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Photochemical Properties of Hydrofluoroethers CH_3OCHF_2, CH_3OCF_3, and $CHF_2OCH_2CF_3$: Reactivity toward OH, IR Absorption Cross Sections, Atmospheric Lifetimes, and Global Warming Potentials

Vladimir L. Orkin,*[†,‡] Victor G. Khamaganov,[†,‡] and Andrey G. Guschin[‡,§]

[†]National Institute of Standards and Technology, Gaithersburg, Maryland 20899, United States
[‡]Institute of Energy Problems of Chemical Physics, Russian Academy of Sciences, Moscow 117829, Russia

S *Supporting Information*

ABSTRACT: Rate constants for the gas phase reactions of OH radicals with three partially fluorinated ethers, CH_3OCF_3 ($k_{HFE-143a}$), CH_3OCHF_2 ($k_{HFE-152a}$), and $CHF_2OCH_2CF_3$ ($k_{HFE-245fa2}$), were measured using a discharge flow–electron paramagnetic resonance technique over the temperature range 298–460 K. The temperature dependences of the rate constants can be represented by the following expressions: $k_{HFE-143a}(T) = (1.10 \pm 0.20) \times 10^{-12} \times \exp\{-(1324 \pm 61)/T\}$ cm^3 molecule^{-1} s^{-1}; $k_{HFE-152a}(T) = (11.6 \pm 4.2) \times 10^{-12} \times \exp\{-(1728 \pm 133)/T\}$ cm^3 molecule^{-1} s^{-1}; and $k_{HFE-245fa2}(T) = (3.04 \pm 0.57) \times 10^{-12} \times \exp\{-(1665 \pm 66)/T\}$ cm^3 molecule^{-1} s^{-1}. The atmospheric lifetimes due to reactions with tropospheric OH were estimated to be 5.2, 1.9, and 5.6 years, respectively. The IR absorption cross sections of these fluorinated ethers were measured between 400 and 2000 cm^{-1}, and their global warming potentials were estimated.
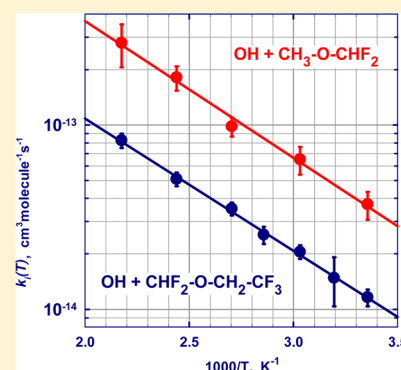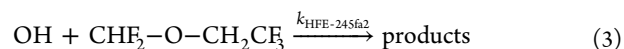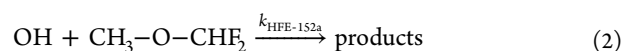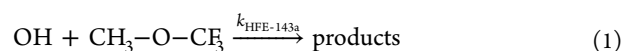
1. INTRODUCTION

Partially fluorinated hydrofluoroethers (HFEs) have been considered as potential alternatives to fully halogenated chlorofluorocarbons (CFCs) and their transitional replacements, partially halogenated hydrochlorofluorocarbons (HCFCs), in various industrial applications. Molecules of hydrofluoroethers do not contain any chlorine and therefore do not contribute to the stratospheric ozone depletion. Nevertheless, these fluorinated compounds may exhibit strong absorption in the Earth's infrared "atmospheric transparency window" between 8 and 12 μm, thus acting as greenhouse gases.

The assessment of the global warming potential (GWP) of a compound requires the knowledge of both its residence time in the atmosphere and its infrared absorption spectrum. The atmospheric lifetimes for most hydrogen-containing trace gases are primarily controlled by their reactions with hydroxyl radicals in the troposphere. The presence of an —O— linkage in the molecules of fluorinated ethers was expected to render these compounds more highly reactive toward hydroxyl radicals resulting in shorter atmospheric lifetime and, therefore, limiting their accumulation in the atmosphere and decreasing their potential impact as greenhouse gases. In contrast with HCFCs and HFCs, there is limited information on reactivity of partially fluorinated ethers (HFEs).[1,2] Only a few studies have been reported on the temperature dependence of such OH reaction rate constants[1] to derive Arrhenius parameters as well as rate constants at the temperatures important for atmospheric modeling. In this paper we report the results of experimental determinations of the rate constants for the reactions between

OH and three hydrofluoroethers: trifluoromethyl methyl ether (HFE-143a), difluoromethyl methyl ether (HFE-152a), and difluoromethyl 2,2,2-trifluoroethyl ether (HFE-245fa2) over the temperature range 298–460 K.

$$OH + CH_3-O-CF_3 \xrightarrow{k_{HFE-143a}} products \qquad (1)$$

$$OH + CH_3-O-CHF_2 \xrightarrow{k_{HFE-152a}} products \qquad (2)$$

$$OH + CHF_2-O-CH_2CF_3 \xrightarrow{k_{HFE-245fa2}} products \qquad (3)$$

Infrared absorption spectra of these molecules were measured between 400 and 2000 cm^{-1}. Integrated IR band intensities are reported here as well as the estimated atmospheric lifetimes and global warming potentials (GWPs) of the three compounds.

2. EXPERIMENTAL SECTION[3]

OH Reaction Rate Constant Measurements. The title reactions have been studied by using the discharge flow/ electron paramagnetic resonance (DF/EPR) apparatus in a quartz tubular reactor of 2.0 cm i.d. coated with a perfluorinated varnish (F-46) to reduce wall loss of OH and to prevent heterogeneous reactions. Detailed descriptions of the apparatus and the experimental methods employed in this study are given elsewhere.[4,5] Thus, only a brief overview of experimental conditions is given here. The temperature of the

flow reactor was controlled (± 0.3 K) with either water (between 298 and 370 K) or mineral oil (between 410 and 460 K) circulated through its outer jacket. OH radicals were produced near the end of the movable quartz injector of H atoms in their fast reaction with NO_2. Both NO_2 and the reactant (fluorinated ether under study) were injected to the flow reactor upstream from the injector tip; they were always in large excess over the hydroxyl radicals (H atoms). The initial OH concentration in this study was 2×10^{11} to 8×10^{11} molecules/cm^3. The average linear gas flow velocity in the reactor was 6−15 m/s, at the total gas pressure of 0.33 kPa (2.5 torr). Flow rates of all gases were determined by direct measurements of the rate of the pressure change in calibrated volumes. Fluorinated ethers were introduced into the metal gas-handling system directly from small metal storage cylinders. The decay rate of OH was measured by varying the distance (4−30 cm) between the movable injector of H atoms and the cavity of the EPR spectrometer. The measured decay rate was then slightly corrected for the axial diffusion (less than 4% correction) to obtain the pseudo-first-order rate coefficients, k, of the OH concentration decay. Finally, the bimolecular reaction rate constant, k_{HFE}, was derived from a linear least-squares analysis of thus obtained k versus the concentration of the fluorinated ether, $[HFE_i]$, using following expression

$$k = k_w + k_{HFE_i} \times [HFE_i]$$

(4)

where k_w is the first-order OH decay rate due to its heterogeneous removal in the absence of the reactant. The technique was described in detail by Orkin and Khamaganov[4,5] and references therein. We estimate the instrumental uncertainty associated with these measurements to be less than ∼7%.

IR Absorption Cross Section Measurements. The IR absorption spectra of CH_3OCF_3 (HFE-143a), CH_3OCHF_2 (HFE-152a), and $CHF_2OCH_2CF_3$ (HFE-245fa2) were measured at NIST by 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}). We used both a liquid-nitrogen-cooled MCT detector and a room temperature DTGS detector. The absorption cross sections obtained with these detectors were compared to avoid a possible systematic error due to differences in their properties. In particular, the DTGS detector was used over the longer wavelength region below 700 cm^{-1} to obtain the reliable data free of artifacts associated with the use of a cold detector.[6] The (10.2 $\pm$ 0.05) cm glass absorption cell fitted with KBr windows was fixed in the spectrophotometer to minimize a baseline shift due to changes in the absorption cell position. The temperature of the cell was measured to be (298 $\pm$ 1) K. Details of the experimental procedure and data treatment and potential complications of these measurements are discussed in a recent paper.[6] The overall instrumental error associated with the optical path length, pressure measurements, and temperature stability was estimated to be ∼0.5%. The uncertainty of the absorption measurements was usually less than ∼1% except in the wavenumber range below ∼700 cm^{-1} where the spectrophotometer noise increases. The majority of measurements were done in pure fluorinated ethers with no bath gas added. Test experiments were done with ∼100 kPa (750 torr) of ultrahigh-purity nitrogen added to check the effect of a broadening gas on the obtained IR absorption spectra.

The complementary measurements of the IR spectra of HFE-143a and HFE-245fa were done at the Institute of Energy Problems of Chemical Physics (InEP) by using a Specord M-80 double beam diffraction spectrophotometer coupled with a computer for data collection and analysis. The absorption cross sections were measured with a 0.5 cm^{-1} spectral slit width and recorded at 0.2 cm^{-1} increments. The (12.16 $\pm$ 0.03) cm glass absorption cell fitted with KBr windows was fixed in the spectrophotometer to prevent a baseline shift. Between measurements the cell was pumped out down to ca. 0.1 Pa and then filled with the gas to be studied. Photometric noise was ca. 0.007 absorption units during these experiments. The temperature of the cell was T = (295 $\pm$ 1) K. These complementary experiments allow comparing the results obtained by using two different IR absorption measurements techniques, FTIR and a diffraction monochromator based instrument.

Materials. The sample of CH_3OCF_3 (HFE-143a) was provided by the Oak Ridge National Laboratory. The purity of the original sample was 99.44% for gas phase sampling and 99.90% for liquid phase sampling. No information on the impurities nature was available. Therefore, the sample was further purified by distillation at the State Institute of Applied Chemistry, Russia, to obtain the material used for reaction rate constant measurements and test experiments. Several fractions with different levels of detected impurities were thus obtained. The impurity levels of various fractions as measured by gas chromatography are listed in Table 1 along with their GC

Table 1. Levels of Impurities in HFE-143a Samples Used in This Study (%)

HFE-143a sample	GC retention time, min				
	1.21	1.40	1.78	1.92	2.80
E0-g	0.16	0.36	0.03	0.01	99.44
E0-l	0.027	0.083	–	–	99.89
E1	0.084	0.158	0.031	0.027	99.7
E2	0.016	–	–	–	99.984
E3	0.006	–	–	–	99.994

retention times. "E0-l" and "E0-g" designate the gas and liquid phase, respectively, of the original sample while E1, E2, and E3 designate the various rectified fractions, E3 being the purest one. Samples of $CHF_2OCH_2CF_3$ (HFE-245fa2) and CH_3OCHF_2 (HFE-152a) were provided by the State Institute of Applied Chemistry, Russia with the stated purity of 99.95% (the main impurities were CHF_2Cl, CF_3OCH_3) and 99.5% (the main impurity was methyl formate), respectively. The stated content of unsaturated halocarbons did not exceed 5 ppm for all samples. The same samples of HFE-143a and HFE-245fa2 were used for IR absorption measurements with the diffraction spectrophotometer at InEP. The samples of all three fluorinated ethers used for IR measurements by using FTIR instrument at NIST were obtained from SynQuest Laboratories, Inc. with the stated purity of better than 99%. Nitrogen dioxide, NO_2, was prepared in the laboratory to appear as white (colorless) snow when frozen in the liquid-nitrogen-cooled trap thus indicating the absence of other nitrogen oxides as impurities. All samples were carefully degassed through multiple freeze−pump−thaw−boil cycles. The carrier flow gas, He, was 99.999% pure, and H_2 was 99.98% pure.

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dx.doi.org/10.1021/jp506377w | J. Phys. Chem. A 2014, 118, 10770−10777

Table 2. Rate Constants Measured in the Present Work for Reactions of OH with CH_3OCF_3, CH_3OCHF_2, and $CHF_2OCH_2CF_3$[a]

T, K	$k_{HFE-143a}(T) \times 10^{14}$, cm^3 molecule^{-1} s^{-1}	$[CH_3OCF_3]$, 10^{15} molecule/cm^3	$k_{HFE-152a}(T) \times 10^{14}$, cm^3 molecule^{-1} s^{-1}	$[CH_3OCHF_2]$, 10^{15} molecule/cm^3	$k_{HFE-245fa2}(T) \times 10^{14}$, cm^3 molecule^{-1} s^{-1}	$[CHF_2OCH_2CF_3]$, 10^{15} molecule/cm^3
298	1.30 ± 0.06	0.2–5.3	3.54 ± 0.65	0.16–0.78	1.13 ± 0.04	0.8–2.5
308	1.50 ± 0.17	0.4–2.2				
313					1.48 ± 0.20	0.9–1.3
319	1.76 ± 0.10	0.4–2.4				
330	1.88 ± 0.21	0.19–2.5	6.45 ± 1.0	0.12–0.76	2.05 ± 0.09	0.5–1.7
342	2.31 ± 0.14	0.5–2.8				
350					2.53 ± 0.18	0.4–1.7
355	2.73 ± 0.11	0.2–2.2				
370	3.08 ± 0.20	0.32–1.2	9.97 ± 0.94	0.21–0.62	3.52 ± 0.13	0.4–1.5
410	4.56 ± 0.27	0.28–1.04	17.4 ± 2.4	0.15–0.33	5.09 ± 0.19	0.3–1.1
460	6.00 ± 0.23	0.28–1.04	27.9 ± 8.0	0.03–0.10	8.25 ± 0.28	0.2–0.9

[a]The uncertainties are 95% confidence intervals from the least-squares fit of a straight line to the measured OH decay rates versus the reactant concentrations and do not include the estimated instrumental uncertainty of 7%.

3. RESULTS AND DISCUSSION

OH Reaction Rate Constants. The rate constants determined for the title reactions are presented in Table 2 and shown in Figures 1 and 2. The Arrhenius parameters derived from the fit to the experimental data are presented in Table 3.
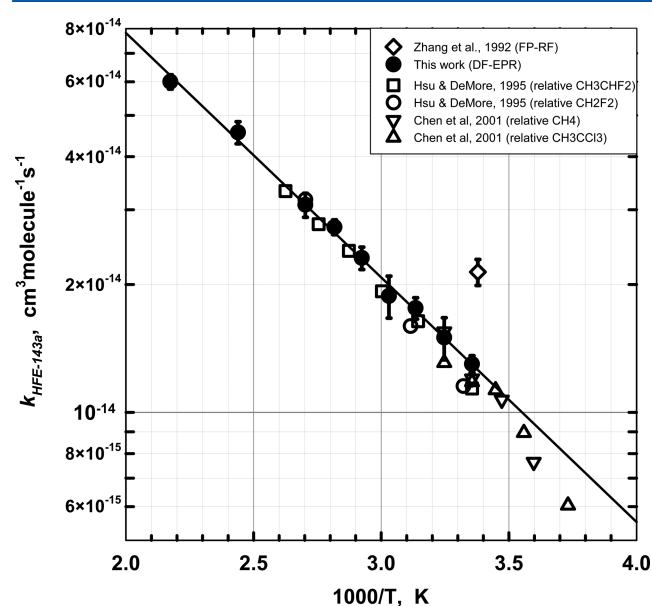

Figure 1. Results of rate constant measurements for the reaction between OH and CH_3OCF_3 (HFE-143a): ($\diamondsuit$) Zhang et al.,[8] ($\bullet$) this study, ($\square$,$\bigcirc$) Hsu and DeMore[9] relative CH_3CHF_2 and CH_2F_2, respectively, and ($\triangle$,$\triangledown$) Chen et al.,[10] relative CH_4 and CH_3CCl_3, respectively.

OH + CH_3−O−CF_3 (HFE-143a). Figure 1 shows all the available data for this reaction. The fit to the data presented in Table 2 yields the following Arrhenius expression

$$k_{HFE-143a}(T) = (1.10 \pm 0.20) \times 10^{-12}$$
$$\times \exp\{-(1324 \pm 61)/T\}$$
$$\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad (5)$$

The results presented in Table 2 were obtained with the purest available sample designated as E3 in Table 1. The impurities in HFE-143a sample were not identified. However, even if we
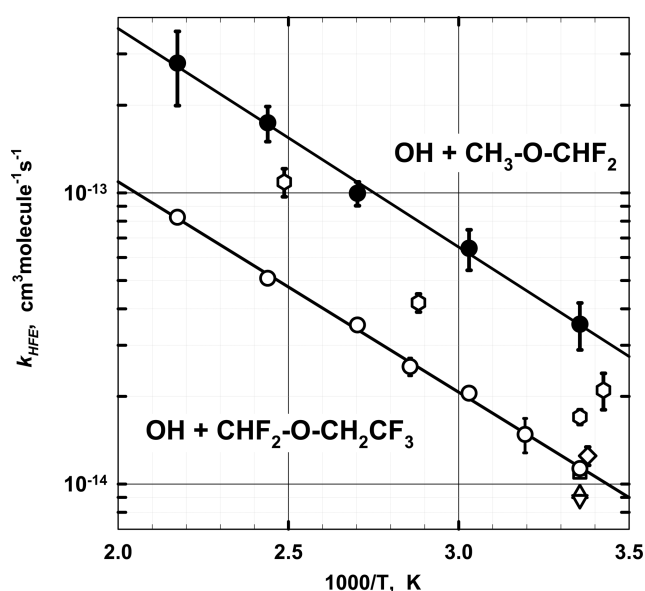

Figure 2. Results of rate constant measurements for the reactions of OH with CH_3OCHF_2 (HFE-152a) and $CHF_2OCH_2CF_3$ (HFE-245fa2). HFE-152a: ($\bullet$) this study; HFE-245fa2: ($\diamondsuit$) Zhang et al.,[8] ($\bigcirc$) this study, ($\square$) Nolan et al.,[12] ($\hexagon$) Beach et al.,[14] and ($\triangle$,$\triangledown$) Oyaro et al.,[13] relative CH_3CCl_3 and CHF_2CH_2F, respectively.

assume that the single impurity in the fraction E3 is the very reactive nonfluorinated dimethyl ether (CH_3OCH_3),[7] its contribution to the measured $k_{HFE-143a}$ would not exceed ∼1%. We did test experiments with different fractions of HFE-143a listed in Table 1 to find no significant difference in the measured rate constants. Thus, we conclude that the measured $k_{HFE-143a}$ presented in this paper is not affected by the presence of reactive impurities within the reported uncertainty. The recommended room temperature rate constant derived in this study is

$$k_{HFE-143a}(298 \text{ K}) = (1.30 \pm 0.14) \times 10^{-14}$$
$$\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad (6)$$

where the indicated total uncertainty includes the statistical two standard error listed in Table 1 and the estimated instrumental uncertainty of ∼7%.

Results of three studies of this reaction are available and shown in Figure 1. Zhang et al.[8] measured the rate constant at room temperature by using absolute FP-RF technique. Hsu and

Table 3. Results of Kinetic Measurements of the Reactions between OH and Fluorinated Ethers^a

molecule (hydrofluoroether)	k_{HFE_i}(298 K) $\times 10^{14}$ molecule/cm^3	$A \times 10^{12}$ molecule/cm^3	E/R, K	temperature range, K	ref
CH$_3$OCF$_3$ (HFE-143a)	1.30 ± 0.05	1.10 ± 0.20	1324 ± 61	298–460	this work
	2.14 ± 0.15			296	8
	1.17 ± 0.05	1.52 ± 0.38	1451 ± 44	298–381	9^b
	1.09 ± 0.02	2.63 ± 0.35	1636 ± 43	301–370	9^b
	1.25 ± 0.08	7.98 ± 12.2	1925 ± 448	278–308	10^b
	1.18 ± 0.11	2.53 ± 3.84	1601 ± 430	268–308	10^b
CH$_3$OCHF$_2$ (HFE-152a)	3.5 ± 0.5	11.6 ± 4.2	1728 ± 133	298–460	this work
CHF$_2$OCH$_2$CF$_3$ (HFE-245fa2)	1.14 ± 0.05	3.04 ± 0.57	1665 ± 66	298–460	this work
	1.25 ± 0.09			296	8
	1.1 ± 0.03			298	12^c
	1.89 ± 0.50	11.5 ± 19.6	1911 ± 558	292–402	14
	0.93 ± 0.02			298	13^b
	0.88 ± 0.03			298	13^b

^{a}The uncertainties are two standard error from the least-squares fits to the reported temperature dependent data and do not include the estimated instrumental uncertainty. The uncertainties of the rate constants measured at room temperature only are those from the original papers. ^{b}The relative rate results were recalculated using the current recommendations for the rate constants of reference reactions.[1] The uncertainties do not include the recommended uncertainties of the reference reaction rate constants. ^{c}Relative rate measurements; the reference reaction is not reported.

DeMore[9] employed a relative rate technique with FTIR detection to measure the rate constant between 298 and 381 K using two different reference compounds, CHF$_2$CH$_3$ and CH$_2$F$_2$. Chen et al.[10] employed a relative rate technique with FTIR detection to measure the rate constant between 268 and 308 K by using two different reference compounds, CH$_4$ and CH$_3$CCl$_3$. We recalculated the results of the relative rate measurements reported in refs 9, 10 using the current recommendations for the rate constants of reference reactions.[1] The Arrhenius parameters derived from the results of these studies are presented in Table 3 along with the room temperature rate constant obtained from the fit to each data set. The result reported by Zhang et al.[8] substantially exceeds all other data probably due to the presence of reactive impurities in their sample of HFE-143a. Although other room temperature data are still scattered between 1.1 and 1.3 $\times$ 10^{-14} cm^3 molecule^{-1} s^{-1}, they are in reasonable agreement when the total uncertainties of measurements are considered. This includes the estimated instrumental uncertainty of our measurements and, at least, the uncertainty of reference reaction rate constants for results reported in refs 9, 10. The data reported by Chen et al.,[10] the only data obtained below room temperature, are somewhat more scattered resulting in large uncertainty of E/R. They are in good agreement with our results at room temperature but indicative of smaller rate constant below room temperature when compared with eq 5.

OH + CH$_3$−O−CHF$_2$ (HFE-152a). The rate constants determined for this reaction are shown in Figure 2 with filled circles. The fit to the data presented in Table 2 yields the following Arrhenius expression

$$k_{HFE\text{-}152a}(T) = (11.6 \pm 4.2) \times 10^{-12}$$
$$\times \exp\{-(1728 \pm 133)/T\}$$
$$cm^3 \text{ molecule}^{-1} \text{ s}^{-1} \qquad (7)$$

Based on the reactivity of methyl formate,[11] the presence of this impurity should not change the measured rate constant by more than ∼3%. The room temperature rate constant derived from our data is

$$k_{HFE\text{-}152a}(298 \text{ K}) = (3.5 \pm 0.7) \times 10^{-14}$$
$$cm^3 \text{ molecule}^{-1} \text{ s}^{-1} \qquad (8)$$

where the indicated total uncertainty includes the statistical two standard error listed in Table 1 and the estimated instrumental uncertainty of ∼7%. To the best of our knowledge, there are no other data available for this reaction.

OH + CHF$_2$−O−CH$_2$CF$_3$ (HFE-245fa2). The fit to the data presented in Table 2 yields the following Arrhenius expression

$$k_{HFE\text{-}245fa2}(T) = (3.04 \pm 0.57) \times 10^{-12}$$
$$\times \exp\{-(1665 \pm 66)/T\}$$
$$cm^3 \text{ molecule}^{-1} \text{ s}^{-1} \qquad (9)$$

The rate constants determined for this reaction are shown in Figure 2 with open circles along with the results of other studies also shown with open symbols. The room temperature rate constant derived from our data is

$$k_{HFE\text{-}245fa}(298 \text{ K}) = (1.14 \pm 0.13) \times 10^{-14}$$
$$cm^3 \text{ molecule}^{-1} \text{ s}^{-1} \qquad (10)$$

where the indicated total uncertainty includes the statistical two standard error listed in Table 1 and the estimated instrumental uncertainty of ∼7%. Results of room temperature studies reported by Zhang et al.[8] (absolute FP-RF measurements), Nolan et al.[12] (relative rate measurements using GC and FTIR), and Oyaro et al.[13] (two relative rate measurements using GC) are in reasonable agreement with the results of our measurements when the total uncertainties are considered. The rate constant measured by Beach et al.[14] between 292 and 402 K (absolute measurements using DF-MS) appears to be overestimated when compared with results from four other research groups (see Table 3).

IR Absorption Cross Section Measurements. The IR absorption spectra of fluorinated ethers are presented in Figures 3, 4, and 5. The spectra were combined as described earlier from the results of measurements at various pressures of compounds: 0.13−13 kPa (1−100 torr) for CF$_3$OCH$_3$, 0.27−17 kPa (2−128 torr) for CHF$_2$OCH$_3$, and 0.2−8.5 kPa (1.5−64 torr) for CF$_3$CH$_2$OCHF$_2$. The top panels in Figures 3, 4, and 5 show the IR spectra of fluorinated ethers between 400

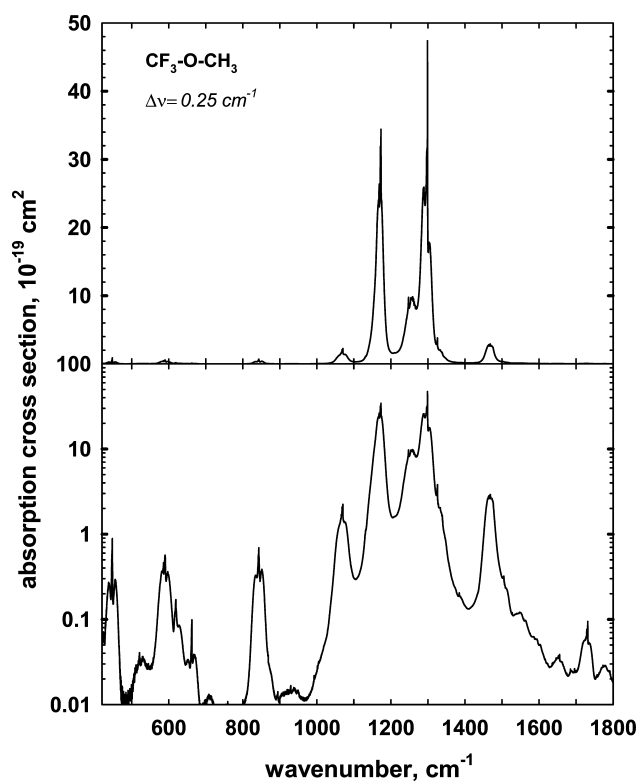**Figure 3.** IR absorption spectrum of CH_3OCF_3 (HFE-143a) obtained with a spectral resolution of 0.25 cm^{-1}.
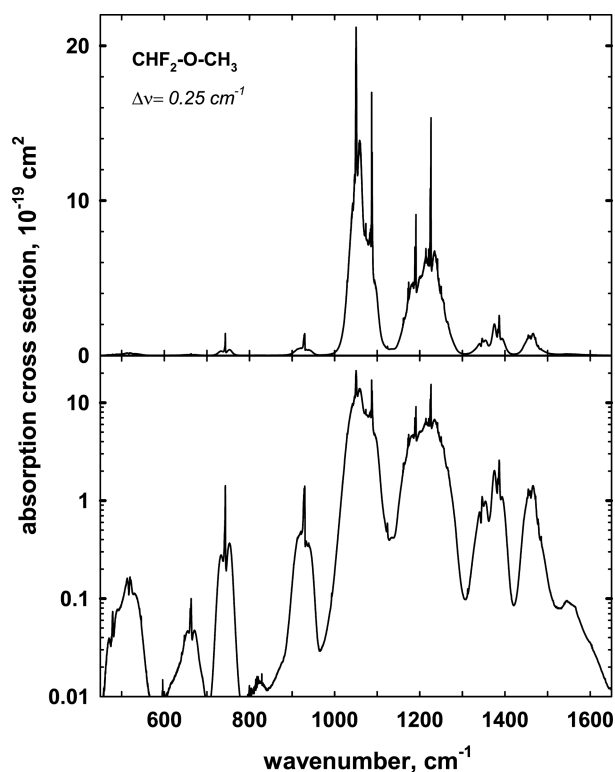

Figure 4. IR absorption spectrum of CH_3OCHF_2 (HFE-152a) obtained with a spectral resolution of 0.25 cm^{-1}.
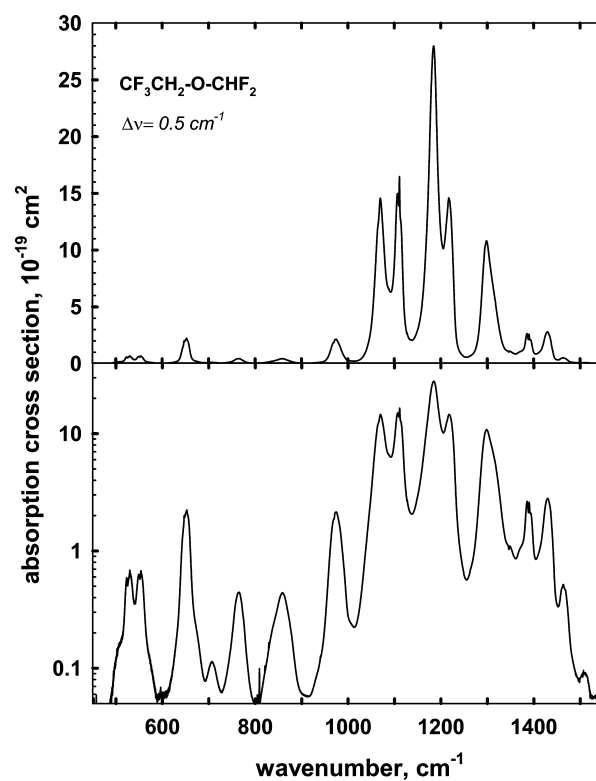
Figure 5. IR absorption spectrum of $CHF_2OCH_2CF_3$ (HFE-245fa2) obtained with a spectral resolution of 0.5 cm^{-1}.

IR spectra of fluorinated ethers have small absorption bands located between 1650 and 2000 cm^{-1} with integrated intensities of less than 0.3% of the total absorption. However, these shorter wavelength absorption bands are not important in the GWP estimations because they are small and the Earth's outgoing radiation flux becomes very small over this spectral range.

IR spectra of mildly fluorinated C2 ethers, CH_3OCHF_2 and CH_3OCF_3, exhibit a few narrow absorption features at the top of their main absorption bands. Test experiments were done to check the effect of broadening gas and spectral resolution on their intensity. The integrated intensities of narrow absorption peaks of HFE-143a located near 1298.9, 1173.3, and 1171.9 cm^{-1} decreased by 8%−12% when the CH_3OCF_3 was pressurized with 100 kPa (750 torr) of nitrogen and the spectral resolution was 0.125 cm^{-1}. The intensities of these small narrow absorption features were barely changed when a 0.25 cm^{-1} spectral resolution was used. Similar variations were observed with the narrow absorption bands of CH_3OCHF_2 located near 1226.2, 1191.0, 1088.3, and 1086.9 cm^{-1}. However, the intensities of these narrow absorption features are less than 0.5% of total absorption of corresponding fluorinated ethers, and possible small variation in their intensities cannot affect GWP estimations for these compounds. Therefore, the spectral resolution of 0.25 cm^{-1} was found to be adequate to represent these spectra without losing any details and a good signal-to-noise ratio. The IR spectrum of the larger ether, $CHF_2OCH_2CF_3$, is very smooth with no pronounced rotational structure. Its absorption spectra obtained with spectral resolutions of 0.125 and 0.5 cm^{-1} do not exhibit any difference.

Our IR absorption measurements of HFE-143a and HFE-245fa2 performed at InEP by using a diffraction spectropho-

and 1650 cm^{-1}, and the lower panels show the same spectra in log scale to illustrate smaller absorption features. IR absorption cross sections are available in the Supporting Information. The

Table 4. Atmospheric Lifetimes of Fluorinated Ethers and Their GWPs

molecule	atmospheric lifetime, years	integrated band intensity, 10^{-17} cm molecule^{-1}	GWPs at time horizons, years			ref
			20	100	500	
CH_3OCF_3, HFE-143a	5.15	21.6[a] (21.4)[b]	2550	739	225	this work
CH_3OCHF_2, HFE-152a	1.79	14.40[a]	1025	291	89	this work
$CHF_2OCH_2CF_3$, HFE-245fa	5.66	26.22[a] (26.34)[b]	3042 (2787)[c]	889 (910)[c]	270	this work
	7.348	26.5	2749	897		13
CFC-11	45	9.74[a]	6730	4750	1620	2

[a]IR absorption cross sections were measured by using a FTIR spectrophotometer at NIST. [b]IR absorption cross sections were measured by using a diffraction spectrophotometer at InEP. [c]GWPs were calculated using our estimation approach and the input parameters (atmospheric lifetimes of HFE-254fa2 and CFC-11 and GWP$_{CFC-11}(t)$) from Oyaro et al.[13] These results can be compared with those from Oyaro et al.[13] shown on the next line.

tometer yielded the total integrated absorption cross section, which differs from our FTIR results by less than 1%. Note that these two sets of IR measurements are absolutely independent as they were done in different laboratories by using different techniques and samples of different origin.

The total integrated absorption cross section of CH_3OCF_3 measured between 450 and 2000 cm^{-1} with a spectral resolution of 0.5 cm^{-1} was reported by Sihra et al.[15] Our value measured over the same interval is ~7.5% larger. These authors also reported the total absorption of $CHF_2OCH_2CF_3$ integrated over the same spectral interval, which is only 0.3% larger than that measured in our work. Oyaro et al.[13] reported the total absorption of $CHF_2OCH_2CF_3$ between 470 and 1550 cm^{-1} to be ~1.3% larger than that measured in our work over the same interval. These authors also report the corrected value from their previous measurements, which is ~0.9% smaller than our value. Thus, all the available data on IR absorption of HFE-245fa2 are in excellent agreement. To the best of our knowledge there are no available data on IR absorption measurements of CH_3OCHF_2 (HFE-152a).

4. ATMOSPHERIC IMPLICATIONS

The atmospheric lifetimes of fluorinated ethers due to their reactions with tropospheric hydroxyl radicals, $\tau_{HFE_i}^{OH}$, can be estimated by using a simple scaling procedure that is based on the results of field measurements[16] and thorough atmospheric modeling[17]

$$\tau_{HFE_i}^{OH} = \frac{k_{MCF}(272)}{k_{HFE_i}(272)} \cdot \tau_{MCF}^{OH} \qquad (11)$$

where $\tau_{HFE_i}^{OH}$ and τ_{MCF}^{OH} are the lifetimes of a compound under study and methyl chloroform, respectively, due to reactions with hydroxyl radicals in the troposphere only, and $k_{HFEi}(272$ K) and $k_{MCF}(272$ K) $= 6.14 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} are the rate constants for the reactions of OH with these substances at $T = 272$ K and with methyl chloroform,[1] respectively. The value of $\tau_{MCF}^{OH} = 6.1$ years[2] was obtained from the measured lifetime of MCF of 5.0 years when an ocean loss of 89 years and a stratospheric loss of 39 years were taken into account.

Based on the available data for the OH reaction rate constants of these fluorinated ethers, we accepted the rate constants given by eqs 7 and 9 for reactions of HFE-152a and HFE-245fa2, respectively. The reaction between OH and HFE-143a was studied most intensively, and consistent data sets are available. The combined fit to all data obtained below 400 K (excluding the obviously overestimated rate constant from Zhang et al.[8]) results in the following Arrhenius expression,

which can be currently recommended to represent $k_{HFE-143a}$ for the purpose of atmospheric modeling

$$k_{HFE-143a}(T) = 1.76 \times 10^{-12} \times \exp\{-1493/T\}$$
$$\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \qquad (12)$$

Thus, based on eqs 7, 9, and 12 we can estimate the atmospheric lifetimes to be 5.15, 1.85, and 5.61 years for HFE-143a, HFE-152a, and HFE-245fa2, respectively.

We can make simple estimations of global warming potentials of fluorinated ethers by combining their estimated atmospheric lifetimes, measured IR absorption spectra and the measured spectrum of Earth's outgoing radiation.[18,19] We first calculate the time-dependent hydrocarbon global warming potentials with CFC-11 as a reference compound, HGWP$_{HFE_i}(t)$. This referencing takes advantage of the fact that the time response functions for both the fluorinated ether under estimation and the CFC-11 reference can be approximated as exponential decays. Hence, HGWP$_{HFE_i}(t)$ can be calculated as follows:[18,20]

$$\begin{aligned} \text{HGWP}_{HFE_i}(t) &= \text{RRF}_{HFE_i}^{CFC-11} \frac{M_{CFC-11}}{M_{HFE_i}} \frac{\int_0^t \exp\{-t/\tau_{HFE_i}\}dt}{\int_0^t \exp\{-t/\tau_{CFC-11}\}dt} \\ &= \text{RRF}_{HFE_i}^{CFC-11} \times \frac{M_{CFC-11}}{M_{HFE_i}} \times \frac{\tau_{HFE_i}}{\tau_{CFC-11}} \\ &\quad \times \frac{1 - \exp\{-t/\tau_{HFE_i}\}}{1 - \exp\{-t/\tau_{CFC-11}\}} \end{aligned} \qquad (13)$$

Here M_{CFC-11} and M_{HFE_i} are molecular masses of CFC-11 and fluorinated ether, respectively, and $\text{RRF}_{HFE_i}^{CFC-11}$ is the relative radiative forcing (using CFC-11 as a reference) for the ether under study

$$\text{RRF}_{HFE_i}^{CFC-11} = \frac{\int_{\nu_1}^{\nu_2} \sigma_{HFE_i}(\nu) \times \Phi(\nu) \, d\nu}{\int_{\nu_1}^{\nu_2} \sigma_{CFC-11}(\nu) \times \Phi(\nu) \, d\nu} \qquad (14)$$

where ν_1 and ν_2 are the integration limits and $\Phi(\nu)$ is the intensity of outgoing Earth's radiation − experimentally measured spectrum of outgoing Earth's radiation obtained from the NIMBUS-4 satellite at a latitude of 15°N[21] that was used in our calculations. Next we use the currently accepted global warming potential of CFC-11 referenced to CO_2 (GWP$_{CFC-11}$), which is calculated using a radiative transfer

model of the atmosphere,[2] to obtain global warming potentials of these fluorinated ethers over various time horizons:

$$\text{GWP}_{\text{HFE}_i}(t) = \text{HGWP}_{\text{HFE}_i}(t) \times \text{GWP}_{\text{CFC-11}}(t) \qquad (15)$$

Thus, calculated GWPs are presented in Table 4 for time horizons of 20, 100, and 500 years. Table 4 also shows the estimated atmospheric lifetimes and the total integrated absorption cross sections of these compounds.

Oyaro et al.[13] used a similar approach suggested by Pinnock et al.[22] with model calculated IR irradiance at the tropopause to estimate GWPs of HFE-245fa2, which are shown in Table 4. Oyaro et al.[13] obtained a very similar IR spectrum of HFE-245fa2, but they used different atmospheric lifetimes of both HFE-245fa2 and CFC-11 and different $\text{GWP}_{\text{CFC-11}}(t)$ in their estimations. These calculations are simple, and the results can be easily compared. We recalculated our GWPs using the same parameters that Oyaro et al.[13] used in their calculations to obtain the values shown in parentheses in Table 4. Thus calculated values can be compared with those from Oyaro et al.[13] shown on the next line. One can see that both estimation techniques yield the same GWPs when the same input data are used. It was also demonstrated in our recent paper[6] where we estimated GWPs of 2,3,3,3-tetrafluoropropene to be identical to those estimated by Papadimitriou et al.[23] who obtained very similar OH kinetic data and IR data and used the same calculation approach as was used by Oyaro et al.[13] Thus, the difference in estimated GWPs is almost entirely due to the differences in input parameters.

ASSOCIATED CONTENT

Ⓢ Supporting Information

The IR absorption cross sections of CH_3OCF_3 (HFE-143a) and CH_3OCH_2F (HFE-152a) obtained with spectral resolutions of 0.25 cm^{-1} and $CHF_2OCH_2CF_3$ (HFE-245fa) obtained with spectral resolutions of 0.5 cm^{-1}. 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.

Present Address

§American University of Armenia, 40 Marshal Baghramian Ave., Yerevan 0019, Armenia.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

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(3) Certain commercial equipment, instruments, or materials are identified in this article in order to adequately specify the experimental procedure. Such identification does not imply recognition or endorsement by both the National Institute of Standards and Technology and the Institute of Energy Problems of Chemical Physics, nor does it imply that the material or equipment identified is necessarily the best available for the purpose.

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