5$, was added to the olefinic carbon to make $(\text{CF}_3)_2\text{C}=\text{CFC}_2\text{F}_5$ from the less substituted $\text{CF}_3\text{CF}=\text{CFCF}_3$.

Perfluoro methyl (ethyl) groups adjacent to the double bond substantially decrease the OH addition rate constant. Thus, the room temperature rate constant of the “parent” perfluorinated alkene, $\text{CF}_2=\text{CF}_2$, is about 140 times greater than the rate constant of its deeply substituted perfluorinated derivative, $(\text{CF}_3)_2\text{C}=\text{CFC}_2\text{F}_5$. The deactivating effect of the $-\text{CF}_3$ group adjacent to the double bond was noticed earlier⁴ and has been shown to be very pronounced in this study. The effect is more pronounced than that of olefinic carbon fluorination ($-\text{F}$ substitution) despite the smaller electron affinity of $-\text{CF}_3$ and the longer distance from the $\text{C}=\text{C}$ double bond. This suggests the importance of a geometrical factor in the delocalization of π -electrons. In the very recent study, Wallington and Hurley²¹ determined the room-temperature OH reaction rate constants of two perfluorinated cycloalkenes: octafluorocyclopentene, $(1.01 \pm 0.16) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, and hexafluorocyclobutene, $(0.96 \pm 0.18) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. These two molecules can be considered as a *cis*- $\text{CF}_3\text{CF}=\text{CFCF}_3$ molecule in which two $-\text{CF}_3$ substitutes are replaced with fluorinated ring connecting both olefinic carbons. As the result, these ring-strained perfluoroalkenes became less reactive toward OH. This can be either due to further delocalization of π -electrons in the presence of the fluorinated ring or due to steric effect of the ring. In both cases, the molecular geometry affects the reactivity of a fluoroalkene. The noticeable difference in the reactivity of stereoisomers also supports the importance of the molecular

geometry. The different OH reactivity of stereoisomers has also been found in case of fluorinated propene, $\text{CHF}=\text{CF}-\text{CF}_3$.²²

Table 2 provides the room-temperature rate constants for OH reactions of fluorinated alkenes (fluorine substitutions are in bold). One can see that the fluorination of the same olefinic carbon does decrease the double bond reactivity (a factor of ~ 1.8 per F atom). However, symmetrically fluorinated perfluoroethene is even slightly more reactive than its "parent" compound, ethene. In contrast with $-\text{CH}_3$ substitution (which increases the ethene reactivity), $-\text{CF}_3$ substitution decreases it by a factor of 6. As soon as this substitution appears, any fluorination of olefinic carbons themselves does not appreciably affect the reactivity. Moreover, it seems that the geometry of the alkene molecule (stereoisomers) containing the $-\text{CF}_3$ adjacent to the double bond is as important for its reactivity toward OH as the fluorination of olefinic carbons.

Atmospheric Implications. The atmospheric lifetimes of the perfluorinated alkenes under study can be estimated from their reactivities toward OH. On the basis of results previously obtained for $\text{CF}_2=\text{CF}_2$ and $\text{CF}_3\text{CF}=\text{CF}_2$,⁴ we can conclude that the absorption cross sections in the tropospheric UV radiation region (above 290 nm) are negligible for all perfluorinated alkenes. Therefore, the reactions with hydroxyl radicals in the troposphere dictate their atmospheric lifetimes, which can be estimated using a simple scaling procedure that is based on the results of field measurements²³ and thorough atmospheric modeling.²⁴

$$\tau_i^{\text{OH}} = \frac{k_{\text{MCF}}(272 \text{ K})}{k_i(272 \text{ K})} \times \tau_{\text{MCF}}^{\text{OH}} \quad (14)$$

In eq 14, τ_i^{OH} and $\tau_{\text{MCF}}^{\text{OH}}$ are the lifetimes of a compound under study and methyl chloroform, respectively, due to reactions with hydroxyl radicals in the troposphere only, and $k_i(272 \text{ K})$ and $k_{\text{MCF}}(272 \text{ K}) = 6.1 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ are the rate constants for the reactions of OH with these substances at $T = 272 \text{ K}$ given by the expressions 7, 8, 10, 11, and 13 and in refs 25 and 26, respectively. The value of $\tau_{\text{MCF}}^{\text{OH}} = 6.0$ years was obtained from the measured lifetime of MCF of 4.9 years when an ocean loss of 89 years and a stratospheric loss of 39 years were taken into account. Applying this method to the title compounds of this study yields estimated atmospheric lifetimes of 1.2, 5.3, 21, 34, and 182 days for $\text{CF}_2=\text{CF}_2$, $\text{CF}_3\text{CF}=\text{CF}_2$, *trans*- $\text{CF}_3\text{CF}=\text{CFCF}_3$, *cis*- $\text{CF}_3\text{CF}=\text{CFCF}_3$, and $(\text{CF}_3)_2\text{C}=\text{CFC}_2\text{F}_5$, respectively. However, it must be emphasized that these derived lifetimes are significantly shorter than the characteristic time of mixing processes in the troposphere and hence are only crude estimates. The use of eq 14 is strictly applicable only for long-lived species that are well mixed throughout the troposphere. The actual residence time of short-lived compounds in the atmosphere depends on the emission location and season as well as local atmospheric conditions.^{27,28} For such species, eq 14 provides only rough estimates of the tropospheric lifetimes with respect to reaction with OH. This is especially true for the first four compounds whose calculated atmospheric lifetimes are much shorter than 0.5 years. Nevertheless, the results of more detailed modeling studies demonstrate that such an estimation procedure gives reasonable average values^{27,28} and provides a useful scaling of the lifetimes of short-lived compounds.

CONCLUSIONS

The reactions between five perfluorinated alkenes and OH radicals were studied between 230 and 480 K. The rate constant for OH addition to the double bond decreases with the number of perfluoro methyl (perfluoro ethyl) substitutes adjacent to the

double bond and spans more than 2 orders of magnitude. The reactivity of stereoisomers of fluorinated alkenes toward OH can be substantially different, thus resulting in different residence times in the atmosphere. The available kinetic information indicates the importance of molecular structure on the reactivity of fluorinated alkenes.

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