High-Accuracy Measurements of OH[•] Reaction Rate Constants and IR and UV Absorption Spectra: Ethanol and Partially Fluorinated Ethyl Alcohols

Vladimir L. Orkin,*^{,†} Victor G. Khamaganov,[†] Larissa E. Martynova,[†] and Michael J. Kurylo[‡]

[†]National Institute of Standards and Technology, Gaithersburg, Maryland 20899, United States

[‡]Goddard Earth Sciences, Technology, and Research (GESTAR) Program, Universities Space Research Association, Greenbelt, Maryland 20771, United States

Supporting Information

ABSTRACT: Rate constants for the gas phase reactions of OH[•] radicals with ethanol and three fluorinated ethyl alcohols, CH₃CH₂OH (k_0), CH₂FCH₂OH (k_1), CHF₂CH₂OH (k_2), and CF₃CH₂OH (k_3) were measured using a flash photolysis resonance-fluorescence technique over the temperature range 220 to 370 K. The Arrhenius plots were found to exhibit noticeable curvature for all four reactions. The temperature dependences of the rate constants can be represented by the following expressions over the indicated temperature intervals: $k_0(220-370 \text{ K}) = 5.98 \times 10^{-13} (T/298)^{1.99} \exp(+515/T) \text{ cm}^3$ molecule⁻¹ s⁻¹, $k_0(220-298 \text{ K}) = (3.35 \pm 0.06) \times 10^{-12} \text{ cm}^3$ molecule⁻¹ s⁻¹ [for atmospheric modeling purposes, $k_0(T)$ is essentially temperature-independent below room temperature, $k_0(220-298 \text{ K}) = (3.35 \pm 0.06) \times 10^{-12} \text{ cm}^3$ molecule⁻¹ s⁻¹], $k_1(230-370 \text{ K}) = 3.47 \times 10^{-14} (T/298)^{4.49} \exp(+977/T) \text{ cm}^3$ molecule⁻¹ s⁻¹, $k_2(220-370 \text{ K}) = 3.87 \times 10^{-14} (T/298)^{4.03} \exp(+578/T) \text{ cm}^3$ molecule⁻¹ s⁻¹. The atmospheric lifetimes due to



reactions with tropospheric OH^{\bullet} were estimated to be 4, 16, 62, and 171 days, respectively, under the assumption of a well-mixed atmosphere. UV absorption cross sections of all four ethanols were measured between 160 and 215 nm. The IR absorption cross sections of the three fluorinated ethanols were measured between 400 and 1900 cm⁻¹, and their global warming potentials were estimated.

1. INTRODUCTION

The international phaseout 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 Earth's climate has stimulated further searches for chemicals that satisfy various industrial needs while having little impact on both stratospheric ozone and climate.^{2,3}

Quantification of the possible role of new compounds as "greenhouse gases" requires accurate information on their atmospheric lifetimes, which are key parameters in determining the environmental consequences of their release into the atmosphere. These data, when combined with IR absorption spectra, allow estimations of radiative forcing and global warming potentials (GWPs) through either radiative-transfer modeling or semiempirical calculations. This search has been particularly focused on chemicals having very short residence times in the lower atmosphere as a result of either photolysis or reaction with hydroxyl radical (OH[•]). Significant photolytic loss is limited to chemicals containing bromine and iodine. Hence, the atmospheric lifetimes of most of the fluorine-containing chemicals being considered as replacements for CFCs and halons are controlled in large part by their reactivities with tropospheric OH[•]. In our laboratory, we have been focusing on precise and accurate measurements of the OH[•] reaction rates of many naturally occurring and anthropogenic halocarbons. Such data are useful not only for screening of new industrial chemicals for environmental acceptability, but also for estimating the reactivities (and lifetimes) of chemicals not yet in production using empirical correlations or more elaborate ab initio calculations.

Fluorinated alcohols are one such class of ozone-friendly chemicals being considered as CFC substitutes in certain industrial applications. These chemicals can be removed from the atmosphere by wet and dry deposition and by reaction with tropospheric OH^{\bullet} , with the latter expected to be the most significant loss process. Hence, OH^{\bullet} reaction rate coefficients

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for such compounds are required to determine their atmospheric lifetimes and possible effects on Earth's radiation budget (i.e., their GWPs). Although the natures and fates of the oxidation products from such reactions are also important in determining environmental acceptability, information on the rate constant of the initial reaction is a necessary first step.

The reactions between OH[•] and the three fluorinated ethanols

$$OH^{\bullet} + CH_{3-i}F_iCH_2OH \xrightarrow{k_i} products, \quad i = 1 - 3$$
(1)

have been studied previously.^{4–9} The CF_3CH_2OH and CH_2FCH_2OH reactions were studied both below and above room temperature, whereas CHF_2CH_2OH was studied only at room temperature.

Ethanol, CH₃CH₂OH, the parent molecule for the abovementioned fluorinated analogues, has both natural and anthropogenic atmospheric sources. It is widely used as a solvent in various industrial applications ranging from perfume, pharmaceutical, and food production; to use in household and industrial cleaning agents and paints; to use as a fuel and fuel additives. Plant fermentation is the main natural source of ethanol. World industrial production of ethanol exceeded 6×10^{10} kg/year and is increasing because of its use as a renewable fuel.¹⁰ Ethanol has been observed in the remote upper troposphere, and its reaction with OH[•] is its main removal process from the atmosphere.

In contrast to the three fluorinated ethanols, the reaction between ethanol and OH[•] has been studied extensively since the mid-1970s, with numerous rate constant measurements performed during the past decade.^{9,11–29} The results reported for the room-temperature rate constant vary by more than 50%. However, in their latest evaluation, the IUPAC panel recommended a value for the room-temperature rate constant with an uncertainty of $\pm 15\%$.³⁰ There are only two comprehensive studies of this reaction at temperatures of atmospheric interest (i.e., below room temperature).^{24,25} These lower-temperature data are somewhat scattered, resulting in some uncertainty in the temperature dependence of the reaction rate constant.

This article reports the results from our recent investigations of the reactions of OH[•] with ethanol and fluorinated ethanols over the temperature range of atmospheric interest. We focused on determining rate constants of both high precision and accuracy so as to clarify their temperature dependences.

2. EXPERIMENTAL SECTION³¹

2.1. OH[•] **Reaction Rate Constant Measurements.** General descriptions of the apparatus and the experimental method used to measure the OH[•] reaction rate constants have been given in previous articles.^{32,33,35} Modifications to the apparatus and the measurement procedure, which resulted in significant improvements in the accuracy of the obtained kinetic data, were recently described in detail.³⁵ In particular, the gas handling system was completely rebuilt, and a new reaction cell and photomultiplier were installed.

The principal component of the flash photolysis-resonance fluorescence apparatus is a double-walled Pyrex reactor (of approximately 180 cm³ internal volume) equipped with quartz windows. The reactor is thermostatted with methanol or water circulated between the outer walls. This reactor is located in a metal housing evacuated to prevent condensation of ambient water during low-temperature measurements. It also prevents extraneous absorption of the UV radiation from the flash lamp



Figure 1. OH[•] reaction decay rate versus ethanol concentration at T = 298 K. Solid circles indicate a common range of decay rates used in our experiments. The rate constant derived from these data by a weighted fit is $k_0(298 \text{ K}) = (3.38 \pm 0.03) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (all data points) and $k_0(298 \text{ K}) = (3.35 \pm 0.03) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (solid circles only).

used to produce OH[•] radicals. Reactions were studied in argon carrier gas (99.9999% or 99.9995% purity) at total pressures of 1.33-26.7 kPa (10.0-200.0 Torr). Flows of dry argon, argon bubbled through water thermostatted at 276 K, and mixtures of argon with each ethanol (containing 0.03-10% of the reactant) flowed through the reactor at total flow rates between 0.21 and 2.4 cm³ s⁻¹, standard temperature and pressure (STP). The reactant mixtures were prepared in glass bulbs (5 or 10 L) equipped with Teflon/glass valves. The concentrations of the gases in the reactor were determined by measuring the gas flow rates and the total pressure with MKS Baratron manometers. Flow rates of argon, H_2O /argon mixture, and the reactant/argon mixtures were measured and maintained using MKS mass flow controllers directly calibrated for each mixture. The procedure and uncertainties associated with gas handling were recently described in detail.35

Hydroxyl radicals were produced by the pulsed photolysis (2.5-10 Hz repetition rate) of H₂O, injected through the 276 K argon/water bubbler. The OH[•] radicals were monitored by their resonance fluorescence near 308 nm ($A^2\Sigma^+ \leftrightarrow X^2\Pi$), excited by a microwave-discharge resonance lamp (0.4 kPa or 3 Torr of a \sim 2% mixture of H₂O in ultra-high-purity helium) focused into the reactor center. Resonantly scattered radiation from the center of the reaction cell was collimated by the reactor window/lens assembly and detected with a cooled photomultiplier operating in photon-counting mode. The photomultiplier operating parameters were chosen so that the photon counting obeyed normal Poisson statistics. The resonance fluorescence signal was recorded on a computer-based multichannel scaler (channel width = 100 μ s) as a sum of 500–20000 consecutive flashes. The entire temporal OH[•] profile was recorded and coadded following each flash, thereby minimizing any possible effects of small flash-toflash variations on the initial OH[•] concentration and drift in the detection radiation intensity.

In the absence of any reactant in the reactor, the temporal decay of the concentration of OH[•] is associated with the diffusion

of OH[•] out of the irradiation (photolysis) zone. This relatively long "background" decay was always recorded with the 2.5 Hz flash repetition rate to ensure the complete disappearance of the OH[•] signal between consecutive flashes. These OH[•] concentration decays were then recorded at various reactant concentrations with a flash repetition rate between 2.5 and 10 Hz. An increased flash repetition rate permits the total signal accumulation time and, therefore, the possible influence of photomultiplier thermal "dark" counting to be decreased. This can be especially advantageous in cases of lower resonance fluorescence signals due to quenching of OH[•](A²\Sigma⁺) at large reactant concentrations. The procedure for deriving the reaction rate constant from such data has been described by Orkin et al.³³ and in subsequent articles.^{35,36}

Figure 1 gives an example of the derived OH[•] reactive decay rates plotted versus the reactant concentrations for the reaction between OH[•] and CH₃CH₂OH. This plot illustrates the wide dynamic range of measurements possible, as well as the potential to make precise measurements at relatively small OH[•] decay rates (i.e., at low concentrations of reactant). Generally, we did not use as broad of a range of OH[•] decay rates as shown in Figure 1. Rather, we preferred to make rate constant measurements under conditions corresponding to the central part of this plot between ~20-40 and 200-250 s⁻¹, corresponding to the solid circles in Figure 1. The ability to make reliable measurements at small decay rates can be very useful at lower temperatures where the reactant concentration can be limited by the saturated vapor pressure. This issue will be discussed later.

At each temperature the rate constant was determined from a fit to all of the decay rates obtained at that temperature (i.e., the slope of a plot similar to Figure 1). The temperatures for the measurements were chosen to be approximately equally distant along the Arrhenius 1/T scale so that they would be equally weighted in the fitting procedure. We increased the number of temperature points for the reaction between OH and CH₃CH₂OH to better clarify the very weak temperature dependence of the rate constant, k_0 . Experiments were always performed at two temperatures that are widely used in other studies, T = 298 K and T = 272 K. The first one is the standard (room) temperature used in the evaluations and presentations of the rate constants, and the second is the temperature used in estimations of the atmospheric lifetime.³⁷

To check for any complications, test experiments were performed with the following variations of experimental parameters: a factor of 4 in the H_2O concentration, a factor of 4 in the flash energy, a factor of 4 in the flash repetition rate (between 2.5 and 10 Hz), a factor of 3 in the residence time of the mixture in the reactor, a factor of 100 in the reactant (ethanol) concentration in the storage bulb, a factor of 12 in the residence time of this reactant mixture in the delivery volume between a storage bulb and a reactor, and a total pressure in the reactor between 1.33 and 16.7 kPa (10 to 200 Torr). No statistically significant changes in the measured reaction rate constant were observed in these test experiments. Note that variations in the H₂O concentration, flash energy, and flash repetition rate result in variations of the OH[•] concentration in the mixture and, possibly, reactant photolysis and product accumulation. Through these test experiments, we explored the possible influence of secondary radical or product reactions on the measured rate constant, thereby enabling the appropriate choice of measurement conditions. Finally, experiments at various pressures were performed to check for a possible pressure dependence of the reaction rate constant.

The measurements performed with various gas flow rates and the reactant concentrations in the storage bulb allowed checking for the potential absorption or desorption of the reactant in the gas handling system. We paid very careful attention to these test experiments especially when more diluted mixtures were used to measure the larger reaction rate constant. In an earlier attempt to study the reaction between OH^{\bullet} and CH_3CH_2OH we used more diluted mixtures of ethanol in the storage bulbs (0.03%) and smaller total flow rates and observed some scattering of and drift in the measured rate constant. We concluded that these complications were due to adsorption of ethanol on the gas handling system walls until the surface became saturated. With the current modified apparatus, such scattering and drift were no longer apparent.

2.2. UV Absorption Cross-Section Measurements. The absorption spectra of undiluted ethanols were measured over the wavelength range of 160-220 nm using a single-beam apparatus consisting of a 1-m vacuum monochromator equipped with a 600 lines/mm grating. The radiation source was a Hamamatsu L1385 deuterium lamp, and the detector was a Hamamatsu R166 photomultiplier. Spectra were recorded at increments of 0.5 nm at a spectral slit width of 0.16 nm. The pressure inside the (16.9 \pm 0.05) cm absorption cell was measured by a MKS Baratron manometer at $T = (295 \pm 1)$ K. The most careful UV absorption measurements were performed for ethanol, CH₃CH₂OH. In addition to the standard optical cell, we also used a shorter (5.02 \pm 0.01) cm absorption cell to extend the ethanol pressure range to between 53 and 720 Pa (between 0.4 and 5.4 Torr) when the main absorption band was measured. A longer (46.71 \pm 0.05) cm absorption cell was used to measure absorption cross sections of ethanol at longer wavelengths. The spectrum of ethanol over the shortest wavelength region between 162 and 165 nm was recorded at increments of 0.1 nm at a spectral slit width of 0.08 nm. Absorption spectra of the evacuated cell and of the cell filled with a gas sample were alternately recorded several times, and the absorption cross sections at the wavelength λ were calculated as

$$\sigma(\lambda) = \frac{\ln[I_0(\lambda)/I_{ROH}(\lambda)]}{[ROH]L}$$
(2)

where [ROH] is the concentration of ethanol in the absorption cell with the optical path length L. I_0 and I_{ROH} are the radiation intensities measured after the absorption cell when the ethanol concentration was zero and [ROH], respectively. The complete spectrum of each compound was constructed from data taken over several overlapping wavelength ranges. Data over each spectral range were obtained at several pressures of each compound to verify adherence to the Beer-Lambert absorption law. The total range of reactant pressures used for these measurements was 0.03-5.3 kPa (0.2-40 Torr). The overall instrumental error associated with uncertainties in the path length, pressure, and temperature stability was estimated to be \sim 0.5%. The uncertainty of the absorption measurements was less than $\sim 2\%$ over most of the wavelength range, increasing to $\sim 10\%$ at 195 nm for the fluorinated ethanols and to ${\sim}20\%$ at 215 nm for ethanol because of the low absorbance in the long-wavelength tails of the spectra.

2.3. IR Absorption Cross-Section Measurements. The IR absorption spectra were measured using a Nicolet 6700 FTIR spectrophotometer with spectral resolutions of 0.125 cm⁻¹ (recorded with a step of 0.06 cm^{-1}), 0.25 cm⁻¹ (recorded with a step of 0.12 cm⁻¹) and 0.5 cm⁻¹ (recorded with a step of 0.25 cm⁻¹). Both a liquid-nitrogen-cooled mercury cadmium telluride (MCT) detector and a room-temperature deuterated triglycine sulfate (DTGS) detector were used. The absorption

cross sections obtained with these detectors were compared to avoid a possible systematic error due to differences in their properties. The DTGS detector, in particular, was used to obtain the reliable data in the longer wavelength region below

Table 1.	Rate Const	ants Measu	red in th	ne Present	Work for
the Reac	tion of OH [•]	with CH ₃ C	$H_2OH^{a_i}$	ı,b	

	$k_0(T) \times 10^{12}$	[CH ₃ CH ₂ OH]	test experiments
T(K)	$(cm^3 molecule^{-1} s^{-1})$	$(10^{13} \text{ molecule/cm}^3)$	conditions
220	3.37 ± 0.03 (32)	0.9-7.21	
230	3.37 ± 0.02 (37)	0.6-7.11	
240	3.32 ± 0.03 (18)	0.9-7.18	
250	$3.35 \pm 0.03 \; (26)$	0.9-7.19	
260	$3.31 \pm 0.03 \; (32)$	0.87 - 7.1	
272	$3.32\pm 0.03\;(19)$	1.0 - 7.2	
285	$3.35 \pm 0.04 \; (16)$	0.97 - 7.1	
298	$3.37 \pm 0.02 \; (43)$	0.58-7.1	
	3.38 ± 0.04	0.9-7.5	$[OH^{\bullet}] \approx 47\%$
	3.36 ± 0.04	1.2-8.1	$[OH^{\bullet}] \approx 210\%$
	3.44 ± 0.03	1.1 - 8.1	$[OH^{\bullet}] pprox 800\%$
	3.35 ± 0.02	1.2-7.2	1.0% mixture in the bulb
	3.39 ± 0.05	0.97-6.8	0.1% mixture in the bulb
	3.45 ± 0.05	0.9-4.6	0.03% mixture in the bulb
	3.32 ± 0.05	0.8-5.7	P = 1.33 kPa (10 Torr)
	3.41 ± 0.09	0.8-7.6	P = 2.67 kPa (20 Torr)
	3.32 ± 0.04	0.7-6.8	P = 26.7 kPa (200 Torr)
313	$3.40 \pm 0.03 \ (9)$	1.0 - 7.2	
330	$3.47 \pm 0.02 \; (17)$	0.9 - 7.1	
350	$3.58 \pm 0.03 \; (9)$	0.8-6.4	
370	$3.75 \pm 0.03 \; (24)$	0.5-5.4	
DDOD	0 = = = 0 /		

RRSD^c 0.75%

^{*a*} The uncertainties are two standard errors from the least-squares fit of a straight line to the measured OH[•] decay rates versus the reactant concentrations. Including estimates for systematic uncertainties, the overall uncertainty of the rate constant (95% confidence limit) was estimated to be ~2%, increasing to 2.5% at the lowest temperatures. ^{*b*} Bold data are results of the fit to all measurements performed at the particular temperature and 4.00 kPa (30.0 Torr) total pressure using a 1% mixture. These data are shown in Figure 1 and were used to derive the temperature dependences. The number of experiments for each temperature is included in parentheses. ^{*c*} Relative residual standard deviation (RRSD) given by eq 9 included to uniformly represent the data deviation from the best-fit modified Arrhenius dependence.

700 cm⁻¹. A (10.2 \pm 0.05) cm glass absorption cell fitted with KBr windows was fixed in the spectrophotometer to minimize any baseline shift due to changes in the absorption cell position. The temperature of the cell was measured to be (295 ± 1) K. Between measurements, the cell was pumped out to \sim 0.01 Pa and then filled with the gas to be studied. Absorption spectra of the evacuated cell and of the cell filled with a gas sample were alternately recorded several times, and the absorption cross sections at the wavenumber ν (cm⁻¹) were calculated. The experimental procedure and data treatment are similar to those described for UV absorption measurements. Details and potential complications of these measurements were discussed in a recent article.35 The overall instrumental error associated with the optical path length, pressure measurements, and temperature stability was estimated to be \sim 0.5%. The uncertainty of the absorption measurements was usually less than \sim 1%, except in the wavenumber range below ~ 700 cm⁻¹, where the spectrophotometer noise increased. All measurements were done in pure fluorinated ethanols with no bath gas added.

Materials. The highest-purity sample of ethanol was used as obtained from Sigma-Aldrich with the stated purity 100.0% (<0.1% of water as the only possible impurity). A sample of 2-fluoroethanol was obtained from Sigma-Aldrich with a stated purity of 97.9%. Our gas chromatography/mass spectrometry (GC/MS), GC/flame ionization detection (FID), and GC/ thermal conductivity detection (TCD) analyses of the liquid sample identified the following impurities, which could affect the results of OH[•] kinetic measurements: dioxane (\sim 1%), acetaldehyde (\sim 0.15%), and 2-chloroethanol (\sim 0.2%). Specific absorption bands of both acetaldehyde and dioxane were observed in the vacuum UV absorption spectrum of the original sample between 160 and 190 nm. This sample was purified to 99.6% using a preparative-scale gas chromatograph, with water being the only remaining impurity detected. GC analysis of the purified sample indicated that impurities other than water were decreased by a factor between 20 and more than 100, thereby eliminating any reactive interference. A sample of 2,2-difluoroethanol obtained from SynQuest Laboratories, Inc., was of 99.35% purity, with water being the only reported impurity. We used this sample in our measurements after GC purification. Finally, two samples

Table 2. Rate Constants Measured in the Present Work for the Reactions of OH^{\bullet} with CH_2FCH_2OH , CHF_2CH_2OH , and $CF_3CH_2OH^{a,b}$

T (K)	$k_1(T) imes 10^{13}$ $({ m cm}^3~{ m molecule}^{-1}~{ m s}^{-1})$	$[CH_2FCH_2OH] \\ (10^{14} \text{ molecule/cm}^3)$	$k_2(T) imes 10^{13} \ ({ m cm}^3 { m molecule}^{-1} { m s}^{-1})$	$[CHF_2CH_2OH] \\ (10^{15} \text{ molecule/cm}^3)$	$k_3(T) imes 10^{14}$ (cm ³ molecule ⁻¹ s ⁻¹)	$[CF_3CH_2OH] \\ (10^{15} \text{ molecule/cm}^3)$
220			$1.48 \pm 0.04 \ (12)$	0.24-0.88	$4.87 \pm 0.07 \ (16)$	0.25-2.7
230	$7.67 \pm 0.38 \ (25)$	0.45-2.1	$1.59 \pm 0.01 \; (18)$	0.12-1.08	$5.43 \pm 0.11 \ (34)$	0.5-3.8
250	$7.75 \pm 0.13 \ (26)$	0.26-2.9	$1.85 \pm 0.02 \ (16)$	0.11-1.3	$6.41 \pm 0.20 \ (20)$	0.5-3.8
272	$8.26 \pm 0.44 \ (10)$	0.38-2.0	$2.21 \pm 0.03 \ (14)$	0.12-1.2	$7.96 \pm 0.16 \ (15)$	0.25-2.9
298	$9.29 \pm 0.18 \ (21)$	0.19-2.5	$2.70 \pm 0.02 \ (16)$	0.12-0.87	$10.1 \pm 0.10 \ (28)$	0.25-2.9
330	10.8 ± 0.50 (7)	0.32-1.2	$3.42 \pm 0.04 \ (17)$	0.11-0.66	$13.5\pm 0.18~(19)$	0.27 - 1.7
370	12.7 ± 0.58 (7)	0.28-1.04	$4.64 \pm 0.10 \ (11)$	0.13-0.45	$18.2 \pm 0.16 \ (17)$	0.13-1.0
RRSD ^c	1.7%		0.45%		1.3%	

^{*a*} Uncertainties are two standard errors from the least-squares fit of a straight line to the measured OH[•] decay rates versus the reactant concentrations. Including estimates for systematic uncertainties, the overall uncertainty of the rate constants (95% confidence limit) for CF₃CH₂OH and CHF₂CH₂OH was estimated to be ~2.5%, increasing to 3% at lowest temperatures. For CH₂FCH₂OH, the overall uncertainty was estimated to be ~6%. ^{*b*} Bold data are results of the fit to all measurements performed at the particular temperature and 4.00 kPa (30.0 Torr) total pressure using a 0.2%, 2%, and 5% mixtures of CH₂FCH₂OH, CHF₂CH₂OH, and CF₃CH₂OH, respectively. These data are shown in the corresponding figures and were used to derive the temperature dependences. The number of experiments for each temperature is included in parentheses. ^{*c*} Relative residual standard deviation (RRSD) given by eq 9 included to uniformly represent the data deviation from the best-fit modified Arrhenius dependence.



Figure 2. (a) Available results of rate constant measurements extended beyond room temperature for the reaction between OH[•] and ethanol, $k_0(T)$. References are given in the legend along with the experimental techniques. Abbreviations: FP–RA, flash photolysis–resonance absorption; FP–RF, flash photolysis–resonance fluorescence; LF–LIF, laser photolysis–laser-induced fluorescence; ShT–RA, shock tube– resonance absorption. The curved line (both solid and dashed parts) shows a three-parameter fit to the data reported in this study. The straight line (both solid and dotted parts) shows the Arrhenius dependence reported by Sivaramakrishnan et al.²⁸ (b) Results of recent rate constant measurements for the reaction between OH[•] and ethanol, $k_0(T)$, at room temperature and below: (□) Jimenez et al.,²⁴ (○) Dillon et al.,²⁵ (●) this study. The solid line shows a three-parameter fit to the data from this study. The dashed line shows $k_0(T) = 3.35 \times 10^{-12}$ cm³ molecule⁻¹ s⁻¹, which can be recommended for T < 298 K.

of 2,2,2-trifluoroethanol were obtained from Sigma-Aldrich and SynQuest Laboratories, Inc., both with a stated purity of 99.9% and water being the only detected impurity. These samples were used without further purification as our own analysis did not reveal any detectable impurity except water. All samples were carefully degassed through multiple freeze–pump–thaw– boil cycles. Note that the absorption spectra were measured much later, and the available samples of fluorinated ethanols were contaminated with small amounts of water. We used 99.9995% and 99.9999% purity argon (Spectra Gases Inc.) as a carrier gas.



Figure 3. Available results of rate constant measurements for the reaction between OH[•] and 2,2,2-trifluoroethanol, CF₃CH₂OH, $k_3(T)$: (*) Wallington et al.,⁴ (+) Inoue et al.,⁵ (Δ , ∇) pulsed photolysis and discharge flow experimental data from Tokuhashi et al.,⁶ (\Box) Hurley et al.,⁷ (\diamond) Sellevag et al.,⁸ (\bigcirc) Kovacs et al.,⁹ (\bullet) this study. The line shows a three-parameter fit to the data from this study. Inset: Temperature-dependent results from Tokuhashi et al.⁶ and this study obtained over the common temperature range between 250 and 375 K. The straight line shows the Arrhenius (two-parameter) fit to the data from this study.

3. RESULTS AND DISCUSSION

3.1. OH' Reaction Rate Constants. The rate constants determined for the title reactions are presented in Tables 1 and 2. The bold data result from fits to all measurements performed at the indicated temperature under our "standard" conditions: 4.00 kPa (30.0 Torr) total pressure, $\sim 6 \times 10^{14}$ molecule/cm³ of H_2O in the reactor, and ~ 0.05 J flash energy. These data were obtained with 0.3% CH₃CH₂OH, 0.2% CH₂FCH₂OH, 2% CHF₂CH₂OH, and 5% CF₃CH₂OH mixtures prepared in the storage bulbs. These particular mixtures were chosen because they were the most convenient to maintain the appropriate reactant concentrations in the reaction cell with our apparatus design. The bold results are shown in the corresponding plots in Figures 2, 3 5, and 6 along with other available data for these reactions. The precision of our measurements allows clear resolution of the curvature in the Arrhenius plots for all four reactions.

The results of some test experiments with ethanol mentioned earlier are also included in Table 1 as the italicized text. These test experiment results indicate the absence of any effect of the gas flow rate (the residence time of the mixture in the system) or of the reactant concentration in the storage bulbs on the measured rate constants. Quantitative IR analysis of the mixtures containing fluorinated ethanols confirmed the content of manometrically prepared mixtures with reactant concentrations as large as 10% and as small as 0.1%. Hence, we used the middle-range concentrations in our experiments.

 $OH^{\bullet} + CH_3CH_2OH$. With all of the modifications and precautions described in an earlier work,³⁵ we were able to obtain very reproducible data over wide ranges of parameters. Figure 1 shows an example of $OH^{\bullet} + CH_3CH_2OH$ measurements at T = 298 K for which the reactant concentration was varied by more than a factor of 120. As stated earlier, despite the wide dynamic ranges

of both the reactant concentration and decay rate that can be measured, we cautiously used the middle part of this range to obtain the most precise and accurate results.

The results of our kinetic measurements for ethanol are presented in Table 1 and shown in Figure 2a,b. The curvature of the Arrhenius plot is clearly resolved in these experiments although, the variation of the reaction rate constant, k_0 , over the entire temperature range is less than 25%. A three-parameter modified Arrhenius dependence fit to the bold data set in Table 1 is shown with curved lines in Figure 2a,b

$$k_0(T) = 5.98 \times 10^{-13} (T/298)^{1.99} \exp(+515/T)$$
 (3)

Our data obtained below room temperature varied by less than 2% and can be represented as being essentially temperatureindependent: $k_0(220-298 \text{ K}) = 3.35 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

All available data from studies of the reaction temperature dependence are shown in Figure 2a. $^{16-18,24,25,27-29}$ Not shown in Figure 2a are results from 10 additional studies performed at room temperature only.^{11–13,15,19,20,22,23,9,26} At T = 298 K, the data range from 2.5×10^{-12} to 3.9×10^{-12} cm³ molecule⁻¹ s⁻¹. Our Arrhenius expression in eq 3 describes the temperature behavior of the available experimental rate constant data up to \sim 600 K reasonably well, as shown by the dashed line in Figure 2a. The most comprehensive studies of this reaction at room temperature and above were conducted by Hess and Tully¹⁸ and recently by Carr at al.,²⁹ which presumably supersede the earlier more scattered results from the same group.²⁷ The data points from refs 18 and 29 lie only a few percent below our fit from eq 3 over the entire range of measurements. Very recent results obtained at high temperatures (857-1297 K) using a shock tube technique²⁸ are also included in Figure 2a. At 1200 K, these new results are about 30% higher than those from an earlier study performed using a similar technique.²⁰ However, this difference might be within the combined uncertainties of these high-temperature measurements. The temperature dependence reported by Sivaramakrishnan et al.²⁸ (shown by the solid line in Figure 2a) is the first temperature dependence of this reaction rate constant obtained at high temperatures. An extrapolation of this dependence down to 720 K (dotted line in Figure 2a) coincides with an extrapolation from a fit to our lower-temperature data (dashed line in Figure 2a). This consistency might be somewhat fortuitous given the scattering of the high-temperature data and the vastly different temperature regions for the fits. Nevertheless, based on the available data, we suggest that the combination of the following two dependences best constrains $k_0(T)$ over the entire temperature range of the measurements

$$k_0(220-720 \text{ K}) = 5.98 \times 10^{-13} (T/298)^{1.99} \exp(+515/T)$$

$$k_0(720-1300K) = 2.5 \times 10^{-11} \exp(-911/T)$$
(4)

There are two fairly recent studies of this reaction extended below room temperature.^{24,25} These data are important for atmospheric implications and are displayed in Figure 2b along with our results. The data reported by Dillon et al.²⁵ are indicative of a temperature-independent rate constant below room temperature. Their reported value of $k_0(298 \pm 2 \text{ K}) = (3.35 \pm 0.17) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ coincides with the results of our measurements.

The data reported by Jimenez et al.²⁴ are more scattered, with the lowest-temperature point being a possible outlier. The scattering of the data prevents an unambiguous determination

of the change of the reaction rate constant with temperature. The reported room-temperature value is $k_0(298 \text{ K}) = (3.1 \pm 0.4) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. In a subsequent article on kinetic studies of 2-fluoroethanol,²⁶ the same group reported an additional measurement of $k_0(298 \text{ K}) = (3.26 \pm 0.08) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, where the uncertainty is the precision only. Thus, the room-temperature rate constants reported by this group agree with the values obtained in our study and reported by Dillon et al.²⁵

Therefore, with the exception of the lowest-temperature point from ref 24, all of the data shown in Figure 2b are indicative of a temperature-independent reaction rate constant below room temperature. In the present study, we eliminated a number of experimental factors affecting both data reproducibility (precision) and accuracy. The precision of our data at each temperature was estimated as ~1%, as shown in Table 1. A number of test experiments were performed to support an estimated combined uncertainty of our measurements of ~2.5%.³⁵

 $OH^{\bullet} + CF_3CH_2OH$. The results of our measurements are presented in Table 2 and shown in Figure 3. The Arrhenius plot exhibits a curvature that is clearly resolved in our experiments. A three-parameter modified Arrhenius expression was used to fit the data set from Table 2 shown in Figure 3

$$k_3(T) = 2.48 \times 10^{-14} (T/298)^{4.03} \exp(+418/T)$$
 (5)

We report a room-temperature rate constant of $k_3(298 \text{ K}) = (9.92 \pm 0.10) \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. The results from six studies of this reaction, four absolute rate constant measurements^{4-6,9} and two relative rate studies,^{7,8} are shown in Figure 3 along with our data. The room-temperature rate constants obtained in the first five studies differ from our value by less than 5% and agree within the reported uncertainties. Thus, the room-temperature data are very consistent, and the rate constant, $k_3(298 \text{ K})$, can be considered as very well-established. Sellevag et al.⁸ determined the room-temperature rate constant by an IR-absorption-based relative rate technique using C₂H₆ as a reference compound. Their reported rate constant is ~30% larger than all other results at room temperature. The reason for this discrepancy is not clear.

The only study of the temperature dependence of this reaction was performed by Tokuhashi et al.⁶ between 250 and 430 K. They reported $k_3(298 \text{ K}) = (10.0 \pm 0.4) \times 10^{-14} \text{ cm}^3$ molecule⁻¹ s⁻¹ derived from experiments using both pulse and discharge flow techniques with LIF detection of OH[•]. They presented the temperature dependence as a standard two-parameter Arrhenius expression. There is excellent agreement between our results and those obtained by Tokuhashi et al.⁶ over the common temperature range. This is illustrated in the inset in Figure 3, where both data sets are plotted between 250 and 375 K only.

It should be noted that the measurements of a relatively small reaction rate constant at low temperature can be complicated by the small saturated vapor pressure of the reactant at that temperature. All ethanols studied in the present work have comparable vapor pressures. However, the smaller reaction rate constants require higher concentrations of the reactant to yield the same OH^{*} decay rates. We faced this problem when studying the reactions of CF₃CH₂OH and CHF₂CH₂OH at the lowest temperature of our experiments, T = 220 K. A complication (possibly due to reactant wall adsorption) clearly manifests itself at reactant partial pressures approaching the saturated vapor





Figure 4. OH[•] reaction decay rate versus fluorinated ethanol concentration at T = 220 K for 2,2-difluoroethanol, (CHF₂CH₂OH, circles) and 2,2,2-trifluoroethanol (CF₃CH₂OH, squares). Data points shown with open symbols are indicative of the loss of the reactant concentration due to adsorption of the compound when its partial pressure approached its saturated vapor pressure. These "open symbols" data were not used in deriving the reaction rate constants $k_2(220$ K) and $k_3(220$ K).

pressure of a compound. Figure 4 presents examples of results obtained at T = 220 K for CF₃CH₂OH and CHF₂CH₂OH. Deviation of the higher-concentration points from a linear dependence is readily apparent, and these highest-concentration data were not considered when the $k_i(220 \text{ K})$ values were derived. We did not observe such "outliers" when CH₂FCH₂OH and CH₃CH₂OH were studied at 220 K because the required reactant partial pressures were well below their saturated vapor pressures at this temperature.

 $OH^{\bullet} + CHF_2CH_2OH$. The results of our measurements are presented in Table 2 and shown in Figure 5, along with other available data. The three-parameter Arrhenius fit to our data results in the following expression

$$k_2(T) = 3.87 \times 10^{-14} (T/298)^{4.25} \exp(+578/T)$$
 (6)

Only two room-temperature studies of this reaction are available.^{8,9} Kovacs et al.⁹ reported the rate constant obtained at T = 300 K that is $\sim 6\%$ below our value at this temperature but coincides well within their reported uncertainty. This agreement is similar to that obtained by these same authors for the reaction of CF₃CH₂OH, where the result of Kovacs et al.⁹ exceeds our value by only 5%. Sellevag et al.⁸ reported a room-temperature rate constant that is $\sim 70\%$ larger than our value for this reaction, an even larger discrepancy than observed for CF₃CH₂OH.

 $OH^{\bullet} + CH_2FCH_2OH$. The results of our measurements are presented in Table 2 and shown in Figure 6. The Arrhenius plot again exhibits a curvature that is clearly resolved in our experiments. A three-parameter modified Arrhenius dependence fit to the data set from Table 2 given by

$$k_1(T) = 3.47 \times 10^{-14} (T/298)^{4.49} \exp(+977/T)$$
 (7)

is shown in Figure 6.

Test kinetic measurements between 298 and 220 K using a sample of 2-fluoroethanol prior to GC purification resulted in



Figure 5. Available results of rate constant measurements for the reaction between OH[•] and 2,2-difluoroethanol, CHF₂CH₂OH, $k_2(T)$: (\diamond) Sellevag et al.,⁸ (\bigcirc) Kovacs et al.,⁹ and ($\textcircled{\bullet}$) this study. The line shows a three-parameter fit to the data from this study.



Figure 6. Available results of rate constant measurements for the reaction between OH[•] and 2-fluoroethanol, CH₂FCH₂OH, $k_1(T)$: (**■**) Rajakumar et al.,²⁶ (\diamond) Sellevag et al.,⁸ and (**●**) this study. The line shows a three-parameter fit to the data from this study. Open squares (\Box) show the data reported by Rajakumar et al.,²⁶ after correction for the difference in UV absorption cross sections at 184.9 nm (see text).

a \sim 15% larger rate constant. Such a difference is reasonably consistent with the amount of detected impurities and their reactivity toward OH[•].³⁸ Based on our analyses of both original and purified samples, we are confident that the data obtained with GC-purified samples are not affected by reactions of impurities.

The available results from two published studies^{8,26} of this reaction are also shown in Figure 6. Sellevag et al.⁸ reported the room-temperature rate constant, which is \sim 50% larger than our value. Again, the reason for this overestimation is not clear, but it is consistent with the results obtained for 2,2,2-trifluoroethanol and 2,2-difluoroethanol.





Figure 7. UV absorption spectra obtained in this study for ethanol and fluorinated ethanols. The single point shown at the wavelength of 184.9 nm is the absorption cross section of 2-fluoroethanol, CH_2FCH_2OH , reported by Rajakumar et al.²⁶

The original data reported by Rajakumar et al.²⁶ are shown as solid squares in Figure 6. They significantly (by $\sim 70-80\%$) exceed the rate constants measured in our study. These authors reported no significant impurities in their sample of 2-fluoroethanol. Their measurements were done using a laser photolysis-LIF absolute technique in which the concentration of the reactant, CH₂FCH₂OH, was determined by in situ measurements of its absorption at 184.9 nm (Hg line) in flow before the reactor. The authors reported the measured UV absorption cross section to be $\sigma(184.9 \text{ nm}) = (6.32 \pm 0.35) \times 10^{-19} \text{ cm}^2/$ molecule, which is shown in Figure 7 along with the UV absorption spectrum of 2-fluoroethanol measured in this study. The absorption cross section at $\lambda = 184.9$ nm measured in the present study is smaller by a factor of \sim 1.82. The use of our absorption cross section would lower the rate constants reported by Rajakumar et al.²⁶ by the same factor of 1.82. These recalculated results, presented in Figure 6 as open squares, are in excellent agreement with the results of the present study and exhibit the same curvature in the Arrhenius plot. In other studies of OH[•] kinetics, our results have generally been in excellent agreement with those from the NOAA group. Thus, the higher UV absorption cross section reported by these authors appears to be the only identifiable reason for the difference in reported rate constants for this reaction.

Precision of OH^{\bullet} Rate Constant Measurements. In our recent article,³⁵ we discussed the precision of individual measurements at each temperature (precision of the pseudo-first-order dependences) and deviation of the measured rate constants from the best-fit curve (modified Arrhenius dependence). One can expect the range of data points scattering around the best-fit line to be consistent with the range of standard errors of the data set. There is an accepted way to present the precision of the final Arrhenius dependence (two-parameter fit) with the standard errors of two parameters: the *A* factor and *E/R*. In contrast, there is no conventional way to present the precision of a threeparameter fit (modified Arrhenius expression) employed to describe the temperature dependence of the reaction rate constant. Because of the nature of three-parameter fit, the standard errors of the obtained parameters of the fit are not very informative. One could use a common statistical value, the residual standard deviation (RSD), as a single parameter describing the precision of the data set and goodness of the fit

$$RSD = \sqrt{\frac{\sum_{j=1}^{N} (\Delta k_j)^2}{(N-p)}}$$
(8)

where Δk_i is the deviation of the measured rate constant from the best-fit curve, N is the number of measured rate constants used in the fit, and *p* is the number of fitted parameters in the model (p = p)2 for an Arrhenius dependence and p = 3 for a modified Arrhenius dependence). However, an obvious disadvantage of using RSD as a measure of data and fit quality is its dependence upon the absolute value of the rate constant, k_i . Indeed, the reaction rate constant can vary significantly (up to an order of magnitude and more) between the highest and lowest temperatures of measurements. Therefore, the largest rate constants, k_i (which give the largest Δk_i values) will contribute most to RSD. Meantime, in the absence of any temperature-dependent systematic errors, the relative precision of the measured rate constant should be independent of temperature rather than the absolute precision. The same shortcoming of RSD does not allow comparing the precision of data obtained for different reaction rate constants. Therefore, we suggest a new relative measure to represent the quality of experimental data and fit: the relative residual standard deviation (RRSD)

$$RRSD = \sqrt{\frac{\sum_{j=1}^{N} [\Delta k_j / k(T_j)]^2}{(N-p)}}$$
(9)

where $k(T_j)$ is the fitted Arrhenius dependence (standard or modified) obtained from the fitting procedure. The summation of these normalized deviations, $\Delta k_j/k(T_j)$, allows one to overcome the above-mentioned disadvantage of the RSD. Thus, the calculated RRSD is expected to be consistent with the relative precision of the individual data points in the data set, $\sigma(T_j)/k(T_j)$, where $\sigma(T_j)$ is the standard statistical error determined for each $k(T_j)$.

The reasonable consistency between RRSD and σ/k is indicative of the absence of additional errors not included in σ . In such a case, either RRSD or σ/k can be accepted as a measure of the uncertainty of measurements associated with data scattering, with the larger value giving the more conservative estimation of the precision. On the other hand, RRSD, which is substantially larger than σ/k , can be indicative of an additional unrecognized source of error due to fluctuations of experimental conditions. We included RRSD in the bottom lines of Tables 1 and 2 for each set of measured reaction rate constants.

In the tables and figures, we show the uncertainty arising from random scattering of the measured OH[•] decay rates; the uncertainties shown here are twice the standard errors derived from the fit. This component of the total uncertainty is useful for identifying trends. However, to obtain a meaningful estimate of the total uncertainty in the absolute rate constant, one must include the standard uncertainty arising from systematic effects.

Total Instrumental Uncertainty and Accuracy of Measurements. The individual sources of systematic uncertainty were discussed in great details in our recent article.³⁵ Based on that analysis, we can conservatively estimate the total instrumental uncertainty as including the following contributions: (1) preparation of the reactant mixtures in the storage bulbs, two pressure measurements (0.1% each) and the temperature stability of the bulb (0.1%); (2) pressure in the kinetic reactor, absolute pressure measurements (0.1%) and pressure fluctuations during the experiment (0.15%); (3) flow controller calibrations, Ar carrier gas flow (0.15%) and reactant mixture flow (0.15%), as well as the potential uncertainty due to fluctuation/ drift of the flow controller "zero" (0.1-0.2%); (4) temperature of the reacting gas mixture in the photolysis/detection region, 0.05% at 298 K, 0.1% at 370 K, and up to 0.5% at 220 K. These uncertainties were combined with the statistical uncertainties presented in Tables 1 and 2. The propagation of the experimental uncertainty was done by combining all statistically obtained uncertainties (type A) as the square-root of the sum of their squares. Systematic (type B) uncertainties were then added to the result. We doubled the resulting uncertainty to yield the 95% total confidence limits ($\sim 2\%$ at room temperature, increasing to \sim 2.5% at 220 K).

For CF₃CH₂OH and CHF₂CH₂OH, an additional 0.5% uncertainty must be added to account for trace amounts of water that could still have been present in the samples. Thus, we estimate the accuracy of the rate constants for these two reactions to be \sim 2.5% at room temperature, increasing to \sim 3% at 220 K. For 2-fluoropropane (CH₂FCH₂OH), the data were obtained before the completion of final modifications to the PF–RF apparatus and measurement procedure. Thus, the estimated systematic uncertainty in the rate constant of this reaction is approximately twice that for the other fluoroethanols, yielding a total uncertainty of \sim 6%.

Discussion of Kinetics. The Arrhenius plots for all four reactions exhibit a noticeable curvature that is clearly resolved in our study. Note that a curvature of the Arrhenius plot is not that uncommon when precise data are available. $^{35,39-41}$ H-atom abstraction from a methylene group, $-CH_2$ -, is the main channel of the OH[•] reaction with ethanol.¹⁴ Fluorination of the methyl group next to the reactive site appears to decrease the roomtemperature reactivity of the methylene group by factors of \sim 3.6, 3.5, and 2.7 for the first, second, and third fluorine, respectively. Ethanol and fluorinated ethanols have different potential reactive sites for OH[•] radicals. Therefore, it is attractive to attribute curvature in the Arrhenius plot to the contribution from OH[•] reactions with (fluoro)methyl and/or hydroxyl groups of (fluoro)ethanols. However, based on our previous experience with the reactivity of fluorinated ethanes, 40 one can similarly speculate on the possibility of reaction pathways involving the reactions of conformers. Tunneling can also contribute to the observed curvature in the Arrhenius plot. For example, Wang et al.⁴² conducted ab initio modeling of the OH[•] reaction with CF₃CH₂OH to find a curvature in the Arrhenius plot due to different reactivities of the -CH2- and -OH groups, with tunneling playing an important role. The availability of very precise experimental data should stimulate further theoretical studies to improve our understanding of chemical mechanisms and develop predictive computational tools.

3.2. UV Absorption Spectra. The ultraviolet absorption spectra obtained in this work are presented in Figure 7. The spectra of all ethanols are quite similar in both shape and maximum band absorption. The main effect of fluorination is a "blue shift" of the longer-wavelength absorption wing, which

increases with the number of F atoms. This shift results in larger differences in absorption cross sections at longer wavelengths. Thus, the absorption cross section at 194 nm decreases by a factor of 8 with the first fluorine in the methyl group and by a factor of \sim 4 with each additional fluorine. The table of measured UV absorption cross sections for all four compounds is available in the Supporting Information.

Unfortunately, very limited quantitative data have been published on the UV absorption cross sections of ethanol, although figures illustrating its UV absorption bands are available in the literature. Such graphical information presented in the original publications was collected and digitized by Keller-Rudek and Moortgat.⁴³ We can compare our results with a few absorption cross sections reported numerically in the original publications.

Harrison et al.⁴⁴ reported the extinction coefficients of CH_3CH_2OH at its absorption minimum near 168 nm and absorption maximum near 182 nm, which exceed our values by 35% and 5%, respectively. Salahub and Sandorfy⁴⁵ reported the extinction coefficient near the 182-nm maximum, which exceeds our value by 7%; the discrepancy is much larger for smaller extinction coefficients measured away from the maximum. Dillon et al.²⁵ reported the absorption cross section of ethanol at the mercury line, 184.9 nm, which exceeds our value by 7%.

To clarify the possible discrepancy near the ethanol absorption maximum, we performed additional measurements between 180 and 187 nm at various experimental conditions. Both the 46.71and 5.02-cm absorption cells were employed. The CH₃CH₂OH concentration ranged from 13 Pa (0.1 Torr) to 1.3 kPa (10 Torr). The PMT detector voltage ranged from 700 to 1000 V. Additional measurements with a spectral resolution of \sim 0.06 nm were performed to complement our standard measurements with 0.16-nm spectral resolution. The statistical treatment of all 30 runs resulted in an absorption maximum of $\sigma_{max}(182 \text{ nm}) = (1.167 \pm 0.005) \times 10^{-18} \text{ cm}^2/\text{molecule}$ and an absorption at the Hg emission line of $\sigma_{\rm Hg}(184.9 \text{ nm}) = (1.106 \pm 0.004) \times$ 10^{-18} cm²/molecule, where the reported errors are 95% statistical confidence intervals. Results of these test measurements near the maximum of the ethanol absorption band agree with the data shown in Figure 7 and available in the Supporting Information. We estimated the presence of water in the ethanol sample by an IR technique to verify the manufacturer stated $\leq 0.1\%$ water impurity, which cannot affect the results of our measurements. With the estimated instrumental uncertainty associated with gas handling of less than 0.5%, we are confident in these measured absorption cross sections.

In contrast to ethanol, our samples of fluorinated ethanols were contaminated with traces of water, which has a very strong absorbance below 180 nm where the maxima of the absorption bands are located. Therefore, we are aware that the measured absorption spectra are somewhat overestimated near their maxima. This overestimation can be up to 10-15% for 2,2,2trifluoroethanol and 2,2-difluoroethanol. It can be even larger for 2-fluoroethanol. A comparison of the absorption maxima of CH₃CH₂OH, CHF₂CH₂OH, and CF₃CH₂OH shows that these compounds have very similar maximum intensities of their absorption bands, which slightly decrease with fluorination of the methyl group. This observation suggests that the maximum of CH₂FCH₂OH absorption does not exceed the absorption maximum of ethanol. However, a water impurity level of more than \sim 15% would be required to explain the measured absorption maximum of CH₂FCH₂OH. Such an impurity level is much larger than indicated by our GC and IR analyses. Additional



Figure 8. IR absorption spectra of 2,2,2-trifluoroethanol, CF_3CH_2OH , obtained with a spectral resolutions of 0.125 cm⁻¹ (top panel) and 0.5 cm⁻¹ (bottom panel). The latter is shown on a logarithmic scale to visualize smaller absorption features.

studies are required if more accurate absorption intensities of fluorinated ethanols below \sim 180 nm are needed. The absorption by water impurity does not affect the measured absorption cross sections of fluorinated ethanols at the longer-wavelength tails of their absorption spectra shown in Figure 7, as water absorption quickly decreases above 180 nm.

The only numerically reported result for fluorinated ethanols is the absorption maximum of CF_3CH_2OH at 165.0 nm (Salahub and Sandorfy⁴⁵), which exceeds the result of our measurements by ~20%. No UV absorption spectra of 2-fluoroethanol and 2,2-difluoroethanol are available. Further, there are no accurate data on the longer-wavelength tails of either the ethanol or 2,2,2-trifluoroethanol absorption bands.

3.3. IR Absorption Spectra. The IR absorption spectra of fluorinated ethanols are presented in Figures 8-10. The spectra were combined as described earlier from the results of measurements at various pressures of compounds restricted by their saturated vapor pressures: 0.4-7.0 kPa (3-52.5 Torr) for CF₃CH₂OH, 0.4–2.4 kPa (3–18 Torr) for CHF₂CH₂OH, and 0.7-2 kPa (5-15 Torr) for CH₂FCH₂OH. The top panels in Figures 8 and 9 show the spectra of CF₃CH₂OH and CHF₂CH₂OH obtained with a spectral resolution of 0.125 cm⁻ to illustrate the main absorption features. The bottom panels show the same spectra recorded with a spectral resolution of 0.5 cm⁻¹ on a logarithmic scale to illustrate smaller absorption features. Figure 10 shows the spectrum of CH₂FCH₂OH between 450 and 1600 cm^{-1} , whereas the inset shows the spectrum obtained with a lower spectral resolution of 1 cm⁻¹ to illustrate its relatively strong absorption at shorter wavelengths. IR absorption cross sections are available in the Supporting Information. IR spectra of less fluorinated ethanols exhibit more pronounced resolved rotational structure of the absorption bands. The spectra obtained with different spectral resolutions are in good



Figure 9. IR absorption spectra of 2,2-difluoroethanol, CHF_2CH_2OH , obtained with spectral resolutions of 0.125 cm⁻¹ (top panel) and 0.5 cm⁻¹ (bottom panel). The latter is shown on a logarithmic scale to visualize smaller absorption features.



Figure 10. IR absorption spectra of 2-fluoroethanol, CH_2FCH_2OH , obtained with a spectral resolution of 0.125 cm⁻¹. The inset shows this spectrum obtained over the spectral interval between 450 and 3800 cm⁻¹ with a spectral resolution of 1 cm⁻¹.

agreement with the exception of very narrow lines where 0.5 cm^{-1} spectral resolution is not adequate.

Samples of fluorinated ethanols, which were used for IR absorption cross-section measurements, were contaminated with small amounts of water. We determined the concentration of water by both IR and GC techniques to make small corrections of the measured IR absorption cross sections of fluorinated ethanols. To do so, we prepared test samples with known small amounts of water added. We then compared the IR band intensities obtained for the original (fluoro)ethanol samples with those obtained for the test samples. When the total pressure in the optical cell is kept constant, the amount of water in any test sample replaces an equal amount of (fluoro)ethanol. The analysis of IR band intensities of H_2O and fluorinated ethanol

(FE) obtained at the same total pressure of both the original and test samples allows determination of the ratios of their concentrations

$$\frac{[H_2O]_{test}}{[H_2O]_0} = \alpha \quad \text{and} \quad \frac{[FE]_{test}}{[FE]_0} = \beta \tag{10}$$

while

$$[FE]_{test} + [H_2O]_{test} = [FE]_0 + [H_2O]_0$$
(11)

Combining these expressions, we obtain the impurity fraction (γ) of water in the original sample as

$$\gamma = \frac{\left[\mathrm{H}_{2}\mathrm{O}\right]_{0}}{\left[FE\right]_{0} + \left[\mathrm{H}_{2}\mathrm{O}\right]_{0}} = \frac{1-\beta}{\alpha-\beta}$$
(12)

Thus, γ can be used for a small correction (increase) in the measured fluoroethanol's IR absorption cross section. This technique does not require knowledge of the absolute amount of water added to the test sample. Therefore, this same method can be used to correct for different amounts of water contained in samples taken from gas and liquid phases of the compound under study. The liquid and gas phases of the same sample often contain different amounts of water. Although the spectral resolution of the spectrophotometer (0.125 cm^{-1}) is not adequate for accurate quantitative determination of H₂O, the comparative measurements of the samples contaminated with small amounts of water performed at equal pressures can provide a reasonable rough estimation of such impurities. As an added check, both the original and test samples were analyzed by GC with thermal conductivity detection to determine the water impurity levels. The results from both techniques were consistent and indicated that the water impurity levels were \sim 4%, 1.9%, and 1.6% in the samples of CH₂FCH₂OH, CHF₂CH₂OH, and CF₃CH₂OH, respectively, used in the IR measurements.

The IR absorption spectra of fluorinated ethanols were measured by Sellevag et al.⁸ (all three compounds) and Rajakumar et al.²⁶ (2-fluoroethanol) to estimate global warming potentials of these compounds. Sellevag et al.⁸ reported integrated absorption intensities (in units of 10^{-17} cm/molecule) of 4.53 \pm 0.14 for CH_2FCH_2OH measured between 460 and 1600 cm⁻¹ 6.2 ± 0.17 for CHF₂CH₂OH measured between 700 and 1550 cm⁻¹, and 13.73 \pm 0.18 for CF₃CH₂OH measured between 610 and 1600 cm⁻¹. The absorption spectra obtained in the present work and integrated over the same spectral intervals give 4.69, 8.39, and 14.5, respectively, in units of 10^{-17} cm/molecule, with an estimated uncertainty of ~2%. Thus, there is reasonable agreement between the integrated intensities for CH₂FCH₂OH (3.5%) and CF₃CH₂OH (5.6%) and a significant difference in the case of CHF₂CH₂OH, with our value being \sim 35% larger. The IR absorption spectra of 2-fluoroethanol and 2,2,2-trifluoroethanol are also available from the Pacific Northwest National Laboratory (PNNL) database.⁴ The integrated absorption intensities measured in this study coincide with those from the PNNL database to better than 1% for CF₃CH₂OH (610-1600 cm⁻¹) and CH₂FCH₂OH $(700-1600 \text{ cm}^{-1})$. The integrated band intensity of CH₂FCH₂OH (between 700 and 1600 cm⁻¹) measured by Rajakumar et al.²⁶ is \sim 18% smaller. Neither PNNL nor Rajakumar et al.²⁶ recorded a longer-wavelength band of CH₂FCH₂OH near 515 cm⁻¹ because a cold MCT detector was used in both laboratories. One can notice that the integrated intensity over the spectral range of climatic interest around 1000 cm⁻¹ (10 μ m)

increases by a factor of \sim 1.7 with each additional F atom. Note that 2-fluoroethanol (CH₂FCH₂OH) has relatively low absorption in this spectral region, which is only about 50% larger than for nonsubstituted ethanol in this range.⁴⁶

4. ATMOSPHERIC IMPLICATIONS

The atmospheric lifetimes of (fluorinated) ethanols, $CH_{3,i}F_iCH_2OH$, due to their reactions with tropospheric hydroxyl radicals, τ_i^{OH} , can be estimated by using a simple scaling procedure that is based on the results of field measurements⁴⁷ and thorough atmospheric modeling³⁷

$$\tau_i^{OH} = \frac{k_{MCF}(272)}{k_i(272)} \tau_{MCF}^{OH}$$
(13)

where τ_i^{OH} and τ_{MCF}^{OH} are the lifetimes of the compound under study and methyl chloroform, respectively, due to reactions with hydroxyl radicals in the troposphere only and $k_i(272 \text{ K})$ and $k_{\text{MCF}}(272 \text{ K}) = 6.14 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ are the rate constants for the reactions of OH^{\bullet} with these substances at T =272 K given by eqs 3, 7, 6, and 5 and in ref 48 respectively. The value of τ_{MCF}^{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 4.0, 16, 62, and 171 days for ethanol, 2-fluoroethanol, 2,2-difluoroethanol, and 2,2,2-trifluoroethanol, 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. These lifetimes can be further shortened if wet deposition plays a significant role as the atmospheric removal process for these compounds. The use of eq 13 is applicable 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.^{49,50} For such species, eq 13 provides only rough estimates of the tropospheric lifetimes with respect to reaction with OH[•]. Nevertheless, the results of more detailed modeling studies demonstrate that such an estimation procedure gives reasonable average values^{49,50} and provides a useful scaling of the lifetimes of short-lived compounds. UV photolysis cannot affect the lifetimes of either the fluorinated ethanols or ethanol even in the case of stratospheric emission of these compounds.

We can make simplified estimations of the global warming potentials of fluorinated ethanols by combining their estimated atmospheric lifetimes, measured IR absorption spectra, and the measured spectrum of Earth's outgoing radiation.⁵¹⁻⁵³ This estimation procedure was described in our earlier articles and yielded results that compared favorably with other simplified estimations and with more rigorous atmospheric model calculations of GWPs.^{35,53} We calculate GWPs in two steps. First, we calculate a halocarbon global warming potential (HGWP) using CFC-11 ($CFCl_3$) as a relative compound with no other modeling data being used at this stage. Second, we use the GWP of CFC-11 relative to CO₂ obtained from rigorous radiative transfer modeling¹ to calculate the GWPs of our compounds relative to CO₂. Table 3 presents the results of these GWP estimations for time horizons of 20, 100, and 500 years. Note that the absorption of Earth's outgoing IR radiation that leads to greenhouse warming of the atmosphere takes place at higher altitudes where

		C			
molecule	atmospheric lifetime (days)	20 years	100 years	500 years	ref
CH ₂ FCH ₂ OH	16	12.5	3.6	1.1	this work <i>a,b</i>
	\sim 14	~ 8	~ 2	~ 1	26 ^{<i>a,c</i>}
	20	3	0.89	0.28	8^d
CHF ₂ CH ₂ OH	62	70	20	6.0	this work <i>a,b</i>
	40	6.03	1.79	0.56	8^d
CF ₃ CH ₂ OH	171	217	62	19	this work <i>a,b</i>
	117	61.4	18.3	5.67	8^d

Table 5. Autospheric Litetimes of Fluorinated Ethanois Due to Reactions with OH and Their Direct Gwr	Table 3.	Atmospheric	Lifetimes of	Fluorinated	d Ethanols	Due to]	Reactions w	vith OH [•]	' and Their	Direct GWPs
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^{*a*} Atmospheric lifetime and GWP calculated under the assumption of a uniform compound distribution in the atmosphere. ^{*b*} Atmospheric lifetime calculated by the method of Spivakovsky et al.³⁷ ^{*c*} Atmospheric lifetime estimated by assuming a diurnally averaged OH[•] radical concentration of 1×10^6 molecule/cm³. ^{*d*} Yearly average atmospheric lifetime and GWP calculated using three-dimensional chemical-transfer and radiative-transfer modeling with midlatitude (Europe and North America) emission scenario.

the air is noticeably colder than the underlying ground. All three fluorinated ethanols have very short atmospheric lifetimes, and therefore, they are not uniformly well-mixed through the troposphere if emitted into the atmosphere from the ground. Their convectional transport to the upper troposphere is comparable to their chemical removal in reactions with OH[•] radicals. This diminishes the thermal impact of such short-lived compounds and the above-calculated GWPs should be considered as upper limits for the majority of emission locations, except for the tropical regions, where extremely fast upwelling can take place.

All of the reported results on the estimated atmospheric lifetimes and GWPs of fluorinated ethanols are listed in Table 3. Unfortunately, we cannot directly compare our estimates of GWPs with those presented by Rajakumar et al.²⁶ and Sellevag et al.8 because different input data and different estimation techniques were used. Rajakumar et al.²⁶ used a lifetime of 2 weeks and calculated GWPs of CH₂FCH₂OH under the assumption of a well-mixed atmosphere to be ~ 8 , ~ 2 , and ~ 1 for the same time horizons of 20, 100, and 500 years, respectively. In a previous work,³⁵ we estimated GWPs for CH₂=CFCF₃ in good agreement with those reported by the same research group⁵⁴ using very similar input data. Therefore, we suggest that any difference in GWPs for CH₂FCH₂OH is due to different input data (estimated lifetimes and IR intensities). Sellevag et al.8 employed a three-dimensional chemistry transport model to make more rigorous calculations of atmospheric lifetimes and GWPs for all three fluorinated ethanols without assuming uniform distribution throughout the troposphere. They reported values of 20, 40, and 117 days for the lifetimes for CH₂FCH₂OH, CHF₂CH₂OH, and CF₃CH₂OH, respectively, using their measured room-temperature rate constants, which are \sim 50%, 70%, and 30% larger than the corresponding values obtained in our study. Their reported lifetimes for CHF₂CH₂OH and CF₃CH₂OH are in reasonable agreement with our estimations when corrected for the rate constant differences. Their calculated lifetime for CH_2FCH_2OH is longer despite the ~50% larger OH[•] reaction rate constant used. This difference might be due to the emission scenario (midlatitude emission only) that was used to model the atmospheric fate of this very short-lived compound. Their calculated GWPs are substantially smaller than those estimated under the assumption of a uniform atmospheric distribution of a compound in both the present work and that of Rajakumar et al.,²⁶ which is reasonable because of both nonuniform altitudinal distribution of these very short-lived substances in the

atmosphere and the modeled emission scenario (midlatitude emission). Thus, the difference is as large as a factor of ~ 2.5 for the longer-lived CF₃CH₂OH, increasing to a factor of ~ 5 for the shorter-lived CHF₂CH₂OH (after scaling for the difference in OH[•] reaction rate constants and IR absorption intensities). Surprisingly, this difference becomes smaller (a factor of only ~ 2.5) for the shortest-lived compound, CH₂FCH₂OH.

ASSOCIATED CONTENT

Supporting Information. UV absorption cross sections of all four compounds and IR absorption absorption cross sections of fluorinated compounds This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*E-mail: vladimir.orkin@nist.gov.

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