Atmospheric gas-phase degradation and global warming potentials of 2-fluoroethanol, 2,2-difluoroethanol, and 2,2,2-trifluoroethanol

Stig Rune Sellevåg\textsuperscript{a}, Claus J. Nielsen\textsuperscript{a,b,*}, Ole Amund Søvde\textsuperscript{b}, Gunnar Myhre\textsuperscript{b}, Jostein K. Sundet\textsuperscript{b}, Frode Stordal\textsuperscript{b}, Ivar S.A. Isaksen\textsuperscript{b}

\textsuperscript{a}Department of Chemistry, University of Oslo, P.O. Box 1033, Blindern, N-0315 Oslo, Norway
\textsuperscript{b}Department of Geosciences, University of Oslo, P.O. Box 1022, Blindern, N-0315 Oslo, Norway

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Abstract

The vapour phase reactions of 2-fluoroethanol, 2,2-difluoroethanol, and 2,2,2-trifluoroethanol with OH radicals and Cl atoms were studied at 298 K and 1013 mbar using long-path FTIR detection. The following reaction rate coefficients were determined by the relative rate method: $k_{298}(OH+CH_2FCH_2OH)=(1.42\pm0.11)\times10^{-12}$, $k_{298}(OH+CHF_2CH_2OH)=(4.51\pm0.06)\times10^{-13}$, $k_{298}(OH+CF_3CH_2OH)=(1.23\pm0.06)\times10^{-13}$, $k_{298}(Cl+CH_2FCH_2OH)=(2.67\pm0.3)\times10^{-11}$, $k_{298}(Cl+CHF_2CH_2OH)=(3.12\pm0.06)\times10^{-12}$, and $k_{298}(Cl+CF_3CH_2OH)=(7.42\pm0.12)\times10^{-13}$ cm$^3$ molecule$^{-1}$ s$^{-1}$; the reported uncertainties represent 3\textsigma from the statistical analyses and do not include any systematic errors or uncertainties in the reference rate coefficients. Quantitative infrared cross-sections of the title compounds at 298 K are reported in the 4000–50 cm$^{-1}$ region.

A 3D chemistry transport model was applied to calculate the atmospheric distributions and lifetimes of the title compounds; the global and yearly averaged lifetimes were calculated as 20 days for CH$_2$FCH$_2$OH, 40 days for CHF$_2$CH$_2$OH, and 117 days for CF$_3$CH$_2$OH. Radiative forcing calculations were carried out assuming either constant vertical profiles or the distribution derived from the chemistry transport model. The Global Warming Potentials for the title compounds are insignificant compared to, e.g. CFC-11 (CCl$_3$F).

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1. Introduction

The Montreal Protocol and amendments (1987) led to the phase out of a series of chlorofluorocarbons, CFCs, in industrialised countries, mainly not only because of their ozone depletion in the stratosphere, but also because of their high global warming potentials, GWPs (Zurer, 1993; IPCC, 1994). An intensive investigation of potential CFC replacements, mainly organic compounds containing hydrogen, fluorine or chlorine atoms was therefore initiated about 10 years ago, in order to estimate their ozone depletion potentials and their GWPs (Fisher et al., 1990; Clerbaux et al., 1993;
Ravishankara et al., 1993, 1994; Pinnock et al., 1995; Christidis et al., 1997; Myhre et al., 1999; Highwood and Shine, 2000).

Partially fluorinated alcohols, FAs, are potential alternatives for CFCs and HCFCs in certain industrial applications. To determine the environmental impact of FAs released into the troposphere, the atmospheric lifetimes and the nature and fate of the resulting oxidation products are needed. This, in turn, requires kinetic data for the atmospheric oxidation processes and information on the degradation mechanisms; the first step of their atmospheric degradation is the reactions with OH radicals.

The aim of this investigation is to calculate the GWPs for CH₃FCH₂OH, CHF₃CH₂OH, and CF₃CH₂OH, and to this purpose infrared absorption cross-sections and reaction rate constants have been determined. Further, degradation products of these fluorinated alcohols have been measured in order to contribute to the understanding of possible environmental impact of these compounds. The compounds studied here react relatively fast in the atmosphere, indicating that these components will not be homogeneously distributed in the troposphere. In previous radiative forcing and GWP studies of CFCs and CFC replacements it has been assumed that the gases have a homogeneous mixing ratio in the troposphere as the lifetime of such gases are typically many years. For gases with a short lifetime the abundance will decrease strongly with altitude. Greenhouse gases are most efficient in long wave radiation trapping around the tropopause level, and therefore the calculated radiative forcing and GWP will be reduced substantially for short-lived components, compared to results assuming a homogeneous mixing ratio in the atmosphere.

Only limited information of direct relevance to the environment is available on the title compounds besides a few preliminary results (Kelly et al., 2001), only rate coefficients for the OH reaction with 2,2,2-trifluoroethane (Wallington et al., 1988; Tokuhashi et al., 1999), and for the Cl atom reactions with the three ethanols are available (Papadimitriou et al., 2003).

2. Experimental details and model description

2.1. Relative rate and product studies

Relative rate experiments and product studies of the alcohol–radical reactions were carried out at 298 ± 2 K and 1013 ± 3 mbar in synthetic air in a 250 L stainless-steel reactor equipped with a multiple reflection White-type mirror system having an optical base path of 2 m and adjusted to give a total optical path of 120 m. The optical system is connected to a Bruker IFS 88 FT-IR spectrometer, allowing in situ analysis of intermediates and final products. Spectra were generally recorded from the time of mixing and to a maximum of 3 h by coadding 100 scan (collection time ca. 60 s) at 0.5 cm⁻¹ instrumental resolution.

In the relative rate method, RR, the reaction rate coefficient for the compound of interest is measured relatively to a reference compound with a known rate coefficient. If the reactants react solely with the same radical and none of the reactants is created in any side reactions, the relative rate coefficient, $k_{rel}$, is given according to the following expression:

$$\ln \left( \frac{[A]_t}{[A]_0} \right) = k_{rel} \ln \left( \frac{[R]_t}{[R]_0} \right),$$

where $A$ is the compound of interest and $R$ is the reference compound. $[A]_0$, $[R]_0$, $[A]_t$ and $[R]_t$ are concentrations of $A$ and $R$ at the start and at the time $t$, respectively, and $k_A$ and $k_R$ are reaction rate coefficients.

OH radicals were produced by photolysis of O₃ in the presence of H₂O employing two Philips TL 20 W/12 fluorescence lamps ($\lambda_{max} \sim 310$ nm) in a quartz tube inserted into the reaction chamber. Cl atoms were generated by photolysis of Cl₂ using two Philips TLD 18 W/08 fluorescence lamps ($\lambda_{max} \sim 375$ nm). Typical initial volume fractions were: alcohols, 2–5 ppm V; reference compounds (acetone, ethane or 1,2-dichloroethane), 2–5 ppm V; Cl₂, 5–10 ppm V; H₂O, 500–1000 ppm V; O₃, 50–100 ppm V. Purified air containing 80% N₂ and 20% O₂ (CO + NO₃ <100 ppb and C₆H₆ <1 ppm) and oxygen gas (99.95%) were delivered from AGA. All organic compounds were purified/degassed by doing three freeze–pump–thaw cycles.

Spectral subtraction was used to find the relative concentrations of the reactants at different time intervals during the reactions. The relative rate coefficients were determined according to Eq. (1) by using a weighted least-squares method that includes uncertainties in the concentration of both reactants (York, 1966). Each relative rate coefficient was determined from three independent measurements. The reported uncertainties in this work represent 3σ from the statistical analyses and do not include any systematic errors or uncertainties in the reference rate coefficients. Based on the residuals in the spectral subtraction, the uncertainty in the relative concentrations of the reactants is estimated to be 0.01.

2.2. Infrared absorption cross-sections

The absorption cross-section of a compound J at a specific wavenumber $\nu$ is according to Beer–Lambert’s law given by $\sigma(\nu) = A_{abs}(\nu)/\nu n_l$, where $A_{abs}(\nu) = -\ln \tau(\nu)$ is the molar absorptance, $\tau$ is the transmittance, $n_l$ is the number density of J and $l$ is the path length where the absorption takes place. The integrated absorption...
intensity, $S_{int}$, is given by

$$S_{int} = \int_{band} \sigma(\nu) \, d\nu.$$  \hspace{1cm} (2)

Infrared spectra of the pure gases at room temperature were recorded in the region 50–4000 cm$^{-1}$ using a Bruker IFS 113v FTIR employing a nominal resolution of 1 cm$^{-1}$ (boxcar apodisation). KBr and Mylar beamsplitters of various thicknesses were used to cover the spectral region. To ensure optical linearity, only deuterated triglycine sulphate (DTGS) detectors were used. Cells of 2.34, 9.89 and 19 cm length equipped with windows of KBr, CsI and high-density polyethylene, respectively, were employed. The partial pressures of the gases in the cells were from 4 to 70 mbar and were measured using MKS Baratron pressure transducers. The cross-sections were obtained from the absorbance spectra assuming that the gas was ideal and applying a baseline correction. The latter was performed by subtracting a polynomial function, obtained by fitting the regions of the spectrum where no absorptions were expected.

2.3. Chemical transport model

The distribution of the three hydrofluoroalcohols is simulated with a Chemical Tracer Model, the Oslo CTM2. The model is run with spin up to make certain that the tracer distribution is representative of the model chemical steady state. The model is run in 5.6 $\times$ 5.6° horizontal resolution and with 19 levels from the surface up to 10 hPa (approximately 32 km). Since the hydrofluoroalcohols are degraded by the hydroxyl radical, which is produced when ozone is photo-dissociated, a comprehensive chemical scheme is included in the calculations. Further, emissions of a range of natural and anthropogenic emissions need to be included, of e.g. a range of ozone precursors. The anthropogenic surface emissions are taken from the EDGAR data base (Olivier et al., 1996) and the natural emissions from GEIA (Yienger and Levy, 1995) and Müller (Muller, 1992). In Acerboni et al. (2001) a similar set up was used to estimate the 3D distribution of short-lived tracers, but there the surface concentrations were set to 1 pptv as the surface boundary for the whole globe. This is unrealistic and has been refined here to make a more realistic pattern of the surface concentrations. We have used emissions for the three hydrofluoroalcohols with a geographical distribution as for CFC-11 emissions, at levels that yield globally averaged surface concentrations of 1 ppbv. This will affect also the vertical distribution of short-lived components under investigation. It is a difficult task to model the vertical transport of such components, since the transport (foremost the convection) and emission patterns must have a high degree of coherence to be able to represent accurately the transport of the tracers to the upper troposphere. The results in Acerboni et al. (2001) were likely an upper limit on the effect of short-lived gases. The result here is probably more realistic in establishing a realistic vertical distribution of short-lived components with surface emissions. Only chemical reaction with OH is included in the CTM calculations, since reaction with Cl will be of much smaller impact for the lifetime and atmospheric distribution of the fluorinated alcohols.

2.4. Radiative transfer model

An emissivity/absorptivity thermal infrared broad band model is used in the radiative forcing calculations. It has been used in several studies of radiative forcing of CFCs and CFC replacements (Myhre and Stordal, 1997; Myhre et al., 1999; Acerboni et al., 2001). A spatial resolution of 10 $\times$ 10° is used in the calculations with climatological values of water vapour, temperature, and clouds (Myhre and Stordal, 1997).

$\text{CH}_3\text{FCH}_2\text{OH}$, $\text{CHF}_2\text{CH}_2\text{OH}$, and $\text{CF}_3\text{CH}_2\text{OH}$ are included in the model with 6, 5, and 8 bands, respectively. The annual mean latitudinal and height distribution as calculated with the CTM is used for the species. To comply with the weak line limit we have scaled down the concentrations from the CTM linearly. The radiative transfer calculations are performed for a global and annual mean surface abundance of 0.1 ppbV. In the radiative forcing calculations we follow the concept described in IPCC (2001) to calculate cloudy sky forcing with stratospheric temperature adjustment included. Our estimates only include the thermal infrared part. However, some of the gases studied here may have a minor contribution at solar wavelengths.

3. Results and discussion

3.1. Kinetic study and degradation products

To determine the atmospheric chemical lifetimes, we have investigated the rate coefficients of the OH and Cl reactions

$\text{CH}_3\text{FCH}_2\text{OH} + \text{OH} + \text{Cl} \rightarrow \text{products}$, \hspace{1cm} (I)

$\text{CHF}_2\text{CH}_2\text{OH} + \text{OH} + \text{Cl} \rightarrow \text{products}$, \hspace{1cm} (II)

$\text{CF}_3\text{CH}_2\text{OH} + \text{OH} + \text{Cl} \rightarrow \text{products}$. \hspace{1cm} (III)

The rate coefficients for the OH reactions were measured using ethane, $\text{CH}_3\text{CH}_3$, as the reference compound. The wavenumber region 2920–2850 cm$^{-1}$, i.e., part of the C–H stretching region, was analysed in order to determine the relative concentrations of $\text{CH}_3\text{CH}_3$ while the 960–900 cm$^{-1}$ region was used to quantify $\text{CF}_3\text{CH}_2\text{OH}$, Fig. 1. FTIR reference spectra of
HCHO, CF₃CH₂OH, C₂H₆, CH₃CHO, HCOOH, H₂O, O₃, H₂O and a sloping baseline were included in the spectral subtractions. An example of the residuals after the spectral subtractions is also included in Fig. 1. Details of the spectral subtractions employed to retrieve the concentrations of the individual reactants are summarized in Table 1.

Fig. 2 shows the decay of CF₃CH₂OH vs. CH₃CH₃ in the presence of OH radicals, plotted according to Eq. (1). As can be seen, there is a clear curvature in the data series suggesting that secondary radical reactions are taking place, and that these are faster for CH₃CH₃ than for CF₃CH₂OH. As will be discussed later CF₃O radicals will eventually be produced in the degradation of CF₃CH₂OH and it is this radical that causes the interfering reactions. It is known that CF₃O radicals react with the reference compound ethane with a rate coefficient of 1.2 × 10⁻¹² cm³ molecule⁻¹ s⁻¹ (Saathoff and Zellner, 1993), which is faster than the corresponding OH reaction. As illustrated in Figs. 3 and 4, the kinetic data for the OH reactions with CHF₂CH₂OH and CH₂FCH₂OH vs. CH₃CH₃ fall on straight lines, indicating that interfering radicals are not produced from these two reactions. Leaving out the data points in the CF₃CH₂OH reaction for a degree of reaction of more than 25% of CH₃CH₃ from the analysis gives a relative rate coefficient of 0.547 ± 0.019 (3σ statistical error) for CF₃CH₂OH vs. CH₃CH₃, and 1.903 ± 0.016 and 5.81 ± 0.19 for the CHF₂CH₂OH and CH₂FCH₂OH, respectively. Using \( k_{989}(\text{OH} + \text{CH₃CH₃}) = 2.4 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \) (Sander et al., 2003) places the OH reaction rate coefficients for CF₃CH₂OH, CHF₂CH₂OH, CH₂FCH₂OH on an absolute scale at respectively (1.31 ± 0.05) × 10⁻¹³, (4.57 ± 0.04) × 10⁻¹³, and (1.39 ± 0.05) × 10⁻¹² cm³ molecule⁻¹ s⁻¹, Table 2.

The rate coefficients for the Cl reactions were measured using different reference compounds; CH₃COO(CH₃)₃ (acetone) and CH₂ClCH₂Cl were used in the case of CF₃CH₂OH, CHF₂CH₂OH was measured relatively to CH₃COO(CH₃)₃, while CHF₂CH₂OH was measured relatively to CH₂ClCH₂Cl. The wavenumber region 3050–3000 cm⁻¹, i.e., part of the C–H stretching region, was analysed in order to determine the relative concentrations of CH₃COO(CH₃)₃. Again the 960–900 cm⁻¹ region was used to quantify CF₃CH₂OH. FTIR reference spectra of CH₃COO(CH₃)₃, CF₃CH₂OH CH₃COCl, CF₂O, HCl, HCOOH, H₂O and a sloping baseline were included in the spectral subtractions.

Fig. 5 shows the decay of CF₃CH₂OH vs. CH₂ClCH₂Cl and vs. CH₂ClCH₂Cl in the presence of Cl atoms, and was plotted according to Eq. (1). In both cases the data fall on straight lines suggesting that the secondary radical reactions interfering in the OH study are of minor importance here. Also the data points from the kinetic studies of CHF₂CH₂OH vs. CH₃COO(CH₃)₃ and CH₂FCH₂OH vs. CH₂ClCH₂Cl fall on straight lines as shown in Figs. 6 and 7, respectively.

The kinetic results are collected in Table 2 and compared with data from the literature. As can be seen, there is good agreement between the different OH reaction rate coefficients reported for CF₃CH₂OH, but the rate coefficients measured by absolute techniques (Wallington et al., 1988; Tokuhashi et al., 1999) are ca. 25% lower than the one from this work measured by the relative rate technique. Some of the apparent discrepancy may be due to error in the value of the reaction rate coefficient of the reference compound, some may be due to secondary radical reactions. Our results for the rate coefficients of the Cl reaction with the three fluorinated alcohols agree with the recent results of
Papadimitriou et al. (2003) taking the uncertainties in the reaction rate coefficients of the reference compounds into account.

The gas-phase degradations of CH$_2$FCH$_2$OH, CHF$_2$CH$_2$OH and CF$_3$CH$_2$OH were studied using chlorine atoms as the oxidizing agent. The corresponding fluoroacetaldehydes CH$_2$FCHO, CHF$_2$CHO and CF$_3$CHO were observed as intermediates in agreement with the results of Papadimitriou et al. (2003). In the case of 2,2,2-trifluoroethanol, both CO and CO$_2$, CF$_3$O, and additional traces of CF$_3$COOH and HF were observed. Papadimitriou et al. (2003) estimated the reaction enthalpies and the C–H and O–H bond enthalpies from B3P86/6-311++G(2df,p) DFT calculations and reported $\Delta_{\text{bond}}^{\text{H}}(\text{CH}_2)$~$\Delta_{\text{bond}}^{\text{H}}(\text{CH}_3)$~$\Delta_{\text{bond}}^{\text{H}}(\text{CH}_3)$~$\Delta_{\text{bond}}^{\text{H}}(\text{OH})$~$60$ kJ mol$^{-1}$. Although the OH reaction is ca. 55 kJ mol$^{-1}$ more exothermic than the Cl reaction ($\Delta_{\text{react}}^{\text{H}}$($\text{HCl+OH}$$\rightarrow$Cl + H$_2$O) = $-57.5$ kJ mol$^{-1}$, calculated at the same level of theory)
it is not unreasonable to assume that the OH and Cl-initiated oxidations will have similar mechanisms. We therefore propose that the first steps in the gas-phase degradation of \( \text{CH}_2\text{FCH}_2\text{OH} \) \((x = 2)\), \( \text{CHF}_2\text{CH}_2\text{OH} \) \((x = 1)\) and \( \text{CF}_3\text{CH}_2\text{OH} \) \((x = 0)\) are

\[
\begin{align*}
\text{CH}_x\text{F}_{3-x}\text{CH}_2\text{OH} & \rightarrow \text{CH}_x\text{F}_{3-x}\text{CHOH} \\
& \rightarrow \text{CH}_x\text{F}_{3-x}\text{CHO}.
\end{align*}
\] (IV)

The atmospheric chemistry of \( \text{CF}_3\text{CHO} \) has recently been studied by Sellevåg et al. (2004). It was found that the atmospheric lifetime of \( \text{CF}_3\text{CHO} \) is mainly determined by its OH reaction rate coefficient: only an upper limit to the photolysis was reported suggesting that photolysis might be of some importance. As far as we are aware of, no experimental data is available on the atmospheric fate of \( \text{CH}_2\text{FCHO} \) and \( \text{CHF}_2\text{CHO} \). Based on the results from the present work and analogies with the reaction of \( \text{CH}_3\text{CHO} \), the gas-phase degradation of the three fluoroacetaldehydes will mainly result in the formation of the corresponding fluoromethyl radicals. The atmospheric chemistry of the \( \text{CF}_3 \) radical has been described in detail by Ko et al. (1994) and by Sehested and Wallington (1993). The \( \text{CH}_2\text{F} \) and \( \text{CHF}_2 \) radicals will likely react with oxygen to form HFCO and \( \text{CF}_2\text{O} \), respectively.

### 3.2. Infrared absorption cross-section

The infrared spectra of \( \text{CH}_2\text{FCH}_2\text{OH}, \text{CHF}_2\text{CH}_2\text{OH}, \) and \( \text{CF}_3\text{CH}_2\text{OH} \) are shown in Fig. 8. The integrated absorption cross-sections (base e) for all three compounds are included in the legends. The quality of our cross-section data has been investigated by comparing with the earlier well-studied \( \text{CHClF}_2, \text{HCFC-22} \) (Ballard et al., 2000). The integrated cross-sections obtained with our Bruker 113v is within 3% of the average value reported in this intercomparison. This in turn suggests that the absolute error limits in our measurements be in the order of ±5%.

### 3.3. CTM2 model results

The spatial distribution of the hydrofluoroalcohols is calculated with the CTM. Figs. 9 and 10 show the

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**Table 2**

<table>
<thead>
<tr>
<th>Molecule</th>
<th>( k_{\text{OH}} ) ((\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}))</th>
<th>( k_{\text{Cl}} ) ((\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}))</th>
<th>Technique and reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{CH}_2\text{FCH}_2\text{OH} )</td>
<td>((1.39 \pm 0.05) \times 10^{-12})</td>
<td>((2.0 \pm 0.4) \times 10^{-11})</td>
<td>VLPRc, RR-FTIR (this work)</td>
</tr>
<tr>
<td>( \text{CHF}_2\text{CH}_2\text{OH} )</td>
<td>((4.57 \pm 0.04) \times 10^{-13})</td>
<td>((2.67 \pm 0.03) \times 10^{-12})</td>
<td>VLPRc, RR-FTIR (this work)</td>
</tr>
<tr>
<td>( \text{CF}_3\text{CH}_2\text{OH} )</td>
<td>((1.31 \pm 0.05) \times 10^{-13})</td>
<td>((7.51 \pm 0.17) \times 10^{-13})</td>
<td>DF-LIF, LP-LIF, FP-LIFg</td>
</tr>
</tbody>
</table>

Errors quoted correspond to 3σ.

- Relative to \( k_{298}(\text{OH} + \text{CH}_3\text{CH}_3) = 2.4 \times 10^{-13} \text{cm}^3\text{molecule}^{-1}\text{s}^{-1} \) (Sander et al., 2003).
- Relative to \( k_{298}(\text{Cl} + \text{CH}_3\text{COCH}_3) = 2.0 \times 10^{-12} \text{cm}^3\text{molecule}^{-1}\text{s}^{-1} \) (Sellevåg and Nielsen, 2003).
- VLPR, very low pressure reactor technique (Papadimitriou et al., 2003).
- Relative to \( k_{298}(\text{Cl} + \text{CH}_3\text{CH}_3) = 5.7 \times 10^{-11} \text{cm}^3\text{molecule}^{-1}\text{s}^{-1} \) (Sander et al., 2003).
- Relative to \( k_{298}(\text{Cl} + \text{CH}_2\text{ClCH}_2\text{Cl}) = 1.3 \times 10^{-12} \text{cm}^3\text{molecule}^{-1}\text{s}^{-1} \) (Wallington et al., 1996).
- FP-RF, flash photolysis resonance fluorescence (Wallington et al., 1988).
- DF, discharge flash; LP, laser photolysis; LIF, laser-induced fluorescence (Tokuhashi et al., 1999).
surface abundance and the zonal mean vertical profile of CF₃CH₂OH, which has the longest lifetime of the three species. The surface pattern shows three distinct maxima over industrialized regions reflecting the surface emissions. Fig. 10 shows a very strong hemispheric difference and that the abundance of CF₃CH₂OH decreases strongly with altitude. The patterns of the atmospheric distribution of the two other hydrofluoroalcohols are similar to the one for CF₃CH₂OH, but with a stronger decrease in abundance with altitude. This is a result of the difference in reaction rates with OH.

The chemical lifetimes calculated with the CTM are 19.8, 39.6, 117.4 days for CH₂FCH₂OH, CHF₂CH₂OH, and CF₃CH₂OH, respectively. This is very short compared to the CFCs and many CFC replacements, but longer than the species investigated in Acerboni et al. (2001).

3.4. Radiative transfer calculations

The radiative forcing calculations for the three hydrofluoroalcohols are shown in Table 3 for atmospheric distribution calculated with the CTM as well as for a distribution which assumes a constant vertical
The radiative forcing due to the hydrofluoroalcohols is very low compared to CFCs and many CFC replacements when applying the atmospheric distribution from the CTM. This is owing to the strong decrease of the species with altitude since the greenhouse gases are most efficient in trapping thermal infrared radiation around the tropopause altitude. The radiative forcings, obtained by applying a distribution with a constant vertical profile, are similar to those of most CFCs and their replacements \(-0.1\text{–}0.35\,\text{Wm}^{-2}\text{ppbv}^{-1}\) (IPCC, 2001). The short lifetimes of the fluorinated alcohols result in a decrease in their concentrations with increasing altitude and in a factor of 2.5–7 lower radiative forcing than calculated using a constant vertical distribution.

Acerboni et al. (2001) introduced a normalized radiative forcing, defined as the radiative forcing divided by the integrated band strength (in \(10^{17}\text{W} \text{m}^{-1}\text{molecule}^{-1}\)). We have calculated this quantity here for the three components under investigation. In the case with constant vertical distribution the normalized radiative forcing is between 1.3 and 1.9 with CHF\(_2\)CH\(_2\)OH and CF\(_3\)CH\(_2\)OH having the highest and lowest value, respectively. CF\(_3\)CH\(_2\)OH has low values owing to some strong absorption bands at high wavenumbers in a spectral region with strong water vapour overlap and with low thermal infrared energy. Most of the CFCs have their absorption bands mainly in the atmospheric window region (about 1200–800 cm\(^{-1}\)) with weak overlap with other gases and thus a higher normalized radiative forcing than these hydrofluoroalcohols, e.g. CFC-11 has a value around 2.5. However, the normalized radiative forcings for the hydrofluoroalcohols in this study are higher than the values for the

![Fig. 8. Infrared absorption cross sections (4000–50 cm\(^{-1}\), base e) of 2-fluoroethanol, 2,2-difluoroethanol, and 2,2,2-trifluoroethanol. Absolute integrated absorption intensities in units of \(10^{17}\text{cm molecule}^{-1}\): \(\text{CH}_2\text{FCH}_2\text{OH}, S_{\text{int}}(1600–460\text{cm}^{-1}) = 4.53\pm0.14\); \(\text{CHF}_2\text{CH}_2\text{OH}, S_{\text{int}}(1550–700\text{cm}^{-1}) = 6.20\pm0.17\); \(\text{CF}_3\text{CH}_2\text{OH}, S_{\text{int}}(1600–610\text{cm}^{-1}) = 13.73\pm0.18\)](image)

![Fig. 9. Atmospheric surface abundance of CF\(_3\)CH\(_2\)OH in ppbV as modelled with the Oslo CTM.](image)
In the case with CTM calculated atmospheric distribution CF\textsubscript{3}CH\textsubscript{2}OH has normalized radiative forcing 0.55 and the two other compounds 0.26.

### Global warming potentials

IPCC (2001) uses global warming potential (GWP) as a simple measure to compare the effectiveness of equal mass emissions of various climate gases. The report discusses its limitations, and gives a background of its concept. The GWP is given relative to another gas, either CO\textsubscript{2} or CFC-11.

GWP calculations are performed here using both CFC-11 and CO\textsubscript{2} as reference gases. For calculations using CO\textsubscript{2} as a reference gas the expression given in IPCC (2001) (same expression as IPCC (1994) with modified constant) is used to establish the radiative forcing with an abundance of CO\textsubscript{2} of 364 ppmv and an increase of 1 ppmv. The lifetime expression for CO\textsubscript{2} is the same as the one adopted in IPCC (2001). With CFC-11 as a reference gas, we use the radiative forcing of 0.25 W m\textsuperscript{-2} ppb\textsuperscript{-1} and lifetime of 45 years from IPCC (2001).

Table 4 shows the GWP for the three hydrofluoroalcohol investigated for 3 time horizons for CO\textsubscript{2} and CFC-11 as reference gases. The three species have very low GWP values compared to various halocarbons (see IPCC, 2001). This is a result of two factors which are both due to the short lifetime of the compounds. First, the radiative forcing is low, since the concentration of the species in the upper troposphere is low as discussed above, and second the lifetime is an important factor for the integrated radiative forcing over a time horizon. However, the GWP values are higher than for the perfluoroalkenes studied in Acerboni et al. (2001). CF\textsubscript{3}CH\textsubscript{2}OH has more than a factor of ten higher GWP values than the two other compounds owing to its longer lifetime.

### Atmospheric implications

The results show that the three fluorinated ethanol have chemical lifetimes in the troposphere ranging from 20 to 120 days and that their primary oxidation products
are fluorinated aldehydes, which in principle are benign to the environment. The secondary gas-phase products are CHFO and CF₂O, which within days will be incorporated into droplets/aerosols and hydrolysed to give CO, CO₂ and HF (Debruyn et al., 1995). The additional fluorine ions in the liquid phase will be negligible compared to the global F⁻ budget (Sehested and Wallington, 1993).

The fluorinated ethanols may, however, also be removed from the troposphere by uptake in cloud droplets and subsequent rainout. Recently, the Henry's law constant for 2,2,2-trifluoroethanol has been measured by Chen et al. (2003). The Henry's law constant varies between 44.6 and 255 M atm⁻¹ in the temperature range from 275 to 299 K, that is 2,2,2-trifluoroethanol is less soluble than ethanol. Chen et al. (2003) also estimated the wet-deposition lifetime to be 343 days, suggesting that 30% of 2,2,2-trifluoroethanol is likely to be oxidised in water droplets in the environment. CF₃CH₂OH may therefore lead to trifluoroacetic acid (TFA, CF₃COOH) in water droplets.

The studied HFA's are CFC replacements with very low GWP values, as a result of their short lifetimes. The GWP values are lower than most of earlier studies for CFCs and CFC replacements.

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References


Table 4

<table>
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<th>Compound</th>
<th>Time horizon (yr)</th>
<th></th>
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</thead>
<tbody>
<tr>
<td></td>
<td>20</td>
<td>100</td>
<td>500</td>
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<tr>
<td>CH₂FCH₂OH</td>
<td>3.00 (0.00046)</td>
<td>0.89 (0.00018)</td>
<td>0.28 (0.00016)</td>
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<td>CHF₂CH₂OH</td>
<td>6.03 (0.00091)</td>
<td>1.79 (0.00037)</td>
<td>0.56 (0.00033)</td>
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<tr>
<td>CF₃CH₂OH</td>
<td>61.4 (0.0093)</td>
<td>18.3 (0.0038)</td>
<td>5.67 (0.0033)</td>
<td></td>
</tr>
</tbody>
</table>

GWP values relative to CFC-11 are in parenthesis.


