Rate Coefficient Measurements and Theoretical Analysis of the OH + (E)-CF₃CH=CHCF₃ ReactionMunkhbayar Baasandorj,^{†,‡,§,¶} Paul Marshall,[§] Robert L. Waterland,^{||,&} A.R. Ravishankara,^{†,§,¶} and James B. Burkholder^{*,†,¶}[†]Earth System Research Laboratory, Chemical Sciences Division, National Oceanic and Atmospheric Administration, 325 Broadway, Boulder, Colorado 80305-3328, United States[‡]Cooperative Institute for Research in Environmental Sciences, University of Colorado, Boulder, Colorado 80309, United States[§]Department of Chemistry, University of North Texas, P.O. Box 305070, Denton, Texas 76203-5070, United States^{||}DuPont Central R&D, Wilmington, Delaware 19880, United States

S Supporting Information

ABSTRACT: Rate coefficients, k , for the gas-phase reaction of the OH radical with (E)-CF₃CH=CHCF₃ ((E)-1,1,1,4,4,4-hexafluoro-2-butene, HFO-1336mzz(E)) were measured over a range of temperatures (211–374 K) and bath gas pressures (20–300 Torr; He, N₂) using a pulsed laser photolysis–laser-induced fluorescence (PLP–LIF) technique. $k_1(T)$ was independent of pressure over this range of conditions with $k_1(296\text{ K}) = (1.31 \pm 0.15) \times 10^{-13}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$ and $k_1(T) = (6.94 \pm 0.80) \times 10^{-13}\text{ exp}[-(496 \pm 10)/T]\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$, where the uncertainties are 2σ , and the pre-exponential term includes estimated systematic error. Rate coefficients for the OD reaction were also determined over a range of temperatures (262–374 K) at 100 Torr (He). The OD rate coefficients were $\sim 15\%$ greater than the OH values and showed similar temperature dependent behavior with $k_2(T) = (7.52 \pm 0.44) \times 10^{-13}\text{ exp}[-(476 \pm 20)/T]$ and $k_2(296\text{ K}) = (1.53 \pm 0.15) \times 10^{-13}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$. The rate coefficients for reaction 1 were also measured using a relative rate technique between 296 and 375 K with $k_1(296\text{ K})$ measured to be $(1.22 \pm 0.1) \times 10^{-13}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$, in agreement with the PLP–LIF results. In addition, the 296 K rate coefficient for the O₃ + (E)-CF₃CH=CHCF₃ reaction was determined to be $< 5.2 \times 10^{-22}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$. A theoretical computational analysis is presented to interpret the observed positive temperature dependence for the addition reaction and the significant decrease in OH reactivity compared to the (Z)-CF₃CH=CHCF₃ stereoisomer reaction. The estimated atmospheric lifetime of (E)-CF₃CH=CHCF₃, due to loss by reaction with OH, is estimated to be ~ 90 days, while the actual lifetime will depend on the location and season of its emission. Infrared absorption spectra of (E)-CF₃CH=CHCF₃ were measured and used to estimate the 100 year time horizon global warming potentials (GWP) of 32 (atmospherically well-mixed) and 14 (lifetime-adjusted).

1. INTRODUCTION

Due to the relevance to atmospheric chemistry and climate change, the OH reactivity of unsaturated hydrofluorocarbon compounds (hydrofluoroolefins, HFOs), which are being considered as replacements for ozone depleting substances and potent greenhouse gases, has been the subject of numerous recent laboratory studies, some from this laboratory^{1–5} (see Burkholder et al.⁶ for an evaluation of the HFO studies), and assessments.^{7,8} Although the kinetic database for this class of compound is not complete, it is apparent that differences in the stereoisomer reactivity with the OH radical can be significant⁶ and lead to differences in atmospheric lifetimes and, thus, environmental impacts. OH radical reactivity is of particular interest for HFOs, because it represents the predominant atmospheric removal process for HFOs via the addition of the OH radical to the carbon–carbon double bond of the molecule. It will also be of interest to fundamental kinetics to evaluate whether stereoisomers could have different reactivities.

Further experimental studies are needed to develop the theoretical and empirical methods, e.g., structure activity relationships (SARs), that adequately describe trends in HFO reactivity and the dependence on molecular structure. In this study, rate coefficients, $k_1(T)$, for reaction 1 were measured as a function of temperature (211–374 K) and pressure (20–300 Torr, He, and 20–200 Torr, N₂) using a pulsed laser photolysis–laser-induced fluorescence (PLP–LIF) technique and a relative rate technique between 296 and 375 K at 100–300 Torr (He).

This study builds on our previous laboratory study of the OH + (Z)-CF₃CH=CHCF₃ reaction rate coefficient² and was designed to investigate the factors most critical in defining the

Received: March 22, 2018

Revised: April 21, 2018

Published: April 25, 2018

OH reactivity of HFO stereoisomers. Rate coefficients, $k_2(T)$, for the OD reaction were also included as part of this study.

The OH reaction rate coefficients for the $\text{CF}_3\text{CH=CHCF}_3$ stereoisomers were found to be significantly different in both absolute magnitude and the sign of the temperature dependence, i.e., [reaction 1](#) displays a positive temperature dependence, while the $(Z)\text{-CF}_3\text{CH=CHCF}_3$ reaction was previously shown to have a slight non-Arrhenius behavior with a weak negative temperature dependence below 296 K. Computational analysis has been employed in this work to explore the physical basis for the differences in reactivity. Infrared and UV absorption spectra of $(E)\text{-CF}_3\text{CH=CHCF}_3$ were also measured as part of this work, and global warming potentials are presented from calculations based on the measured infrared spectrum. In addition, the rate coefficient for the $(E)\text{-CF}_3\text{CH=CHCF}_3$ reaction with ozone is reported. During the course of our study, Østerstrom et al.⁹ reported a room temperature (296 K) relative rate study of [reactions 1](#) and [2](#), which will be compared with the present results.

2. EXPERIMENTAL METHODS

Rate coefficients for [reaction 1](#) were measured as a function of temperature (211–374 K) and pressure (20–300 Torr) using a pulsed laser photolysis (PLP)–laser-induced fluorescence (LIF) technique. The temperature range included in this study enables a direct experimental determination of the OH reactivity at temperatures relevant to the upper troposphere–lower stratosphere and a reliable determination of the reaction activation energy. The PLP–LIF apparatus has been used previously in our laboratory,^{5,10} and the details relevant to the present study are described briefly here. The rate coefficient for [reaction 1](#) was also determined using a relative rate (RR) technique at temperatures between 296 and 375 K at 100 Torr (He), which is described separately below.⁵ UV and infrared absorption cross section measurements for $(E)\text{-CF}_3\text{CH=CHCF}_3$ are also presented.

2.1. Pulsed Laser Photolysis–Laser-Induced Fluorescence Apparatus. A 150 cm³ Pyrex LIF temperature jacketed reactor was used in this study. The reactor temperature was controlled by circulating fluid from a temperature-regulated reservoir, and the gas temperature in the reaction zone (the intersection of the photolysis and probe laser beams) was measured with a retractable thermocouple to within ± 1 K.

Rate coefficients were measured under pseudo first-order conditions in OH, $[\text{HFC}] \gg [\text{OH}]$, with OH radicals produced via the 248 nm (KrF excimer laser) pulsed laser photolysis of H_2O_2 (hydrogen peroxide) or $(\text{CH}_3)_3\text{COOH}$ (t-butyl hydrogen peroxide)

where the OH quantum yield for [reaction 3](#) is 2⁶ and unity for [reaction 4](#).¹¹ H_2O_2 photolysis was used for kinetic measurements at temperatures >250 K. $(\text{CH}_3)_3\text{COOH}$ photolysis was used over the temperature range 211 to 298 K. The initial OH radical concentration, $[\text{OH}]_0$, was estimated from the precursor concentration, its absorption cross section at 248 nm, and the photolysis laser power measured at the exit of the LIF reactor with a calibrated power meter. The photolysis laser fluence was varied between 3 and 17 mJ

cm^{−2} pulse^{−1} over the course of our study. The concentrations of H_2O_2 and $(\text{CH}_3)_3\text{COOH}$ in the LIF reactor were estimated from the pseudo first-order rate coefficients measured in the absence of $(E)\text{-CF}_3\text{CH=CHCF}_3$, as described later.

OD radicals were produced using 248 nm pulsed laser photolysis of O_3 ($[\text{O}_3] \approx 4 \times 10^{12}$ molecules cm^{−3}) in a He bath gas to produce $\text{O}(^1\text{D})$ followed by its reaction with D_2O ($[\text{D}_2\text{O}] \approx 3 \times 10^{16}$ molecules cm^{−3}).

The D_2O concentration was sufficient to remove 99% of the $\text{O}(^1\text{D})$ within 1 μs after the photolysis pulse and quench vibrationally excited OD that was produced.

OH radical fluorescence was detected following pulsed laser excitation in the $\text{A}^2\Sigma^+(\nu=1) \leftarrow \text{X}^2\Pi(\nu=0)$ transition near 282 nm using the frequency doubled output from a Nd:YAG pumped dye laser. OD fluorescence was detected following excitation near 287.6 nm. The probe laser beam propagated through the LIF reactor at a right angle to the larger diameter photolysis laser beam. The photolysis and probe beams intersected in the middle of the reactor. Fluorescence from the reaction zone was detected by a photomultiplier tube (PMT) orthogonal to the plane of the photolysis and probe laser beams. A band-pass filter (308 nm, fwhm = 10 nm) mounted in front of the PMT was used to isolate the OH fluorescence in the $\text{A}^2\Sigma^+(\nu=0) \rightarrow \text{X}^2\Pi(\nu=0)$ transition. The PMT signal was averaged for 100 laser shots with a gated charge integrator. OH temporal profiles were measured by varying the delay between the photolysis and the probe lasers (i.e., the reaction time) between 10 μs –20 ms. Both the photolysis and probe lasers were operated at 10 Hz.

OH temporal profiles followed the integrated first-order rate expression

$$\ln\left(\frac{[\text{OH}]_t}{[\text{OH}]_0}\right) = \ln\left(\frac{S_t}{S_0}\right) = -(k_1[(E)\text{-CF}_3\text{CH=CHCF}_3] + k_d)t = -k't \quad (1)$$

where S_t is the measured OH signal at time t , which is proportional to $[\text{OH}]_t$, $[(E)\text{-CF}_3\text{CH=CHCF}_3]$ is the $(E)\text{-CF}_3\text{CH=CHCF}_3$ concentration in the LIF reactor, and k' and k_d are the first-order rate coefficients for loss of OH in the presence and absence of $(E)\text{-CF}_3\text{CH=CHCF}_3$, respectively. k' values were obtained from a nonlinear least-squares fit of S_t versus time. k_d represents the loss of OH due to its reaction with the OH precursor and diffusion out of the detection volume. k_d values depended on the OH radical precursor and its concentration and were in the 50–500 s^{−1} range. OH temporal profiles were measured over a range of HFO concentrations at each temperature and pressure. Rate coefficients, $k_1(T)$, were determined from a linear least-squares fit of k' versus $[(E)\text{-CF}_3\text{CH=CHCF}_3]$ weighted by the measurement precision. k_d values measured in the absence of the reactant and obtained from the [eq 1](#) fit agreed to within 5%.

2.2. Relative Rate Measurements. In the relative rate (RR) method, the loss of the reactant compound, HFO, was measured relative to the loss of a reference compound that has a well-established rate coefficient. Provided the reactant and reference compounds are lost solely via the OH reaction the rate coefficients for the two reactions are related by

$$\ln\left(\frac{[(E)\text{-CF}_3\text{CH=CHCF}_3]_0}{[(E)\text{-CF}_3\text{CH=CHCF}_3]_t}\right) = \frac{k_E}{k_{\text{ref}}}\ln\left(\frac{[\text{ref}]_0}{[\text{ref}]_t}\right) \quad (11)$$

where $[(E)\text{-CF}_3\text{CH=CHCF}_3]_0$, $[(E)\text{-CF}_3\text{CH=CHCF}_3]_t$, $[\text{ref}]_0$, and $[\text{ref}]_t$ are the initial reactant and reference concentrations at time zero and the concentrations following reaction at the time t . k_E and k_{ref} are the rate coefficients for the $(E)\text{-CF}_3\text{CH=CHCF}_3$ and reference reaction with OH, respectively. C_2H_6 was used as the reference compound where $k(T) = 7.66 \times 10^{-12} \exp(-1020/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for the $\text{OH} + \text{C}_2\text{H}_6$ reaction with NASA/JPL defined uncertainty parameters of $f(298 \text{ K}) = 1.07$ and $g = 50$.⁶ Several experiments were performed using $\text{CH}_3\text{CH}_2\text{Cl}$ as the reference compound; however, deviations from eq II, which we attribute to secondary Cl-atom chemistry, were observed and particularly noticeable at higher extent of reaction.¹² Results using $\text{CH}_3\text{CH}_2\text{Cl}$ as the reference compound were not included in the final analysis.

The apparatus used for the relative rate measurements has been described elsewhere.⁵ Basically, the apparatus consists of a 100 cm long reaction cell (5 cm i.d.) coupled to a Fourier transform infrared spectrometer (FTIR) for monitoring the loss of reactants. OH radicals were produced via 248 nm pulsed laser photolysis of O_3 in a He bath gas and an excess of H_2O (>10 Torr) to produce $\text{O}(^1\text{D})$ followed by its reaction with H_2O .

Experiments were performed by first filling the reactor with $(E)\text{-CF}_3\text{CH=CHCF}_3$, C_2H_6 , H_2O vapor, and ~ 100 Torr of He bath gas. The gases were thoroughly mixed using a Teflon diaphragm circulation pump, and the initial infrared spectrum was recorded. Ozone was then slowly added to the circulating gas mixture, while the photolysis beam was passed along the length of the reactor. The residence time of the gas in the reaction cell was ~ 6 s. The steady-state concentration of O_3 was estimated to be $\sim 1 \times 10^{14} \text{ molecules cm}^{-3}$.

The loss of the reactant and the reference compounds were measured by infrared absorption, while the gas mixture was circulated between the reactor and the infrared absorption cell. Infrared spectra were recorded at a spectral resolution of 1 cm^{-1} between 500 and 4000 cm^{-1} in 20 coadditions. The loss of C_2H_6 was determined by monitoring the change in the absorption band near 820 cm^{-1} , while the loss of $(E)\text{-CF}_3\text{CH=CHCF}_3$ was monitored using the absorption band near 1320 cm^{-1} . Dark experiments performed under conditions identical to those used in the RR experiments, but without the photolysis laser beam, showed no observable change, $<0.5\%$, in the measured infrared spectra of the reactant compounds over a period of ~ 2 h.

The photolysis laser fluence was in the $12\text{--}26 \text{ mJ cm}^{-2} \text{ pulse}^{-1}$ range over the course of the study. The initial $(E)\text{-CF}_3\text{CH=CHCF}_3$ and C_2H_6 concentrations were in the range of $(3\text{--}8) \times 10^{14}$ and $(3\text{--}10) \times 10^{15} \text{ molecules cm}^{-3}$, respectively. Several experiments were performed with ~ 2 Torr of O_2 added to the reaction mixture and found to agree with experiments with no O_2 added to within the measurement precision, with agreement to within 5%, or better.

2.3. O_3 Rate Coefficient. Room temperature rate coefficients for the reaction of O_3 with $(E)\text{-CF}_3\text{CH=CHCF}_3$ were measured under static conditions at 100–250 Torr (He) using infrared absorption to monitor the loss of reactant in the presence of excess O_3 . Reaction rate coefficients were measured under pseudo first-order conditions in $(E)\text{-CF}_3\text{CH=CHCF}_3$, $[\text{O}_3] \gg [(E)\text{-CF}_3\text{CH=CHCF}_3]$. Experiments were performed using the same setup used in the relative rate measurements

described above. Experiments were also performed using the multipass infrared absorption cell as the reactor, i.e., without circulation of the gases. The O_3 concentration was in the range of $(1.9\text{--}8.6) \times 10^{16} \text{ molecules cm}^{-3}$ and was quantified using its infrared absorption band near 2100 cm^{-1} ($1.36 \times 10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$).^{13,14} The $(E)\text{-CF}_3\text{CH=CHCF}_3$ concentration was in the range of $(3.9\text{--}7.5) \times 10^{14} \text{ molecules cm}^{-3}$ and $[\text{O}_2]$, when added, was in the range of $(0.5\text{--}10) \times 10^{16} \text{ molecules cm}^{-3}$. Rate coefficients were obtained from a linear least-squares fit of k' versus $[\text{O}_3]$.

2.4. UV and Infrared Absorption Measurements. UV and infrared absorption cross sections of $(E)\text{-CF}_3\text{CH=CHCF}_3$ were determined in this work for use in monitoring the $[(E)\text{-CF}_3\text{CH=CHCF}_3]$ online in the PLP–LIF kinetic measurements and for the determination of their global warming potentials. Absorption cross sections were determined at room temperature, 296 K, using absolute pressure measurements under static conditions with manometrically prepared mixtures of $(E)\text{-CF}_3\text{CH=CHCF}_3$ (0.01 and 9% in a He bath gas).

UV (184.9 nm) absorption was measured using a Hg pen-ray lamp light source, a 100 cm long absorption cell, and a 185 nm band-pass filter mounted in front of a solar-blind photodiode detector. Absorption cross sections were determined from measurements made over a range of $(E)\text{-CF}_3\text{CH=CHCF}_3$ concentrations using Beer's Law

$$A = -\ln\left(\frac{I}{I_0}\right) = \sigma L[(E)\text{-CF}_3\text{CH=CHCF}_3] \quad (\text{III})$$

where I and I_0 are the transmitted intensity through the cell with and without $(E)\text{-CF}_3\text{CH=CHCF}_3$, respectively, σ is the $(E)\text{-CF}_3\text{CH=CHCF}_3$ absorption cross section at 184.9 nm, and L is the path length of the cell. A range of $(E)\text{-CF}_3\text{CH=CHCF}_3$ concentrations, $(7.35\text{--}27.5) \times 10^{16} \text{ molecules cm}^{-3}$, were used. The absorbance, A , obeyed eq III, and a linear least-squares analysis of A versus $[(E)\text{-CF}_3\text{CH=CHCF}_3]$ yielded the absorption cross section of $(5.72 \pm 0.04) \times 10^{-20} \text{ cm}^2 \text{ molecule}^{-1}$, where the quoted uncertainties are the fit precision. Absorption cross sections obtained using independently prepared sample mixtures were identical to within the precision of the measurement.

Infrared absorption spectra were recorded using a FTIR equipped with a low-volume multipass absorption cell (500 cm^3 , 485 cm optical path length) and an HgCdTe detector. Spectra were measured between 500 and 4000 cm^{-1} with a spectral resolution of 1 cm^{-1} . During the PLP–LIF kinetic experiments, infrared absorption measurements were made either before or after the LIF reactor. The $(E)\text{-CF}_3\text{CH=CHCF}_3$ concentration determined from the UV and infrared absorption measurements was scaled to account for the differences in pressure and temperature between the absorption cells and the LIF reactor to obtain its concentration in the LIF reactor.

2.5. Materials. He (UHP, 99.999%), N_2 (UHP, 99.99%), N_2 (UHP, < 0.5 ppm of O_2), O_2 (UHP, 99.99%), and $(\text{CH}_3)_3\text{COOH}$ (70 wt % in H_2O) were used as supplied. Concentrated H_2O_2 ($>95\%$) was prepared by bubbling N_2 through a sample that was initially $\sim 60\%$ mole fraction. H_2O_2 and $(\text{CH}_3)_3\text{COOH}$ were introduced into the gas flow by passing a small flow of He through a bubbler containing the liquid samples. H_2O_2 and $(\text{CH}_3)_3\text{COOH}$ were added to the main gas flow just prior to entering the LIF reactor. O_3 was

Table 1. Summary of Experimental Conditions and Rate Coefficients Obtained in This Work for the OH + (E)-CF₃CH=CHCF₃ reaction, $k_1(T)$

T (K)	P (Torr)	bath gas	[O ₂] (10 ¹⁶ molecules cm ⁻³)	ν (cm s ⁻¹)	laser fluence (mJ cm ⁻² pulse ⁻¹)	[precursor] (10 ¹⁴ molecules cm ⁻³)	[OH] ^a (10 ¹¹ molecules cm ⁻³)	[(E)-CF ₃ CH=CHCF ₃] (10 ¹⁵ molecules cm ⁻³)	k_1^c (10 ⁻¹³ cm ³ molecule ⁻¹ s ⁻¹)
211	200	He	—	6.1	8.0	0.60	0.12 ^a	2.54–28.8	0.679 ± 0.01
211	200	He	4.50	6.1	8.0	0.60	0.12 ^a	2.21–29.0	0.673 ± 0.01
219	200	He	—	6.2	8.1	1.05	0.21 ^a	1.59–22.2	$k_1(211\text{ K}) = 0.668 \pm 0.01^d$
219	200	He	4.37	6.2	8.1	0.75	0.15 ^a	2.50–28.8	0.741 ± 0.01
220	200	N ₂	—	6.6	7.6	0.62	0.12 ^a	2.60–19.0	0.730 ± 0.01
240	200	He	—	6.5	6.54	1.24	0.20 ^a	1.88–48.0	0.725 ± 0.02
240	200	He	4.15	6.5	6.54	1.24	0.20 ^a	1.21–36.9	$k_1(220\text{ K}) = 0.726 \pm 0.01^d$
253	100	He	—	6.8	9.7	0.47	1.86 ^b	1.60–95.4	0.877 ± 0.01
252	100	N ₂	—	6.3	8.0	0.59	1.90 ^b	0.95–65.7	0.878 ± 0.01
252	100	N ₂	4.65	6.3	8.0	0.59	1.90 ^b	1.30–68.0	0.940 ± 0.01
270	100	He	—	7.1	8.8	0.49	1.60 ^b	2.92–70.4	0.962 ± 0.01
296	20	He	—	20.6	4.0	1.43	2.56 ^b	1.02–38.0	$k_1(252\text{ K}) = 0.962 \pm 0.01^d$
296	52	He	—	8.6	4.8	1.25	2.00 ^b	0.98–67.0	1.11 ± 0.01
296	54	He	3.4	8.4	4.8	1.25	2.00 ^b	9.00–74.2	$k_1(270\text{ K}) = 1.11 \pm 0.01^d$
296	100	He	—	10	9.7	0.45	1.76 ^b	0.65–47.0	1.32 ± 0.02
296	200	He	—	8.1	6.5	1.54	0.25 ^a	4.09–40.8	1.31 ± 0.02
296	300	He	—	7.8	5.3	0.31	0.66 ^b	3.43–40.4	1.31 ± 0.02
297	25	N ₂	—	6.7	5.5	0.45	0.57 ^b	1.49–47.6	1.29 ± 0.01
296	200	N ₂	—	7.4	5.5	0.46	0.57 ^b	2.20–71.0	1.29 ± 0.01
296	200	N ₂	4.39	7.4	5.5	0.46	0.57 ^b	0.17–2.10	1.32 ± 0.02
319	100	He	—	7.7	15.9	0.49	1.77 ^b	2.33–55.5	1.31 ± 0.02
341	100	He	—	7	3.8	0.55	0.48 ^b	1.44–51.0	$k_1(296\text{ K}) = 1.31 \pm 0.01^d$
357	100	He	—	7.9	15.9	0.52	1.87 ^b	1.80–45.3	1.47 ± 0.01
374	100	He	—	10	4.4	0.65	0.65 ^b	0.81–48.8	1.60 ± 0.06
374	100	N ₂	3.76	9.8	14.3	0.43	1.29 ^b	0.80–46.0	1.73 ± 0.02
374	100	N ₂	—	9.8	14.3	0.43	1.29 ^b	0.80–46.0	1.82 ± 0.05
									1.88 ± 0.04
									1.84 ± 0.05
									$k_1(373\text{ K}) = 1.84 \pm 0.03^d$

^a*t*-C₄H₉OOH was used as the OH precursor. ^bH₂O₂ was used as the OH source. ^cThe quoted uncertainties are the 2σ precision from the linear least-squares fit of k' versus [(E)-CF₃CH=CHCF₃]. ^dDetermined from a weighted linear least-squares fit to all ($k' - k_d$) versus [(E)-CF₃CH=CHCF₃].

stored in a 195 K silica gel trap and swept into the reactor by passing a He bath gas flow through the trap.

The (*E*)-CF₃CH=CHCF₃ (99.95% purity) sample was degassed in several freeze–pump–thaw cycles before use. Quoted sample impurities for (*E*)-CF₃CH=CHCF₃ included (*Z*)-CF₃CH=CHCF₃ (0.04 wt %) and HCFC-122 (CHCl₂CClF₂) (0.01 wt %). Mixtures of the samples in a He bath gas were prepared manometrically in 12 L Pyrex bulbs. Mixing ratios in the range of 10–35% were used during the course of the experiments. The bulb content was monitored using infrared absorption and found to be stable to within ~1% over the duration of our study.

Gas flows were measured with calibrated mass flow meters, and pressures were measured using capacitance manometers. The gas flow velocity in the PLP–LIF experiments was in the range of 6–20 cm s^{−1} ensuring a fresh sample of gas in the LIF reaction volume for each photolysis pulse. Uncertainties quoted herein are 2σ unless noted otherwise.

3. RESULTS AND DISCUSSION

3.1. OH Reaction Rate Coefficients Obtained Using PLP–LIF. Rate coefficients for reaction 1 were measured over the temperature range of 211–374 K at pressures between 20 and 300 Torr (He, N₂). A summary of the experimental conditions and the rate coefficients obtained is given in Table 1. The reaction was found to be independent of pressure to within the precision of the measurements at all temperatures included in this study. Representative measured OH decay profiles are provided in Figure S1 of the Supporting Information. The OH decay profiles followed pseudo-first-order kinetics, i.e., single exponential decays, under all experimental conditions.

Figure 1 shows the second-order plots for reaction 1 obtained at 296 K and the temperature extremes, 211 and 374 K, included in this study. The obtained (*k*' − *k*_d) values varied

Figure 1. Pseudo first-order rate coefficient data for the reaction of OH with (*E*)-CF₃CH=CHCF₃ obtained in this work at 296 K and the temperature extremes included in this study. Error bars on the individual data points are suppressed for clarity. The precision in (*k*' − *k*_d) is 100 s^{−1}, or less, and the absolute uncertainty in [(*E*)-CF₃CH=CHCF₃] is ~5% (see text). The lines are linear least-square fits of the data to eq 1. A summary of the experimental results is given in Table 1.

linearly with the (*E*)-CF₃CH=CHCF₃ concentration over the entire range of concentrations employed and with changes in various experimental parameters such as [OH]₀, photolysis laser fluence, OH radical precursor, and linear gas flow velocity as outlined in Table 1. The measured rate coefficients were independent of O₂ addition to the reaction mixture. In the final analysis, *k*₁(*T*) was obtained from a weighted linear least-squares fit (eq 1), including all data obtained at a given temperature. The fits shown in Figure 1 reproduce the experimental data very well with *k*₁(296 K) = (1.31 ± 0.01) × 10^{−13} cm³ molecule^{−1} s^{−1}, where the quoted uncertainty is the linear least-squares fit precision.

Figure 2 shows the temperature dependence of the measured rate coefficients for reaction 1. *k*₁(*T*) has a positive temperature

Figure 2. Rate coefficient temperature dependence for the OH (filled circles and triangles) and OD (open circles) reaction with (*E*)-CF₃CH=CHCF₃ measured in this work using the pulsed laser photolysis–laser-induced fluorescence (PLP–LIF) and relative rate (RR) (green squares) techniques. The different colored symbols represent experiments performed in He (blue), N₂ (red), and with O₂ added (solid triangles). The solid and dashed lines are least-squares Arrhenius expression fits to the data. The gray shaded region represents the estimated range of absolute uncertainty for reaction 1. The Arrhenius expression for the OH + (*Z*)-CF₃CH=CHCF₃ reaction taken from Baasandorj et al.² is included for comparison (dotted line).

dependence over the entire temperature range, 211–374 K, that is described by the Arrhenius expression *k*₁(*T*) = (6.94 ± 0.24) × 10^{−13} exp[−(496 ± 10)/*T*] cm³ molecule^{−1} s^{−1}, where the quoted uncertainties are the fit precision.

In a relative rate study, Østerstrom et al.⁹ reported *k*₁(296 K) to be (1.72 ± 0.42) × 10^{−13} cm³ molecule^{−1} s^{−1}, which is ~30% greater than the present PLP–LIF and RR results. Their value does, however, agree with our value within the combined uncertainties of the two studies.

3.1.1. OD + (E)-CF₃CH=CHF. The OD + (E)-CF₃CH=CHCF₃ reaction rate coefficients, $k_2(T)$, were measured over the temperature range 262–374 K. A summary of the experimental conditions and rate coefficients obtained in these experiments is given in Table 2. The OD temporal profiles followed pseudo first-order kinetics under all experimental conditions. Combining all of the measurements obtained at 296 K yielded $k_2(296\text{ K}) = (1.53 \pm 0.02) \times 10^{-13}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$, where the uncertainty is the fit precision. $k_2(T)$ is systematically about 15% greater than the rate coefficients obtained for the OH reaction, which implies that the reaction mechanism is predominately controlled by radical addition to the double bond. Note that the modest increase in OD reactivity is similar to that reported for the OH/OD reactions with the HFOs CH₂=CHF and CH₂=CF₂ reported from our laboratory.¹⁵

The temperature dependence of the rate coefficient for reaction 2 is similar to that of reaction 1 with $k_2(T) = (7.52 \pm 0.44) \times 10^{-13} \exp[-(476 \pm 20)/T]\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$, where the quoted uncertainties are from the precision of the fit. The rate coefficient data for reaction 2 is included in Figure 2 for comparison with the rate coefficients obtained for the OH reactions.

Østerstrom et al.⁹ reported $k_2(296\text{ K})$ as part of their relative rate study. Their value of $5.61 \times 10^{-13}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$ is a factor of 3.7 greater than that obtained in the present study. Their reported $k_2(296\text{ K})/k_1(296\text{ K})$ ratio is 3.3, which is in poor agreement with our measured ratio of 1.17. On the basis of theoretical calculations, Østerstrom et al.⁹ interpreted the significantly enhanced OD reactivity to a reduced barrier height for the OD reaction. It is worth noting that the Østerstrom et al.⁹ study also included OH and OD radical relative rate measurements for the (Z)-CF₃CH=CHCF₃ stereoisomer. In this case, they report a $k_2(296\text{ K})/k_1(296\text{ K})$ ratio of 1.65, which is greater but much closer to the value reported in Baasandorj et al.² from our laboratory, 1.17, which was based on absolute PLP–LIF measurements. The source of the discrepancy in the OD rate coefficient results between the present work and Østerstrom et al.⁹ is presently unclear.

3.2. Relative Rate (RR) Measurements. Figure 3 shows the results obtained in the relative rate coefficient measurements for reaction 1 at 296, 315, 340, 348, and 375 K. The results are given in Table 3 and included in Figure 2 for comparison with the absolute PLP–LIF measurement results. The RR results are in agreement, to within the combined uncertainties of the measurements, with the PLP–LIF results over the entire temperature range.

3.3. O₃ Reaction Rate Coefficient. Rate coefficients for the reaction of O₃ with (E)-CF₃CH=CHCF₃ were measured at 296 K.

The experimental data are plotted in Figure S2 of the Supporting Information. The decay of the HFO in the presence of excess O₃ followed pseudo first-order kinetics, and there was no observable change, <0.5%, in the (E)-CF₃CH=CHCF₃ concentration under similar conditions in the absence of O₃. O₃ losses of ≤30% were observed over the 1 to 3 h duration of an experiment that were not due to reaction 7. An average O₃ concentration was used for the rate coefficient determination. The rate coefficient for reaction 7 was found to be independent of the O₂ concentration to within the precision of the measurements, with a value of $k_7(296\text{ K}) = (5.16 \pm 0.40) \times$

Table 2. Summary of Experimental Conditions and Rate Coefficients Obtained in This Work for the OD + (E)-CF₃CH=CHCF₃ Reaction

<i>T</i> (K)	<i>P</i> (Torr, He)	<i>ν</i> (cm s ^{−1})	photolysis laser fluence (mJ cm ^{−2} pulse ^{−1})	[O ₃] (10 ¹² molecules cm ^{−3})	[D ₂ O]/[O ₂] (10 ¹⁶ molecules cm ^{−3})	[OH] ₀ (10 ¹¹ molecules cm ^{−3})	[(E)-CF ₃ CH=CHCF ₃] (10 ¹⁵ molecules cm ^{−3})	<i>k</i> ^a (10 ^{−13} cm ³ molecule ^{−1} s ^{−1})
262	100	8.52	8.1	4.0	3.26/–	9.8	1.99–35.9	1.26 ± 0.02
262	100	8.52	8.1	4.0	3.26/3.28	9.8	1.94–31.8	1.25 ± 0.01
296	100	9.3	9.4	3.7	3.03/–	9.5	1.70–30.8	<i>k</i> (262 K) = 1.25 ± 0.01 ^b
296	100	9.5	9.4	3.6	3.03/2.9	9.2	1.37–2.8	1.53 ± 0.02
339	100	9.5	9.4	3.25	2.79/–	8.4	1.27–22.8	1.53 ± 0.03
339	100	9.5	9.4	3.25	2.79/2.67	8.4	1.33–22.6	<i>k</i> (296 K) = 1.53 ± 0.02 ^b
374	100	11.4	6.5	3.0	2.48/–	5.4	1.00–22.3	1.84 ± 0.02
374	100	11.4	6.5	3.0	2.48/–	5.4	1.20–20.7	1.83 ± 0.02
								<i>k</i> (339 K) = 1.84 ± 0.01 ^b
								2.14 ± 0.02
								2.12 ± 0.02
								<i>k</i> (374 K) = 2.13 ± 0.02 ^b

^aThe quoted uncertainties are 2σ of the measurement precision. ^bDetermined from a weighted linear least-squares fit to all (*k*′ – *k*_d) versus [(E)-CF₃CH=CHCF₃].

Figure 3. Relative rate data for the OH + (E)-CF₃CH=CHCF₃ reaction obtained in this work at 296 K (circles), 315 K (dashed red line, closely overlaps the fit of the 296 K data), 340 K (dashed green line), 348 K (dashed blue line), and 375 K (triangles). The data points obtained at 315, 340, and 348 K are omitted for clarity, while the range of the dashed line represents the range of the experimental data. Error bars on the individual data points are suppressed for clarity but are approximately ± 0.01 for both the CF₃CH=CHCF₃ and C₂H₆ measurement precision. The lines are linear least-squares fits to all the data obtained at each temperature (Table 3).

Table 3. Summary of OH + (E)-CF₃CH=CHCF₃ Relative Rate Results^a

T (K)	experiments	k_E/k_{ref}^b	k_1 (10^{-13} cm ³ molecule ⁻¹ s ⁻¹)
296	4	0.500 ± 0.04	1.22 ± 0.10
315	1	0.480 ± 0.04	1.44 ± 0.11
340	2	0.404 ± 0.03	1.54 ± 0.12
348	1	0.413 ± 0.03	1.69 ± 0.14
375	3	0.354 ± 0.03	1.77 ± 0.14

^aC₂H₆ reference compound, $k_{ref}(T) = 7.66 \times 10^{-12} \exp(-1020/T)$ cm³ molecule⁻¹ s⁻¹ for OH + CH₃CH₃.⁶ ^bValue obtained from fit of all data at the given temperature.

10^{-22} cm³ molecule⁻¹ s⁻¹, where the uncertainty is the fit precision. This measurement adequately establishes that the O₃ reaction is a minor atmospheric loss process for (E)-CF₃CH=CHCF₃ and that this reaction did not contribute to the measured OH reaction rate coefficient using the relative rate method. The reactivity of (Z)-CF₃CH=CHCF₃ was found in our previous study to also be unreactive toward O₃, $< 6 \times 10^{-21}$ cm³ molecule⁻¹ s⁻¹. Østerstrøm et al.⁹ reported a rate coefficient for reaction 7 of $(4.14 \pm 0.42) \times 10^{-22}$ cm³ molecule⁻¹ s⁻¹ at 296 ± 2 K, which is in reasonable agreement with the present result.

3.4. Uncertainty Analysis. The determinations of $k_1(T)$ and $k_2(T)$ include uncertainties in the experimental measurements as well as the determination of [(E)-CF₃CH=CHCF₃] in the LIF reactor. The precision of the measurements was high with rate coefficients measured under different experimental conditions at a given temperature agreeing to better than 2%, see Tables 1 and 2. Kinetic measurements were carried out over

a range of experimental conditions and the uncertainty in pressure ($\pm 1\%$), flow rate ($\pm 2\%$), and temperature (± 1 K) made minor contributions to the potential systematic error of the measurements.

The (E)-CF₃CH=CHCF₃ concentration was determined using online infrared and UV absorption measurements as well as measured gas flows. The three methods agreed to better than 6% under all experimental conditions including absorption measurements made before and after the LIF reactor that demonstrated no significant loss of (E)-CF₃CH=CHCF₃ in the apparatus. The uncertainty in the determination of the absorption cross sections was estimated to be $< 3\%$.

The agreement obtained between the PLP–LIF and RR rate coefficient values indicates that sample impurities did not significantly influence the absolute rate coefficient determinations, which is consistent with the sample purity analysis. The uncertainty in the relative rate measurement is primarily determined by the uncertainty in the reference compound rate coefficient. The rate coefficient for the OH + C₂H₆ reaction is well-known with an uncertainty of $\sim 7\%$ (1σ).⁶ We estimate the overall uncertainty in the relative rate measurement to be $\sim 11\%$.

Reactions 1 and 2 are in their high-pressure limits under the conditions included in this study, and the overall uncertainty in $k_1(T)$ and $k_2(T)$ is estimated to be 9% with $k_1(T) = (6.94 \pm 0.25) \times 10^{-13} \exp[-(496 \pm 10)/T]$ cm³ molecule⁻¹ s⁻¹ and $k_2(T) = (7.52 \pm 0.44) \times 10^{-13} \exp[-(476 \pm 20)/T]$, where the measured room temperature rate coefficients are $k_1(296 \text{ K}) = (1.30 \pm 0.13) \times 10^{-13}$ and $k_2(296 \text{ K}) = (1.53 \pm 0.15) \times 10^{-13}$ cm³ molecule⁻¹ s⁻¹. The pre-exponential factors include the estimated systematic uncertainty. Uncertainty factors consistent with the NASA/JPL data evaluation are $f(298 \text{ K}) = 1.05$ and $g = 0$ over the temperature range included in this study.

3.5. Infrared Spectrum. The infrared absorption spectrum of (E)-CF₃CH=CHCF₃ measured in this work at 296 K is shown in Figure 4. Absorption spectra were measured over a (E)-CF₃CH=CHCF₃ concentration range of $(0.90\text{--}29.7) \times 10^{14}$ molecules cm⁻³, obeyed Beers' law, and were independent of bath gas pressure (30–500 Torr, He). The absorption spectrum shows strong absorption bands in the 1100–1400 cm⁻¹ region, which overlaps with the high wavenumber region of the atmospheric infrared window. Absorption band strengths were determined by a linear least-squares analysis of the integrated absorbance versus [(E)-CF₃CH=CHCF₃] and are given in Table 4. The infrared spectrum reported in the Østerstrøm et al.⁹ study is in good agreement with the present results. The theoretically calculated infrared absorption spectrum obtained in this work, derived via density functional theory using the B3LYP functional and the 6-311G(d,p) basis set, is included in Figure 4 for comparison, and a table of the band centers and band strengths is included in the Supporting Information. These quantities have also been tabulated there based on the M06-2X functional and the aug-cc-pVTZ basis set. As seen in Figure 4, the latter method is not more accurate. As shown in Table 4, the theoretical band strengths are in good agreement with the experimental values, although the band strengths for the individual bands in the 1100 to 1400 cm⁻¹ region show some differences. Overall, the theoretical calculations reproduce the experimental spectrum and could be used in cases where experimental data are not available. The vibrational bands shown in Figure 4 are due to coupled motions within the molecule but are qualitatively described as follows: H–C–C–H bend (1329 cm^{-1}), coupled H–C–C–H wag and

Figure 4. Infrared absorption spectrum of (E) - $\text{CF}_3\text{CH}=\text{CHCF}_3$ measured in this work at 296 K using Fourier transform infrared spectroscopy with 1 cm^{-1} resolution is shown in the upper panel. The theoretically calculated spectrum obtained in this work with B3LYP/6-311G(d,p) and M06-2X/aug-cc-pVTZ theory (unscaled frequencies) with the bands represented as 20 cm^{-1} fwhm Gaussians is included in the upper panel for comparison. The lower panel shows the Earth's irradiance taken from Hodnebrog et al.¹⁶ (black) and the radiative efficiency spectrum of (E) - $\text{CF}_3\text{CH}=\text{CHCF}_3$ (red) on the right axis.

CF_3 deformation combination (1265 cm^{-1}), CF_3 deformation (1162 cm^{-1}), C–F stretch (1128 cm^{-1}), H-atoms motion out-of-plane (1007 cm^{-1}), C–C stretch (853 cm^{-1}), and CF_3 breathing motion (619 cm^{-1}), where the values in parentheses are the unscaled band centers computed with B3LYP.

4. STEREOISOMER REACTIVITY COMPARISON AND THEORETICAL ANALYSIS

The observed significant positive temperature dependence for the rate coefficients for reactions 1 and 2, $E/R \approx 500\text{ K}$, and the significant difference in reactivity compared to the (Z) - $\text{CF}_3\text{CH}=\text{CHCF}_3$ stereoisomer as shown in Figure 2, was not expected. The $\text{OH} + (Z)\text{-CF}_3\text{CH}=\text{CHCF}_3$ rate coefficient was determined in our previous study to be $k(T) = (5.73 \pm 0.10) \times 10^{-13} \times T^2 \times \exp[(680 \pm 5)/T]\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$ over a similar temperature range. The temperature dependence for reaction 1 is also not consistent with the temperature dependence of a typical $\text{OH} +$ unsaturated hydrocarbon reaction, i.e., OH addition to a carbon–carbon double bond, which typically displays a negative temperature dependence near room temperature with E/R values in the range of -500 to

-1000 K .⁶ Yet, our OD kinetic results are, however, consistent with a radical addition reaction mechanism.

The lower reactivity of $(E)\text{-CF}_3\text{CH}=\text{CHCF}_3$ may be due to several contributing factors, e.g., steric hindrance imposed by the CF_3 groups to the OH attack on the $>\text{C}=\text{C}<$ double bond, hydrogen bonding, and differences in dipole attraction. It has been observed that $\text{CF}_2=\text{CF}_2$ and $\text{CF}_3\text{CF}=\text{CF}_2$, perfluoroolefins (PFOs), are significantly more reactive than their partially fluorinated counterparts, which implies a steric influence.^{15,17,18} Fluorination is also known to influence the temperature dependence of the OH reaction rate coefficients. OH radical reactions with C2 and C3 hydrofluoroalkenes^{15,18,19} show negative temperature dependencies that are consistent with the mechanism of OH addition to the carbon–carbon double bond. In our study, $k_1(T)$ was found to have a positive temperature dependence and follow an Arrhenius behavior. A slight non-Arrhenius behavior is often associated with a change in reaction mechanism. However, a mechanism shift for alkenes is generally observed at elevated temperatures, as the addition pathway becomes unimportant due to the rapid decomposition reaction of the OH –alkene adduct back to reactants, while H-atom abstraction, if available, becomes more important.²⁰ The computational analysis presented below addresses some of these issues.

Initially, the CBS-QB3 method²¹ was applied to estimate the binding energy in the common $\text{OH} + \text{CF}_3\text{CH}=\text{CHCF}_3$ adduct, where rotation around the central C–C bond is possible, because the π -bond in the reactant is broken. The results are $\Delta H_0 = 122$ and 142 kJ mol^{-1} for the E - and Z -isomers, respectively. So, the addition reaction for the Z -isomer is both faster and more exothermic than the corresponding reaction for the E -isomer. The difference in C–O bond dissociation enthalpies at 0 K is a reflection of the Z -isomer being 20 kJ mol^{-1} less stable than the E -stereoisomer. We then focused attention onto the transition state (TS) for OH addition. A challenge for standard computational approaches is the high spin contamination in the TS region for OH addition to alkenes, where $\langle S^2 \rangle \approx 1.0$ rather than the ideal value of 0.75 for a spin doublet.²² We adopted the method employed by Zhu et al.²³ to rationalize $\text{OH} + \text{C}_2\text{H}_4$ kinetics, namely, evaluation of the spin-projected PMP2/aug-cc-pVQZ energy at the spin-unrestricted UMP2/cc-pVTZ geometry. We verified that the TS geometries were the lowest energy conformation with respect to rotation of the OH group about the forming C–O bond. Greenwald et al.²² suggested that the UMP2/cc-pVTZ vibrational zero-point energy (ZPE) for the $\text{OH} + \text{C}_2\text{H}_4$ TS is adversely affected by the extensive spin contamination and instead employed density functional values at the UB3LYP/cc-pVTZ level. Complications arose here, because the unrestricted UB3LYP functional does not yield a distinct saddle point along the reaction coordinate. Instead, we used the unrestricted

Table 4. Infrared Absorption Band Strengths for $(E)\text{-CF}_3\text{CH}=\text{CHCF}_3$ at 296 K

integration range (cm^{-1})	band strength ($10^{-17}\text{ cm}^2\text{ molecule}^{-1}\text{ cm}^{-1}$)		
	Østerstrom et al. ⁹	this work (experimental) ^a	this work (theoretical) ^b
590–700		1.05 ± 0.02	1.0
800–1040		1.02 ± 0.02	1.22
1050–1400		28.7 ± 0.2	29.9
550–2000	29.6 ± 1.5	30.2 ± 0.2	32.1

^aUncertainties are fit precision. Note that the spectrum included in the SI is one of multiple spectra used to derive the recommended band strengths and does not match the recommended band strengths exactly. ^bTheoretical spectrum calculated with B3LYP/6-311G(d,p) theory.

Table 5. Ab Initio Energies for OH + Alkene Reactions

species	PMP2/aug-cc-pVQZ ^a	ZPE ^b (kJ mol ⁻¹)	$\Delta E_0^{\ddagger c}$ (kJ mol ⁻¹)
OH	-75.648639	22.33	
C ₂ H ₄	-78.427688	134.55	
OH + C ₂ H ₄ TS	-154.081545	164.86	-5.1
(Z)-CF ₃ CH=CHCF ₃	-751.935262	166.32	
OH + (Z)-CF ₃ CH=CHCF ₃ entrance adduct	-827.589106	189.58	-6.6
OH + (Z)-CF ₃ CH=CHCF ₃ TS	-827.587273	195.98	-0.9
(E)-CF ₃ CH=CHCF ₃	-751.943960	166.48	
OH + (E)-CF ₃ CH=CHCF ₃ TS	-827.593329	195.98	7.0

^aSpin-projected energy in a.u. (1 au $\approx$ 2625.5 kJ mol⁻¹). ^bZero-point vibrational energy at the UM06-2X/aug-cc-pVDZ level of theory, unscaled. ^cTS energy relative to reactants at 0 K, including ZPE scaled by 0.972 and a -0.83 kJ mol⁻¹ spin-orbit correction to the energy of OH.

UM06-2X functional, which does, together with the aug-cc-pVDZ basis set, and scaled the ZPE by a standard factor of 0.972. This step forms part of the approach employed by Liu and co-workers in their analyses of fluorinated alkenes.²⁴ All calculations were carried out with the Gaussian 09 program suite.²⁵ The ² Π ground electronic state of the hydroxyl radical exhibits two closely spaced energy levels split by 140 cm⁻¹ arising from spin-orbit coupling, an effect not included in these nonrelativistic calculations, which return an average energy. Accordingly, the PMP2/aug-cc-pVQZ energy of this species is corrected down by half of this quantity, i.e., by 0.83 kJ mol⁻¹. We also sought bound adducts in the entrance as evidence of long-range interaction between the reactants. The above methodology located an adduct for the Z-isomer with a C–O distance of about 2.9×10^{-10} m, but while a similar adduct for the E-isomer was located using M06-2X theory, it was not a local minimum using UMP2/cc-pVTZ theory.

The results are summarized in Table 5. As a check, we have analyzed OH + C₂H₄ and obtain an energy for the addition TS (at 0 K, including changes in ZPE) of $\Delta E_0^{\ddagger} = -5.1$ kJ mol⁻¹ relative to the reactants. This compares well with the value of -3.3 kJ mol⁻¹ derived by Zhu et al.²³ and the range of -0.4 ± 8.4 kJ mol⁻¹ derived by Greenwald et al.²² on the basis of detailed modeling, with a best estimate adjusted to fit experiment of -4.6 kJ mol⁻¹. It is tempting to compare this submerged barrier directly with the negative activation energy (E_a) observed for the OH + C₂H₄ reaction at the high-pressure limit below 600 K, but Greenwald et al.²² argued that the temperature variation depends on both this “inner TS” and the effects of bottlenecks in the long-range interaction of OH and C₂H₄. Various kinds of long-range potential were explored by Georgievskii and Klippenstein²⁶ who obtained rate constants generally above 10^{-10} cm³ molecule⁻¹ s⁻¹, orders of magnitude larger than observed here, and it was noted that in particular for OH addition to alkenes, the presence of the inner TS reduces the reactivity below that derived from long-range transition-state theory. A similar situation holds for OH + (Z)-CF₃CH=CHCF₃, where the computed barrier is below the reactants, at $\Delta E_0^{\ddagger} = -0.9$ kJ mol⁻¹, and is qualitatively consistent with the slightly negative observed activation energy. Ai and Liu obtained a more negative barrier height of -6.3 kJ mol⁻¹.²⁴ For the E-isomer, we compute the TS to be less stable and find it lies at $\Delta E_0^{\ddagger} = 7.0$ kJ mol⁻¹ above the reactants. These results are summarized in Figure 5. While our computations successfully reproduce the differences in activation energies, a question is why the two TSs have these different stabilities relative to the respective reactants.

The computed structures of the E- and Z-stereoisomers of CF₃CH=CHCF₃ are shown in Figure 6, and the Cartesian

Figure 5. Schematic potential energy diagram for OH + CF₃CH=CHCF₃ isomers, based on PMP2/cc-pVQZ energies and M06-2X/cc-pVDZ vibrational frequencies (see text). Final product enthalpy based on CBS-QB3 theory.

coordinates are provided in Table S1 of the Supporting Information. The TSs for OH addition are also shown in Figure 5. In both cases, the C–O distance is ~ 2.03 Å (1 Å = 1×10^{-10} m). In the E-isomer TS, it may be seen that the OH group is pointed away from the CF₃ groups, with a closest H–F separation of 2.94 Å, whereas in the Z-isomer TS the OH group is pointed toward an F atom, with a closest distance of 2.43 Å. This close approach may allow weak hydrogen bonding between the OH and the CF₃ groups that could stabilize the Z-isomer TS.

The Z-isomer is of C₂ symmetry, while the E-isomer has C_{2h} symmetry and is therefore nonpolar. An alternative interpretation is that the interaction between the permanent dipole moments of OH and (Z)-CF₃CH=CHCF₃ lowers the energy of the Z-isomer TS relative to that of the E-conformation. The dipole moments, μ , of OH and (Z)-CF₃CH=CHCF₃, with the aug-cc-pVQZ basis set, are 1.76 and 3.22 D, respectively (1 D $\approx 3.34 \times 10^{-30}$ C m). The two dipoles are approximately parallel in the Z TS and the corresponding relation for the potential energy²⁷

$$V = -\frac{\mu_1 \mu_2}{4\pi\epsilon_0 r^3} \quad (\text{IV})$$

yields $V \approx -40$ kJ mol⁻¹ for $r = 2.0 \times 10^{-10}$ m. This is more than enough to stabilize the TS, although eq IV is only valid when r is much greater than the charge separations in the dipoles, which is not the case here. We propose that the Z-reaction path may be stabilized relative to the E-path by internal

Figure 6. UMP2/cc-pVTZ structures for $(E)\text{-CF}_3\text{CH=CHCF}_3$, $\text{OH} + (E)\text{-CF}_3\text{CH=CHCF}_3$ TS, $(Z)\text{-CF}_3\text{CH=CHCF}_3$, $\text{OH} + (Z)\text{-CF}_3\text{CH=CHCF}_3$ TS. Selected distances are in units of 10^{-10} m.

hydrogen bonding and/or interaction of OH with the dipole of $(Z)\text{-CF}_3\text{CH=CHCF}_3$.

An indication of significant long-range interaction is the weakly bound adduct in the entrance channel for $\text{OH} + (Z)\text{-CF}_3\text{CH=CHCF}_3$, computed to lie 12.9 kJ mol^{-1} lower in energy than the reactants (before any allowance for zero-point vibrational energy, which alters this energy difference to 6.6 kJ mol^{-1}). With a separation of $2.9 \times 10^{-10} \text{ m}$ in the entrance complex, eq IV yields $V \approx -13 \text{ kJ mol}^{-1}$, remarkably close although as noted it is an oversimplification. No adduct was found using PMP2/cc-pVTZ theory for $\text{OH} + (E)\text{-CF}_3\text{CH=CHCF}_3$ as indicated above, but at the M06-2X geometry, the predicted PMP2/cc-pVTZ binding energy is only -1.0 kJ mol^{-1} before ZPE. Thus, it is plausible that dipole–dipole forces could contribute to the potential, which controls the reactivity of the *Z*-isomer.

5. ATMOSPHERIC IMPLICATIONS

On the basis of the rate coefficients determined in this study, the lifetime of $(E)\text{-CF}_3\text{CH=CHCF}_3$ with respect to reaction with OH is estimated to be ~ 90 days for an OH concentration of $1 \times 10^6 \text{ molecules cm}^{-3}$.²⁸ The atmospheric lifetime is only approximate, because the loss of $(E)\text{-CF}_3\text{CH=CHCF}_3$ will actually depend on the time and location of its emission. The rate coefficient for the $\text{O}_3 + (E)\text{-CF}_3\text{CH=CHCF}_3$ reaction at 296 K was measured to be $5.2 \times 10^{-22} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, which makes this atmospheric loss process insignificant under background O_3 conditions, with a >60 year lifetime for an O_3 abundance of 30 ppm.

The tropospheric degradation mechanism and stable end-product formation is expected to be the same as that for the $(Z)\text{-CF}_3\text{CH=CHCF}_3$ stereoisomer as discussed in our previous studies.^{4,5} The photochemical ozone creation potential (POCP)^{29,30} of $(E)\text{-CF}_3\text{CH=CHCF}_3$ is estimated to be ~ 1 , which is a factor of 3.2 less than that of the $(Z)\text{-CF}_3\text{CH=CHCF}_3$ stereoisomer² due to its lower OH reactivity. The POCPs for both the (E) - and $(Z)\text{-CF}_3\text{CH=CHCF}_3$ stereoisomers are low in comparison with common unsaturated hydrocarbons, e.g., 112 for $\text{CH}_3\text{CH=CH}_2$.

Figure 4 shows the overlap of the infrared absorption spectrum $(E)\text{-CF}_3\text{CH=CHCF}_3$ with Earth's irradiance reported in Hodnebrog et al.¹⁶ The overlap is greatest for the absorption bands in the 1000 to 1250 cm^{-1} region, while the strongest absorption band near 1325 cm^{-1} is attenuated significantly by the decreasing irradiance. The $(E)\text{-CF}_3\text{CH=CHCF}_3$ radiative efficiency (RE) was calculated to be 0.35 (atmospherically well-mixed) and 0.15 (lifetime-adjusted) $\text{W m}^{-2} \text{ ppb}^{-1}$ using the estimation methods given in Hodnebrog et al.¹⁶ Although there are differences in the vibrational band centers and band strengths, the RE of $(E)\text{-CF}_3\text{CH=CHCF}_3$ is very similar to that of $(Z)\text{-CF}_3\text{CH=CHCF}_3$, $0.38 \text{ W m}^{-2} \text{ ppb}^{-1}$.² The global warming potentials for $(E)\text{-CF}_3\text{CH=CHCF}_3$, calculated relative to CO_2 , are greater than for $(Z)\text{-CF}_3\text{CH=CHCF}_3$ due to its longer atmospheric lifetime. The well-mixed GWPs for $(E)\text{-CF}_3\text{CH=CHCF}_3$ for the 20, 100, and 500 year time horizons are 114 (49), 32 (14), and 10 (4), respectively, using the CO_2 radiative forcing given in WMO³¹ with GWPs obtained using lifetime-adjusted RE values given in parentheses.

6. CONCLUSIONS

Rate coefficients for the $\text{OH} + (E)\text{-CF}_3\text{CH=CHCF}_3$ reaction were determined in this study over a range of temperatures (211–374 K) and bath gas pressures (20–300 Torr; He, N_2). The rate coefficient was independent of pressure within the precision of the measurements and expected to be in the high-pressure limit. The measurements are well-represented by the Arrhenius expression $k_1(T) = (6.94 \pm 0.80) \times 10^{-13} \exp[-(496 \pm 10)/T] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, where the measured room temperature rate coefficient is $k_1(296 \text{ K}) = (1.30 \pm 0.15) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. The quoted uncertainties are 2σ and include estimated systematic errors. On the basis of the OH rate coefficients determined in this study, the atmospheric lifetime of $(E)\text{-CF}_3\text{CH=CHCF}_3$ was estimated to be ~ 90 days. The photochemical ozone creation potential (POCP) of $(E)\text{-CF}_3\text{CH=CHCF}_3$ was estimated to be small, and its global warming potential was determined to be low, ~ 14 (lifetime-adjusted), for the 100 year time horizon.

The present kinetic results clearly demonstrate that the OH reactivity of the *E*- and *Z*-stereoisomers of $\text{CF}_3\text{CH=CHCF}_3$ differ significantly. This study and results of previous studies from this laboratory for $\text{OH} + (E)\text{-}$ and $(Z)\text{-1-chloro-3,3,3-trifluoropropene-1 (CF}_3\text{CH=CHCl)}^{12}$ and $\text{OH} + \text{CH}_3\text{OC}_7\text{F}_{13}$ (methyl-perfluoroheptene ethers)³² reactions have highlighted that stereoisomers of halogen substituted olefins display significant differences in OH radical reactivity, and temperature dependence, that is not observed in olefinic hydrocarbon reactions. Other examples of the haloolefin stereoisomer reactivity dependence are available in the literature.⁶ For example, the $\text{OH} + \text{CHF=CFCF}_3$ and $\text{CF}_3\text{CF=CFCF}_3$ reactions show a stereoisomer reactivity dependence, although somewhat less in these reactions than observed in the present study. In addition, the *E*-stereoisomers of CHF=CFCF_3 and $\text{CF}_3\text{CF=CFCF}_3$ are more reactive than the *Z*-stereoisomers, which is opposite to what was observed for the $\text{CF}_3\text{CH=CHCF}_3$ stereoisomers. Computational methods were applied in this study to rationalize the reactivity differences for the $\text{CF}_3\text{CH=CHCF}_3$ reaction, which are most likely attributed to differences in H-bonding, although contributions based on differences in the polarity of the reaction adducts cannot be ruled out. Further laboratory and theoretical studies of haloolefin stereoisomer reactivity would aid the further development of a more general understanding of the reactivity trends.

■ ASSOCIATED CONTENT

■ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpca.8b02771.

Representative OH radical PLP–LIF decay profiles, second-order kinetic plot for the $\text{O}_3 + (E)\text{-CF}_3\text{CH=CHCF}_3$ reaction, infrared band strength Beer's law plots for $(E)\text{-CF}_3\text{CH=CHCF}_3$, tables of computational parameters for the $\text{OH} + (E)\text{-}$ and $(Z)\text{-CF}_3\text{CH=CHCF}_3$ reaction, theoretically calculated infrared band centers and bands strengths for $(E)\text{-CF}_3\text{CH=CHCF}_3$, digitized experimental $(E)\text{-CF}_3\text{CH=CHCF}_3$ infrared spectrum (PDF)

$(E)\text{-CF}_3\text{CH=CHCF}_3$ IR spectrum (TXT)

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We thank Barbara Minor and Mark Robin of DuPont Fluoroproducts for providing the samples and sample purity analysis. This work was supported in part by NOAA's Climate Goal and NASA's Atmospheric Composition Program. P.M. thanks Prof. Wes Borden for valuable discussions and the R.A. Welch Foundation (Grant B-1174) for support. Computer facilities were purchased in part with support from the National Science Foundation (Grant CHE-0741936).

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