JOURNAL OF GEOPHYSICAL RESEARCH, VOL. 103, NO. D21, PAGES 28,181–28,186, NOVEMBER 20, 1998

Lifetimes and global warming potentials for dimethyl ether and for fluorinated ethers: CH_3OCF_3 (E143a), CHF_2OCHF_2 (E134), CHF_2OCF_3 (E125)

D. A. Good and J. S. Francisco

Department of Chemistry and Department of Earth and Atmospheric Science, Purdue University
West Lafayette, Indiana

A. K. Jain and D. J. Wuebbles

Department of Atmospheric Science, University of Illinois Urbana-Champaign, Urbana

Abstract. Using recent kinetic data, two-dimensional (2-D) chemical-transport modeling of the atmospheric lifetimes of dimethyl ether and fluorinated ethers CH_3OCF_3 (E143a), CHF_2OCHF_2 (E134), and CHF_2OCF_3 (E125) shows that E134 and E125 have substantially larger lifetimes than previously estimated. Dimethyl ether has a short atmospheric lifetime of 5.1 days and a relatively insignificant radiative forcing leading to a relatively low global warming potential. Increasing fluorination is accompanied by slower rates of reaction with hydroxyl radical and ultimately longer lifetimes. E143a, E134, and E125 were found to have lifetimes of 5.7, 29.7, and 165 years, respectively. In addition, our work uses ab initio methodology to determine IR absorption cross sections for each ether. Our study finds that E134 and E125 have significant infrared absorption and thus relatively high radiative forcing values. These two properties together yield global warming potentials for E134 and E125 of 5720 and 14,000, respectively, integrated over a 100 year period.

1. Introduction

Dimethyl ether is a proposed diesel fuel substitute while fluorinated ethers are proposed CFC/HCFC replacements in foam blowing and refrigeration applications [*Sehested et al.*, 1996; *Zhang et al.*, 1992; *Hsu and Demore*, 1995]. Attractive features of these ethers include the absence of chlorine and the incorporation of hydrogen. Chlorine is known to catalytically degrade ozone in the stratosphere, thus its removal in the troposphere lowers the molecule's ozone depletion potential (ODP) (a measure of a molecule's potential effects on ozone defined as the change in total ozone concentration per unit mass emission of the gas) [*Wuebbles*, 1995]. The incorporation of hydrogen allows removal of the ether via hydrogen abstraction by tropospheric hydroxyl radical. In addition to affecting its influence on ozone, the rate of removal determines the molecule's atmospheric lifetime, which in turn influences global warming properties. A molecule's relative ability to affect climatic change is quantitatively described by the global warming potential (GWP) which incorporates both the molecule's lifetime and the ability to absorb radiation (its radiative forcing). A molecule's radiative forcing is a measure of the change in net irradiance (W m^{-2}) at the tropopause after allowing for stratospheric temperatures to readjust to stratospheric equilibrium. The time-integrated radiative forcing resulting from the instantaneous release of a kilogram of trace gas expressed relative to that of a kilogram of a reference gas, usually CO_2, defines a molecule's GWP [*Intergovernmental Panel on Climate Change* (*IPCC*), 1990, 1996]. GWPs, however, are integrated over a range of time periods (rather than to steady state) due to the complexity of the carbon cycle effects on CO_2 concentrations. Previous experimental and theoretical studies of these ethers suggest shorter lifetimes than analogous fluorinated hydrocarbons [*Cooper et al.*, 1992; *Zhang et al.*, 1992]. Shorter atmospheric lifetimes generally translate into lower GWPs depending on where and how strongly the molecule absorbs infrared radiation. Below 7 μm (1400 cm^{-1}), water in the atmosphere absorbs infrared radiation, while above 12 μm (800 cm^{-1}), both water and CO_2 effectively absorb. This leaves a window between 7 and 12 μm where there is less infrared radiation absorption. CFCs and other anthropogenic substances with absorption features in this region can absorb, effectively closing this window at specific wavelengths and can significantly affect global climate [*IPCC*, 1990; *Ramanathan et al.*, 1985]. Information on where and how strongly a molecule absorbs is obtained through a determination of the molecule's vibrational profile, i.e., band position and band strength. This work uses prior evaluation of the vibrational profile of dimethyl and fluorinated ethers. By combining this with evaluations of their lifetimes, the environmental significance of these species is determined relative to their ability to affect global climate. Presented in this work are lifetimes, relative radiative forcings, and global warming potentials calculated for dimethyl ether and the fluorinated ethers CH_3OCF_3 (E143a), CHF_2OCHF_2 (E134), and CHF_2OCF_3 (E125).

Paper number 98JD01880.
0148-0227/98/98JD-01880$09.00

2. Lifetime

A molecule's lifetime is defined as the ratio of its atmospheric burden to that of its combined loss mechanisms and is the time it takes for a substance to decrease by $(1/e)$ 36.8% of

Table 1. Lifetime of Ether Species Due to OH Loss Only

Species	Rate Expression	Scaling Relative to *Prinn et al.* [1995] (4.9 years)		Scaling Relative to *WMO* [1995] (5.9 years)	
		Calculated	Model	Calculated	Model
CH_3OCH_3	[a]$6.7 \times 10^{-12}e^{-300/T}$	0.014	0.012	0.017	0.014
CH_3OCF_3	[b]$1.9 \times 10^{-12}e^{-1555/T}$	4.7	4.7	5.7	5.7
CHF_2OCHF_2	[b]$1.9 \times 10^{-12}e^{-2006/T}$	24.1	24.6	29.0	29.7
CHF_2OCHF_2	[b]$4.7 \times 10^{-13}e^{-2095/T}$	134.0	137.0	162.0	165.0

All values expressed in years.
[a]*Wallington et al.* [1988].
[b]*Hsu and Demore* [1995].

its original concentration [e.g., *WMO*, 1995; *Wuebbles*, 1995]. For the molecules evaluated, photolysis should be relatively unimportant, implying reaction with hydroxyl radical (OH) is the principal removal mechanism. The UV-vis absorption of the fluorinated ethers has been neither measured nor calculated. The first excited state of dimethyl ether is found to be about 185 nm [*Bremner et al.*, 1991]. Ethers released into the atmosphere will not encounter radiation of this energy until they reach past the stratosphere. For this reason the lifetimes of fluorinated ethers are expected to be dominated by their reaction with tropospheric hydroxyl radical. The expression for a molecule's lifetime is shown in (1) where k is the rate constant for reaction with hydroxyl radical at a specified temperature taken as the globally averaged atmospheric temperature, 277 K [*Prather and Spivakovsky*, 1990].

$$\tau = 1/k[\mathrm{OH}] \tag{1}$$

Rate constants are those of *Hsu et al.* [1995] and *Wallington et al.* [1988]. The concentration of hydroxyl radical is taken from the work of *Prinn et al.* [1995] who determined a global weighted-average lower-atmospheric OH concentration of $9.7 \pm 0.6 \times 10^5$ radicals cm^{-3} based on their observations of methyl chloroform concentration and evaluation of its budget. The derived atmospheric lifetime of methyl chloroform (4.9 years due to tropospheric OH loss and 4.8 years due to total atmospheric OH loss) along with its atmospheric concentration are used to estimate the globally averaged OH concentration.

Another approach to lifetime determinations can be made through the use of global atmospheric chemical-transport models that represent all of the known relevant processes. The zonally averaged two-dimensional chemical-radiative-transport model used in this study to determine the atmospheric lifetimes of the ethers determines the distributions of important trace constituents in the troposphere, stratosphere, and mesosphere. The photochemical mechanism typically represents the chemical and physical interactions of about 50 chemical species and stratospheric aerosols and accounts for about 150 chemical and photochemical reactions in the atmosphere [*Wuebbles et al.*, 1995, 1997; *Kinnison et al.*, 1994].

A common practice for more accurately evaluating atmospheric lifetimes of gases reacting primarily with OH is to scale the lifetime of a particular species, x, relative to methyl chloroform such that

$$\tau_x/\tau_{CH_3CCl_3} = k_{CH_3CCl_3}/k_x \tag{2}$$

The methyl chloroform-hydroxyl radical rate expression is $1.8 \times 10^{-12}e^{-1550/T}$ [*DeMore et al.*, 1994]. In Table 1, columns 3 and 5 list the atmospheric lifetime of each species using (2). Column 3 uses a methyl chloroform lifetime of 4.9 years as determined by *Prinn et al.* [1995] for tropospheric OH loss, while column 5 uses a 5.9 year methyl chloroform lifetime as recommended by *WMO* [1995]. Columns 4 and 6 list lifetimes of the ethers as computed from the chemical transport model. Column 4 is scaled with the 4.9 year methyl chloroform lifetime, while column 6 uses the 5.9 year chloroform lifetime. Plate 1 illustrates the results of the chemical transport model. The concentration of each ether is shown as a function of altitude. Dimethyl ether with its fast rate of reaction with hydroxyl radical degrades very quickly within the troposphere. From model calculations the lifetime of dimethyl ether is found to be ~0.015 years (~5.1 days). Little dimethyl ether would be transported into the stratosphere and would thus have little impact on the stratosphere's ozone layer if reactions from its degradation products could affect ozone. Slower reaction rates and longer lifetimes accompany increasing fluorination. CHF_2OCHF_2, (E134) and CHF_2OCF_3, (E125) are shown in Table 1 to have substantial lifetimes, with E125 having a lifetime of 134–165 years. These ethers are predicted to reach well beyond the troposphere; see Plate 1. Previous evaluations implied shorter lifetimes for fluorinated ethers; however, our analysis contradicts these conclusions [*Cooper et al.*, 1992; *Zhang et al.*, 1992]. In the kinetic investigation by *Hsu et al.* [1995] a relative rate technique was used which negates the effects of unwanted side reactions caused by impurities. As a result, the rate data from *Hsu et al.*'s [1995] investigation are substantially slower than those of *Zhang et al.* [1992]. Slower reaction rates lead to longer atmospheric lifetimes and may impart significant global warming properties to these ethers depending on the molecule's specific infrared absorption features.

3. Radiative Forcing

Band positions and band strengths for each ether have been determined from ab initio methodology in a previous study [*Good et al.*, 1998]. Optimizations were performed with Becke nonlocal three parameter exchange and correlation functional with the Lee-Yang-Parr correctional functional method (B3LYP). The B3LYP calculations were performed with the large 6-311++G(3df,3pd) basis set. This method was found to have a rms error of 2.7% in determining band positions of these ethers [*Good et al.*, 1998]. Absorption cross sections were integrated over a spectral width of 100 cm^{-1}. Integrated band strengths predicted by ab initio calculations lie between 10 to

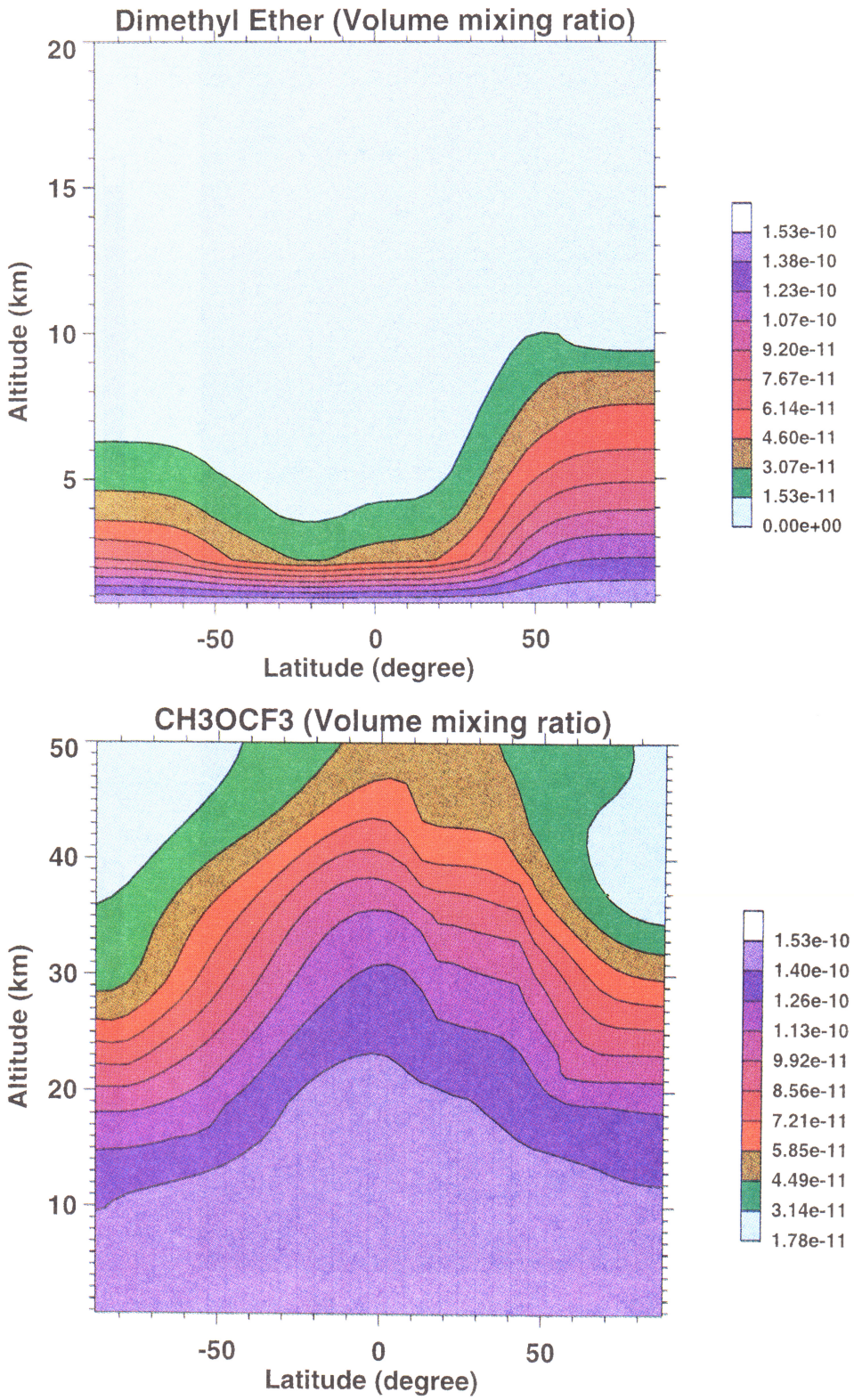
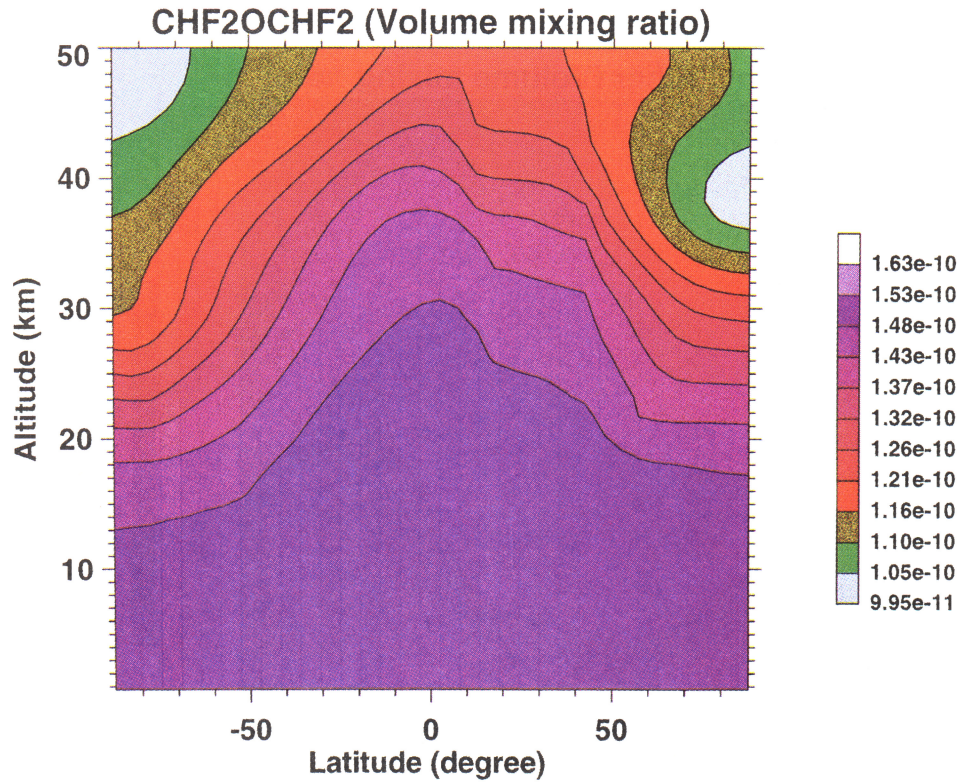


Plate 1. Atmospheric concentration distribution of dimethyl ether, CH_3OCF_3 (E143a), CHF_2OCHF_2 (E134), and CHF_2OCF_3 (E125), from 2-D chemical-transport model. The model is first run to steady state with current surface mole fractions specified for major source gases. Since the current atmospheric abundances of the ethers studied here are expected to be quite small, their global distributions in the background atmosphere are assumed to be zero. The surface abundances of dimethyl ether, E143a, E134, and E125, are then perturbed with 1ppb one at a time, and the model is run to steady state.



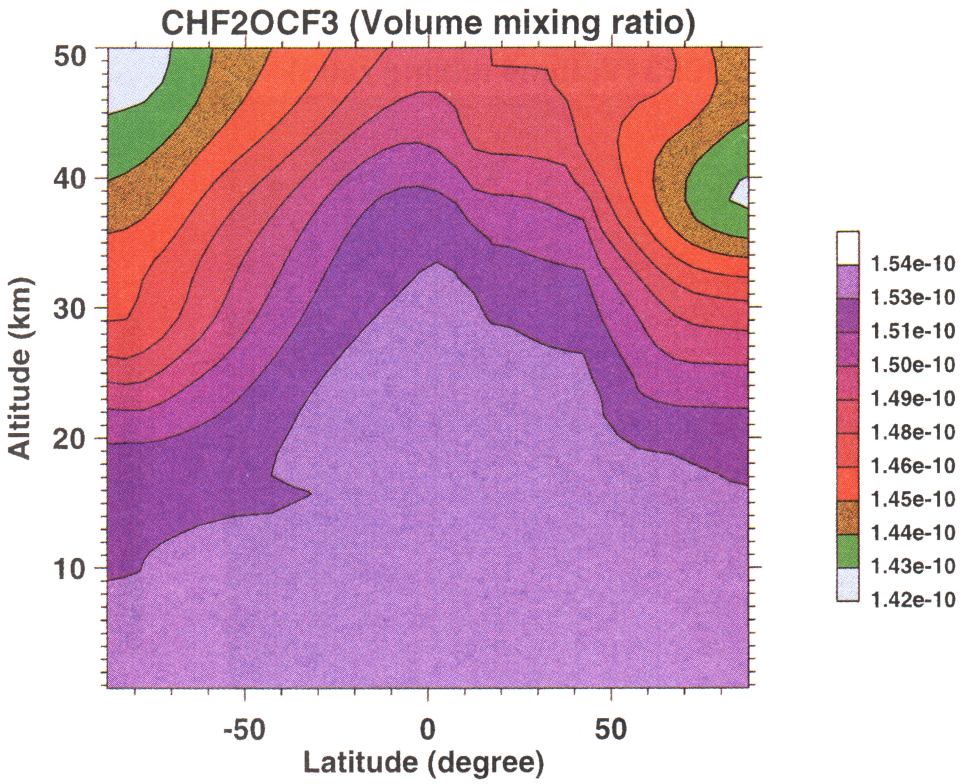


Plate 1. (continued)

15% above experimentally derived results. This error is within the deviation of 10–25% between experimentally determined cross-section data [*Pinnock et al.*, 1995]. Band strengths are then used with a radiative transfer model for the global atmosphere to determine radiation budgets as a function of altitude. The longwave and shortwave radiation schemes of this model have been used in the climate community model (CCM) of the National Center for Atmospheric Research (NCAR) to compute long wave and short wave radiation [*Briegleb*, 1992]. This narrowband model incorporates integrated cross sections into 30, 100 cm^{-1} bands extending from 0.0 to 3000 cm^{-1}. The radiative transfer model contains vertical profiles of pressure

Table 2a. Radiative Forcings (W m^{-2} ppb^{-1}) Using Experimental Vibrational Data

Forcing Agent	Calculated			Average (IPCC)	Relative to CFC-11 per Unit Molecule
	McDaniel et al.	Clerbaux et al.	Varanasi et al.		
CFC-11	0.24	···	0.25	0.245 (0.22)	1.00
CFC-12	0.29	0.32	0.32	0.31 (0.28)	1.27 (1.27)
HCFC-22	0.20	0.23	0.22	0.216 (0.19)	0.88 (0.86)

Table 3. Global Warming Potentials Calibration Relative to *IPCC* [1996] Values

Greenhouse Gas	20 year Integration	100 year Integration	500 year Integration[a]
CFC-11	4700 (4900)	3680 (3800)	1320 (1400)
CFC-12	7520 (7800)	7890 (8100)	3900 (4200)
HCFC-22	3860 (4000)	1460 (1500)	450 (520)

IPCC values are in parentheses. All values expressed relative to CO_2. Instantaneous injection of 1 kg of each gas.
[a]from *Wuebbles* [1995].

and temperature. Vertical mixing ratios of H_2O, O_3, CO_2, CH_4, and N_2O over 35 levels as well as cloud coverage at three levels are incorporated. Calculated radiative forcings for CFC-11, CFC-12, and HCFC-22 using experimentally derived band strengths compare well with *IPCC* [1996] estimates. Table 2a compares the model-estimated radiative forcing values as well as their ratio to CFC-11 with recent *IPCC* [1996] estimates. The band strengths used were those of *McDaniel et al.* [1991], *Varanasi et al.* [1988], and *Clerbaux et al.* [1993]. The average of the three data sets differs from IPCC estimates by 11.4, 10.7, and 13.7% for CFC-11, CFC-12, and HCFC-22, respectively. Column 6 in Table 2a shows that the relative ratio to CFC-11 compares extremely well with *IPCC* [1996] estimates.

Table 2b also lists radiative forcing values for species using absorbance cross sections as determined from ab initio methodology. Structurally similar HFC analogs to the fluorinated ethers were investigated for comparative purposes. For all species the raw radiative forcing values are overestimated (Table 2b, column 2). Their relative values, however, compare reasonably well with literature values. Column 3 of Table 2b lists forcing values relative to CFC-11 and scaled by the *IPCC* [1996] forcing value for CFC-11 (0.22 W m^{-2} ppb^{-1}). Column 4 of Table 2b lists forcing values relative to CFC-12 and scaled by the *IPCC* [1996] forcing value for CFC-12 (0.28 W m^{-2} ppb^{-1}).

Dimethyl ether, as expected, has a very low radiative forcing as predicted from its vibrational spectra. Dimethyl ether's intense CH stretching bands resonate around 3000 cm^{-1} well outside the 7–12 μm window region. Each of the fluorinated ethers in Table 2 has a forcing value considerably larger than its HFC analog. E143a has a forcing value slightly lower than that of CFC-12, while the remaining two ethers, E134 and E125, have larger radiative forcings per unit amount in the atmosphere. The C-F and C-O stretching modes of these ethers resonate within the 7–12 μm band; thus increases in fluorination are accompanied by an increase in the molecule's radiative forcing [*Good et al.*, 1998].

4. Global Warming Potentials

GWP calculations integrate the molecule's atmospheric lifetime and its radiative forcing into one expression to evaluate the cumulative effect of emissions of a greenhouse gas on climate. The time-integrated radiative forcings for CO_2 are based on the approach of *IPCC* [1996], using a CO_2 decay response calculated by Siegenthaler and Joos carbon cycle model [*IPCC*, 1996; *Siegenthaler and Joos*, 1992].

Table 3 tabulates estimated global warming potentials for CFC-11, CFC-12, and HFC-22 relative to CO_2 compared to *IPCC* [1996] estimates shown in parentheses. An average error of 3.3% exists between this work and the *IPCC* [1996] estimates. Table 4 lists global warming potentials for the ethers. As expected, the long lifetimes and intense absorption features within the 7–12 μm window of E134 and E125 result in substantial global warming potentials. Table 4 also compares GWP values for HFCs structurally similar to each ether. Lifetimes and global warming potentials for each HFC were taken from *IPCC* [1996]. HFC-125 has a lifetime of 32.6 years, thus its GWP decreases substantially over longer integration periods. Conversely, the GWP of E125 increases from 20 to 100 year integrations and then declines due to its relatively large lifetime of 165 years. E134 has a lifetime longer than both HFC-134 and HFC-134a, thus leading to higher global warming potentials across all integration periods. Over short integration periods the GWP of E134 is similar in magnitude to that of E125 due to similarities in their radiative forcings (0.49 and 0.47 W m^{-2} ppb^{-1} for E125 and E134, respectively). Over longer integration periods however, the differences in lifetimes begins to dominate the GWP. Over a 100 year integration the

Table 2b. Radiative Forcings (W m^{-2} ppb^{-1}) Using ab Initio Vibrational Data

Forcing Agent	Raw Forcing Value	Forcing Scaled Relative to CFC-11 (0.22 W m^{-2} ppb^{-1})	Forcing Scaled Relative to CFC-12 (0.28 W m^{-2} ppb^{-1})	Literature Value
CFC-11	0.29	0.22	0.24	0.22[a]
CFC-12	0.34	0.26	0.28	0.28[a]
CF_3CH_3 (HCF143a)	0.18	0.14	0.15	0.168[b]
CHF_2CHF_2 (HFC134)	0.25	0.19	0.21	0.18[b]
CF_3CHF_2 (HFC125)	0.36	0.27	0.29	0.25[b]
CH_3OCH_3	0.02	0.02	0.02	···
CH_3OCF_3 (E143a)	0.31	0.24	0.26	···
CHF_2OCHF_2 (E134)	0.57	0.43	0.47	···
CHF_2OCF_3 (E125)	0.60	0.46	0.49	···

[a]*IPCC* [1996].
[b]From *Pinnock et al.* [1995].

Table 4. Comparison of Alternative Hydrocarbons

Species	Chemical Formula	Lifetime, years	Global Warming Potential, 20 years	Global Warming Potential, 100 years	Global Warming Potential, 500 years
HFC-125	CHF_2CF_3	32.6	4600	2800	920
E125	CHF_2OCF_3	165.2	11800	1400	9120
HFC-134	CHF_2CHF_2	10.6	2900	1000	310
E134	CHF_2OCHF_2	29.7	9760	5720	1830
HFC-134a	CH_2FCF_3	14.6	3400	1300	420
HFC-143a	CH_3CF_3	48.3	5000	3800	1400
E143a	CH_3OCF_3	5.7	2200	656	202
HFC-143	CH_2FCHF_2	3.8	1000	300	94
DME	CH_3OCH_3	0.015	1.2	0.3	0.1

HFC values from *IPCC* [1996].

GWP for E134 (5720) is 41% that of the E125 GWP (14,000), while over a 500 year integration the GWP of E134 (1830) is only 20% that of the E125 GWP (9120). E143a has a lifetime and thus GWP intermediate to that of HFC-143 and HFC-143a over all time integrations.

5. Conclusions

Dimethyl ether appears to be atmospherically benign with respect to its ability to affect global climate. A short atmospheric lifetime and a lack of significant absorption features in the window region combine to yield a small GWP. Unless there are unrealistically large emissions, dimethyl ether should not contribute significantly to global warming.

E143a appears to be an improvement over analogous halocarbons, while E134 and E125 are long-lived species with significant global warming properties. Plate 1 indicates that substantial concentrations of these ethers will reach the stratosphere. For these ethers, photolysis may become an important removal mechanism capable of competing with reaction with hydroxyl radical. The importance of photolysis as a removal mechanism and the atmospheric fate of formed degradation products are needed to fully characterize the environmental significance of these ethers.

Acknowledgments. Work at the University of Illinois was supported in part by the NASA ACMAP and by the U.S. EPA.

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J. S. Francisco and D. A. Good, Department of Chemistry and Department of Earth and Atmospheric Sciences, Purdue University, West Lafayette, IN 47907-1393. (e-mail: jfrancis@chem.purdue.edu)

A. K. Jain and D. J. Wuebbles, Department of Atmospheric Sciences, University of Illinois Urbana-Champaign, Urbana, IL 61801.

(Received May 4, 1998; revised May 21, 1998; accepted May 29, 1998.)