1,1,1,3,3,-Pentafluorobutane (HFC-365mfc): Atmospheric Degradation and Contribution to Radiative Forcing

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ABSTRACT: The rate constant for the reaction of the hydroxyl radical with 1,1,1,3,3-pentafluorobutane (HFC-365mfc) has been determined over the temperature range 278-323 K using a relative rate technique. The results provide a value of $k(OH + CF_2CH_2CF_2CH_2) = 2.0 \times 10^{-12}$ $exp(-1750 \pm 400/T)$ cm³ molecule⁻¹ s⁻¹ based on $k(OH + CH_3CCl_3) = 1.8 \times 10^{-12}$ exp $(-1550 \pm 150/T)$ cm³ molecule⁻¹ s⁻¹ for the rate constant of the reference reaction. Assuming the major atmospheric removal process is via reaction with OH in the troposphere, the rate constant data from this work gives an estimate of 10.8 years for the tropospheric lifetime of HFC-365mfc. The overall atmospheric lifetime obtained by taking into account a minor contribution from degradation in the stratosphere, is estimated to be 10.2 years. The rate constant for the reaction of Cl atoms with 1,1,1,3,3-pentafluorobutane was also determined at 298 ± 2 K using the relative rate method, $k(Cl + CF_2CH_2CF_2CH_2) = (1.1 \pm 0.3) \times 10^{-15}$ cm^3 molecule⁻¹ s⁻¹. The chlorine initiated photooxidation of CF₂CH₂CF₂CH₄ was investigated from 273-330 K and as a function of O₂ pressure at 1 atmosphere total pressure using Fourier transform infrared spectroscopy. Under all conditions the major carbon-containing products were CF₂O and CO₂, with smaller amounts of CF₃O₃CF₃. In order to ascertain the relative importance of hydrogen abstraction from the $-CH_2$ and $-CH_3$ groups in CF₂CH₂CF₂CH₂, rate constants for the reaction of OH radicals and Cl atoms with the structurally similar compounds CF₂CH₂CCl₂F and CF₂CH₂CF₂ were also determined at 298 K k(OH + CF₂CH₂CCl₂F) = $(8 \pm 3) \times 10^{-16}$ cm³ molecule⁻¹ s⁻¹; k(OH + CF₂CH₂CF₂) = $(3.5 \pm 1.5) \times$ 10^{-16} cm³ molecule⁻¹ s⁻¹; $k(Cl + CF_3CH_2CCl_2F) = (3.5 \pm 1.5) \times 10^{-17}$ cm³ molecule⁻¹ s⁻¹]; $k(Cl + CF_2CH_2CF_2) < 1 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. The results indicate that the most probable site for H-atom abstraction from CF₃CH₂CF₂CH₃ is the methyl group and that the formation of carbonyl compounds containing more than a single carbon atom will be negligible under atmospheric conditions, carbonyl difluoride and carbon dioxide being the main degradation products. Finally, accurate infrared absorption cross-sections have been measured for CF₃CH₂CF₂CH₃, and jointly used with the calculated overall atmospheric lifetime of 10.2 years, in the NCAR chemical-radiative model, to determine the radiative forcing of climate by this CFC alternative. The steady-state Halocarbon Global Warming Potential, relative to CFC-11, is 0.17. The Global Warming Potentials relative to CO₂ are found to be 2210, 790, and 250, for integration time-horizons of 20, 100, and 500 years, respectively. © 1997 John Wiley & Sons, Inc. Int J Chem Kinet **29:** 607–617, 1997.

INTRODUCTION

1,1,1,3,3-pentafluorobutane is envisioned as an eventual replacement for CCl₂FCH₂ (HCFC-141b) which is used as a blowing agent for polyurethane foams. HCFC-141b is itself the main substitute for CFC-11 (CCl₂F) in this application, but under the provisions of the Montreal Protocol on Substances that Deplete the Ozone Layer, its uses will be phased down starting in 2004, with virtual elimination occurring by 2020. Earlier phase-out will be required in the USA, the European Union, and Japan. The long atmospheric lifetimes of CFCs allow them to be transported to the stratosphere, where they release chlorine, resulting in the catalytic destruction of ozone [1-3]. Hydrochlorofluorocarbons (HCFCs) and hydrofluorocarbons (HFCs) resemble CFCs in their physical and chemical characteristics, but the presence of at least one hydrogen atom in these compounds means that they are degraded largely in the troposphere following reaction with the hydroxyl radical [4-6]. Although the replacement of CFCs by HCFCs results in considerably reduced ozone loss, the presence of chlorine in these compounds means that the small amounts entering the stratosphere give rise to some ozone depletion. Since HFCs do not contain chlorine, their contribution to stratospheric ozone depletion is expected to be negligible; however, it is important to determine their environmental impact with respect to their Global Warming Potential (GWP) and degradation products.

The purpose of this work was to determine the rate constant for the reaction of OH radicals with $CF_3CH_2CF_2CH_3$ as a function of temperature, to identify the products arising from its oxidation under atmospheric conditions, to measure the infrared absorption cross-sections of $CF_3CH_2CF_2CH_3$ and to calculate its Global Warming Potential. These data are required in order to evaluate the environmental impact of $CF_3CH_2CF_2CH_3$.

EXPERIMENTAL

Rate Constants and Degradation Mechanisms

Relative rate and product studies were carried out at atmospheric pressure in an FEP Teflon cylindrical reaction vessel (volume ca. 50 litre) surrounded by fluorescent lamps. Photolysis experiments in the range 300-450 nm were carried out using 10 sunlamps (Philips TL 20/09) and 10 blacklamps (Philips TL 20/08). Twenty Philips TUV 15W germicidal lamps were used as a source of radiation at 254 nm. The vessel and lamps were enclosed in a thermostatically controlled chamber which allowed reactions to be studied over the temperature range 273-330 K. Electric fans positioned below the reaction vessel helped provide a uniform reaction temperature, which was monitored by two chromel/alumel thermocouples placed within the chamber. Light intensity was varied by switching off various sets of lamps. All pressure measurements were made using MKS Baratron capacitance manometers. Measured amounts of reagents were flushed from calibrated Pyrex bulbs into the reaction vessel by a stream of zero-grade nitrogen (Air Products); the vessel was then filled to its full capacity with either ultra-pure air (Air Products) or mixtures of zero-grade nitrogen and zero-grade oxygen (Air Products). Reaction mixtures were allowed to mix for at least 30 min prior to the start of photolysis. Quantitative analyses were carried out using gas chromatography (Shimadzu Model 14A, with flame ionization detection) and FTIR spectroscopy (Mattson Polaris). Samples of reaction mixtures were drawn through a Valco gas sampling valve for gas chromatographic analysis. Infrared spectra were obtained using an evacuable 2 litre Teflon-coated Wilks cell, containing a multipass White mirror arrangement, mounted in the cavity of the spectrometer. After various periods of photolysis, the reaction mixtures were expanded into the cell through 3 mm inner diameter Teflon tubing. Spectra were recorded using a 10 m path length at 5 minute intervals, the spectral range was 500 to 3500 cm⁻¹ with a resolution of 4 cm⁻¹ and the spectra derived from 128 scans. Reference spectra and calibration curves for each com-

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pound were obtained by expanding known pressures of authentic samples of the compounds into the IR cell. Ozone concentrations were determined by a Monitor Labs 8810 UV photometric ozone analyzer.

Infrared Absorption Cross-Sections

High-resolution absorption cross-sections for HFC-365mfc were determined at room temperature in the infrared atmospheric window spectral range. The infrared spectra were recorded using the procedure and set-up described in detail in previous publications [7,8]. The gas was introduced into a laboratory-built thermostated cell [9] maintained at 287 ± 0.5 K. The cell was placed inside the air evacuated chamber of the FTIR spectrometer (Bruker IFS120HR). Infrared spectra were obtained between 600 and 1500 cm⁻¹ at 0.03 cm⁻¹ spectral resolution. For each of the 6 pressures investigated, ranging from 1 to 5 torr, 100 scans of the moving mirror were co-added in order to obtain a good signal-to-noise ratio.

Materials

1,1,1,3,3-pentafluorobutane (99 wt.%), 1,1,1,3,3hexafluoropropane (>97 mol%), and 1,1-dichloro-1,3,3,3-tetrafluoropropane (99.8 mol%) were obtained from Solvay S.A., Belgium and vacuum distilled. Chlorine, HCl (Matheson, research grade), CF₂O, CCIFO, CF₃COCF₃, CH₃CCl₂F, (Fluorochem Ltd.), and 1,1,1-trichloroethane (Fluka) were used as received. Ozone was produced by passing zero-grade oxygen through an ozone generator (Monitor Labs) directly into the reaction chamber.

RESULTS AND DISCUSSION

Rate Constants and Degradation Mechanisms

(*i*) *Relative Rate Studies:* The rate constant for the reaction of OH radicals with $CF_3CH_2CF_2CH_3$ was determined relative to that for reaction with CH_3CCl_3

$$OH + CF_3CH_2CF_2CH_3 \longrightarrow products \qquad (1)$$

$$OH + CH_3CCl_3 \longrightarrow products$$
 (2)

Ozone was photolyzed in the presence of water vapor to generate OH radicals.

$$O_3 + h\nu(\lambda = 254 \text{ nm}) \longrightarrow O(^1D) + O_2$$
 (3)

$$O(^{1}D) + H_{2}O \longrightarrow OH + OH$$
 (4)

Assuming that substrate and reference are consumed only by OH radicals it can be shown that:

$$\ln\{[CF_3CH_2CF_2CH_3]_0/[CF_3CH_2CF_2CH_3]_t\} = k_1/k_2\ln\{[CH_3CCl_3]_0/[CH_3CCl_3]_t\}$$
(I)

where the subscripts 0 and *t* indicate concentrations before irradiation and at time *t*, respectively. Direct photolytic loss of $CF_3CH_2CF_2CH_3$ and CH_3CCl_3 was unimportant and the reaction mixtures were stable in the dark for at least 5 h.

Mixtures of O₃, H₂O, CF₃CH₂CF₂CH₃, and CH₃CCl₃ in air were photolyzed for about 25 min in the temperature range 278-323 K with $[CF_3CH_2CF_2CH_3]_0$ and $[CH_3CCl_3]_0 = 1-10$ ppm; $[O_3]_0 = 100 - 1,000 \text{ ppm};$ and $[H_2O]_0 = 2,000 - 1,000 \text{ ppm};$ 10,000 ppm, (1 ppm = 2.46×10^{13} molecule cm⁻³ at 298 K, and 760 torr total pressure). Under the reaction conditions employed the substrate and reference compound were found to decay by approximately 20% during the experiments. Data for the runs were plotted in the form of eq. (I), Figure 1, and show the expected linear relationship. The rate constant $k_1/k_2 = 0.58 \pm 0.04$, (error is $\pm 2\sigma$ and represents precision only), was independent of relative reactant concentration, reaction time, and light intensity in agreement with the proposed mechanism. A possible source of error is the reaction of $O(^1D)$ with $CF_3CH_2CF_2CH_3$ and CH_3CCl_3 . The rate constant for the reaction of $O(^{1}D)$ with $H_{2}O$, $k_4 = 2.2 \times 10^{-10} \,\mathrm{cm}^3$ molecule⁻¹ s⁻¹ [10] is sufficiently high that under the experimental conditions employed with $H_2O \ge 100 [CF_3CH_2CF_2CH_3]_0$ or [CH₃CCl₃]₀, O(¹D) is efficiently scavenged in reaction (4). Based on the rate of reactant loss in the reac-



Figure 1 Concentration-time data for the reaction of OH radicals with CF₃CH₂CF₂CH₃ and CH₃CCl₃ at 298 K.

tor, the steady-state concentrations of OH and O(¹D) are estimated to be around 2.5×10^{10} and 2.5×10^{2} molecules cm⁻³, respectively. Hence depletion of CF₃CH₂CF₂CH₃ and CH₃CCl₃ by reaction with O(¹D) will be unimportant compared to loss by reaction with OH. Variations in water vapor pressure from 1–10 torr had no measurable effect on the value of k_1/k_2 , thus providing support for this assumption. Chlorine atoms are generated from the reaction of OH with CH₃CCl₃ in the presence of O₂ [11], however, this species will be rapidly removed by reaction with O₃.

Using recent absolute rate constant measurements for the reaction of OH + CH₃CCl₃ at 298 K, $(k_2 =$ 1.0×10^{-14} [12], $k_2 = 0.95 \times 10^{-14}$ [13], and $k_2 = 1.1 \times 10^{-14}$ [14] cm³ molecule⁻¹ s⁻¹), provides a value for $k_1(OH + CF_3CH_2CF_2CH_3) =$ $(5.9 \pm 0.4) \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K}.$ The error in the rate constant for the reference reaction probably adds a further 15% to the uncertainty in k_1 . The values of k_1/k_2 obtained at five different temperatures over the range 278-323 K show little variation with temperature and are plotted in Arrhenius form in Figure 2. A linear least-squares fit of the data gives $k_1(OH + CF_3CH_2CF_2CH_3)/$ $k_2(OH + CH_3CCl_3) = 1.13 \exp(-202 \pm 200/T).$ Taking a value of $k_2(OH + CH_3CCl_3) = 1.8 \times$ $10^{-12} \exp(-1550 \pm 150/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} [15],$ provides an estimate of $k_1(OH + CF_3CH_2CF_2CH_3) =$ $2.0 \times 10^{-12} \exp(-1750/T)$ cm³ molecule⁻¹ s⁻¹ with total estimated errors of $\Delta(E/R) = \pm 400$ K. Mellouki et al. [16] have reported a value of $k_1 = (1.68 \pm 0.21) \times 10^{-12} \exp(-1585 \pm 80/T) \text{ cm}^3$ molecule⁻¹ s⁻¹ using a pulsed laser photolysis-laser induced fluorescence technique. The rate constant determined at 298 K, $k_1 = (8.69 \pm 0.74) \times 10^{-15} \text{ cm}^3$



Figure 2 Arrhenius plot for the ratio of rate constants for the reactions of OH radicals with $CF_3CH_2CF_2CH_3$ and CH_3CCl_3 .

molecule⁻¹ s⁻¹, is almost a factor of 1.5 higher than the rate constant determined in this work. DeMore [17] has recently described an empirical method for the estimation of the rate constants for reaction of OH with halocarbons based on the available experimental data for a wide range of halogenated methanes and ethanes. Typically, the rate constants derived from the method are within a factor of 1.3 of the experimental values. A value of $k_1 = 4.9 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1}$ s⁻¹ was calculated using the group contributions given by DeMore [17] and is in reasonable agreement with the experimental rate constant obtained in this study. The higher rate constant value determined by Mellouki et al. [16] is likely to be due to the presence of reactive impurities in the sample of CF₂CH₂CF₂CH₂ used by these authors. The tropospheric lifetime for HFC-365mfc, which may be assumed to degrade essentially by reaction with the OH radical in the troposphere, may be calculated by means of the equation:

$$\tau(\text{HFC-365mfc})/\tau(\text{CH}_3\text{CCl}_3)$$

= k(OH + CH_3\text{CCl}_3)/k(OH + HFC-365mfc)

where τ (HFC-365mfc) is the tropospheric lifetime of HFC-365mfc, τ (CH₃CCl₃) is the lifetime of CH₃CCl₃ with respect to reaction with OH in the troposphere, and the OH rate constants refer to a temperature of 277 K [18]. Using the numerical values τ (CH₃CCl₃) = 5.9 years [19], k(OH + CH₃CCl₃) = $1.8 \times 10^{-12} \exp(-1550/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} [15],$ and k(OH + HFC-365mfc) from this work, one can calculate that the tropospheric lifetime of HFC-365mfc is 10.8 years. On the other hand, using the value of k(OH + HFC-365mfc) from [16], the lifetime would be 7.1 years. In order to determine the overall atmospheric lifetime of HFC-365mfc, τ , a correction must be applied to the tropospheric lifetime τ (HFC-365mfc), to allow for degradation in the stratosphere using the equation $(1/\tau) =$ $1/\tau$ (HFC-365mfc) + $1/\tau$ (strat), where τ (strat) is the lifetime with respect to transport to the stratosphere and degradation there. Degradation of HFC-365mfc in the stratosphere is expected to be mainly initiated via reaction with OH, since photolysis and reaction with $O(^{1}D)$ are likely to play only a minor role [20]. An estimate of τ (strat) = 170 years for HFC-365mfc was derived from the AER-2D model for structurally similar HFCs [21] and provides an estimate of 10.2 years for the overall atmospheric lifetime of HFC-365mfc.

In a similar series of experiments Cl_2 was photolyzed in the presence of $CF_3CH_2CF_2CH_3$ /reference compound/air mixtures with reactant concentrations



Figure 3 Concentration-time data for the reaction of Cl atoms with $CF_3CH_2CF_2CH_3/CH_3CCl_2F$ and $CF_3CH_2CCl_2F/CF_3CH_2CF_2CH_3$ mixtures at 298 K.

in the range 1-20 ppm. Chlorine atoms react with CF₃CH₂CF₂CH₃ and the reference, here CH₃CCl₂F:

 $Cl_2 + h\nu(\lambda = 300 - 450 \text{ nm}) \longrightarrow 2Cl$ (5)

 $Cl + CF_3CH_2CF_2CH_3 \longrightarrow products$ (6)

 $Cl + CH_3CCl_2F \longrightarrow products$ (7)

and

$$\begin{split} &\ln\{[CF_{3}CH_{2}CF_{2}CH_{3}]_{0}/[CF_{3}CH_{2}CF_{2}CH_{3}]_{t}\} \\ &= k_{6}/k_{7}\ln\{[CH_{3}CCl_{2}F]_{0}/[CH_{3}CCl_{2}F]_{t}\} \quad (II) \end{split}$$

Rate data plotted in the form of eq. (III) gave a good straight line, Figure 3, with slope $k_6/k_7 = 0.52 \pm 0.06$. Taking a value of $k_7(\text{Cl} + \text{CH}_3\text{CCl}_2\text{F}) = (2.2 \pm 0.2) \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} [22-25] k_6(\text{Cl} + \text{CF}_3\text{CH}_2\text{CF}_2\text{CH}_3) = 1.1 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K}$ with an estimated uncertainty of around 25%.

(*ii*) Degradation Studies: The reaction of OH radicals with $CF_3CH_2CF_2CH_3$ takes place via hydrogen atom abstraction:

$$OH + CF_3CH_2CF_2CH_3 \longrightarrow CF_3CH_2CF_2CH_2 + H_2O \quad (1a)$$

$$OH + CF_3CH_2CF_2CH_3 \longrightarrow CF_3CHCF_2CH_3 + H_2O \quad (1b)$$

Under atmospheric conditions the alkyl radicals formed will react consecutively with O_2 and NO [4,5] to give the corresponding alkoxy radicals:

$$CF_{3}CH_{2}CF_{2}CH_{2} + O_{2} + M \longrightarrow CF_{3}CH_{2}CF_{2}CH_{2}O_{2} + M$$
(8)

$$CF_{3}CH_{2}CF_{2}CH_{2}O_{2} + NO \longrightarrow CF_{3}CH_{2}CF_{2}CH_{2}O + NO_{2} \quad (9)$$

$$CF_{3}CHCF_{2}CH_{3} + O_{2} + M \longrightarrow CF_{3}CHO_{2}CF_{2}CH_{3} + M \quad (10)$$

$$CF_3CHOCF_2CH_3 + NO \longrightarrow CF_3CHOCF_2CH_3 + NO_2 \quad (11)$$

An accurate study of product formation from the reaction of OH radicals with $CF_3CH_2CF_2CH_3$ using FTIR spectroscopy proved impossible on account of interfering bands from the high concentrations of O₃ and H₂O required for the kinetic investigations of the reaction. However, the reaction of Cl atoms with the halocarbon can be used to produce the required haloalkyl radicals.

$$Cl + CF_{3}CH_{2}CF_{2}CH_{3} \longrightarrow CF_{3}CH_{2}CF_{2}CH_{2} + HCl \quad (6a)$$
$$Cl + CF_{3}CH_{2}CF_{2}CH_{3} \longrightarrow$$

$$CF_3CHCF_2CH_3 + HCl$$
 (6b)

Cl₂ (20–30 ppm) and CF₃CH₂CF₂CH₃ (5–10 ppm) in mixtures of N₂ and O₂ were photolyzed over the temperature range 278–330 K. The major products identified in all the runs were CF₂O, CO₂, and HCl together with small amounts of CF₃O₃CF₃. Figure 4 gives the infrared spectra obtained following the photolysis for 30 min of 30 ppm Cl₂ with 10 ppm CF₃CH₂CF₂CH₃ in air at 760 torr and 298 K after successive subtraction of reference spectra of CF₃CH₂CF₂CH₃ and CF₂O, respectively. The residual spectrum indicates the presence of very small



Figure 4 (a) Infrared spectra obtained following photolysis for 30 min of 30 ppm Cl_2 with 10 ppm $CF_3CH_2CF_2CH_3$ in air at 760 torr and 298 K and after successive subtraction of reference spectra of (b) reactants and (c) CF_2O .



Figure 5 Concentration-time profiles of $CF_2CH_2CF_2CH_3$ and CF_2O in the photolysis of Cl_2 (30 ppm) and $CF_3CH_2CF_2CH_3$ (10 ppm) in air at 760 torr and 298 K.

amounts of CF₃O₃CF₃. The results confirm the absence of carbon containing products other than CF₂O, CF₃O₃CF₃, and CO₂. Concentration-time profiles of the reactant, CF₃CH₂CF₂CH₃, and CF₂O from an experiment in which 30 ppm Cl₂ and 10 ppm CF₃CH₂CF₂CH₃ were photolyzed in air at 760 torr and 298 K are shown in Figure 5 and the yield of CF₂O is plotted as a function of the loss of CF₃CH₂CF₂CH₃ in Figure 6. The results shown that for conversions of CF₃CH₂CF₂CH₃ \leq 60%, the yield of CF₂O is close to 200%, and that of the minor product, CF₃O₃CF₃, less than 5%, within the experimental error (estimated to be ±5%).

The experimental data can be rationalized in terms of the following reactions:





Figure 6 Plot of the yield of CF_2O against the loss of $CF_3CH_2CF_2CH_3$ from the photolysis of Cl_2 (30 ppm) and $CF_3CH_2CF_2CH_3$ (10 ppm) in air at 760 torr and 298 K.

$$2CF_{3}CHO_{2}CF_{2}CH_{3} \longrightarrow 2CF_{3}CHOCF_{2}CH_{3} + O_{2} \quad (13)$$

By comparison with the reported data for alkoxy radicals of general structure R—CH₂O (where R is a halogenated alkyl group) [11,26–28], reaction with O₂ is likely to be the only significant loss for the CF₃CH₂CF₂CH₂O radical in both laboratory experiments and the atmosphere:

$$CF_{3}CH_{2}CF_{2}CH_{2}O + O_{2} \longrightarrow CF_{3}CH_{2}CF_{2}CHO + HO_{2}$$

Since aldehydes are expected to react with Cl atoms with rate constants which are orders of magnitude higher than for the parent halocarbons [29], CF₃CH₂CF₂CHO formed in reaction (14) will be rapidly removed by reaction with Cl atoms under the experimental conditions employed.

$$Cl + CF_{3}CH_{2}CF_{2}CHO \longrightarrow CF_{3}CH_{2}CF_{2}CO + HCl \quad (15)$$

$$\begin{array}{c} CF_{3}CH_{2}CF_{2}CO \,+\,O_{2}\,+\,M \longrightarrow \\ CF_{3}CH_{2}CF_{2}C(O)O_{2}\,+\,M \quad (16) \end{array}$$

$$2CF_{3}CH_{2}CF_{2}C(0)O_{2} \longrightarrow 2CF_{3}CH_{2}CF_{2}C(0)O + O_{2} \quad (17)$$

$$CF_3CH_2CF_2C(O)O \longrightarrow CF_3CH_2CF_2 + CO_2$$
 (18)

$$CF_{3}CH_{2}CF_{2} + O_{2} + M \longrightarrow CF_{3}CH_{2}CF_{2}O_{2} + M$$
(19)

$$2CF_{3}CH_{2}CF_{2}O_{2} \longrightarrow 2CF_{3}CH_{2}CF_{2}O + O_{2} \quad (20)$$

Carbon-carbon bond scission may be assumed to be the only important reaction pathway for the $CF_3CH_2CF_2O$ radical by comparison with the data for CF_3CF_2O [30–32], CHF_2CF_2O [33], CH_2FCF_2O [34], and CH_3CF_2O [30,31] radicals.

$$CF_3CH_2CF_2O \longrightarrow CF_3CH_2 + CF_2O$$

Further reactions of the CF_3CH_2 radical give rise to the formation of CF_3CHO [11,26–28] which subsequently reacts with Cl in the presence of O₂ to form CF_3 radicals and CO₂ [28]. CF_3 radicals will lead to the production of CF_2O or $CF_3O_3CF_3$.

$$CF_3 + O_2 + M \longrightarrow CF_3O_2 + M$$
 (22)

$$2CF_3O_2 \longrightarrow 2CF_3O + O_2 \qquad (23)$$

$$CF_3O_2 + CF_3O \longrightarrow CF_3O_3CF_3$$
 (24)

$$CF_3O \xrightarrow{\text{several steps}} CF_2O$$
 (25)

The yield of $CF_3O_3CF_3$ was relatively low and hence the conversion of CF_3O_2 radicals to CF_2O must be virtually quantitative. It is possible that CF_3O radicals formed in reaction (23) produce CF_3OH by hydrogen atom abstraction from $CF_3CH_2CF_2CH_3$, followed by heterogeneous loss of CF_3OH to give CF_2O [35]. Reaction of CF_3O with fluorocarbons has been shown to be relatively slow [36] and is unlikely to be the major source of CF_2O . Previous work from this laboratory has shown that the generation of CF_3O from the photolysis of $CF_3O_2CF_3$ in air gives high yields of CF_2O in the presence of Cl atoms [37]. Generation of CF_2O in the present system is consistent with the exothermic reactions (26) or (27).

$$CF_3O_2 + Cl \longrightarrow CF_2O + ClOF$$
 (26)

$$CF_3O + CI \longrightarrow CF_2O + CIF$$
 (27)

Abstraction of a hydrogen atom may also occur from the $-CH_2$ — group in $CF_3CH_2CF_2CH_3$, reaction (6b), leading to the formation of the alkoxy radical $CF_3CHOCF_2CH_3$ via reactions (10) and (13). This species may either decompose by C—C bond cleavage or react with O₂:

$$CF_3CHOCF_2CH_3 \longrightarrow CF_3 + CH_3CF_2CHO$$
 (28a)

$$CF_3CHOCF_2CH_3 \longrightarrow CF_3CHO + CH_3CF_2$$
 (28b)

$$CF_{3}CHOCF_{2}CH_{3} + O_{2} \longrightarrow CF_{3}C(O)CF_{2}CH_{3} + HO_{2} \quad (29)$$

Further reactions of the products of reaction (28) will yield CF_2O and $CF_3O_3CF_3$ in a series of reactions analogous to those described above. An authentic sample of $CF_3C(O)CF_2CH_3$, the product of the bimolecular reaction of $CF_3CHOCF_2CH_3$ with O_2 , was not available, however, the infrared spectrum of this compound is expected to exhibit similar features to that of $CF_3C(O)CF_3$. There was no evidence for the formation of $CF_3C(O)CF_2CH_3$ even at 273 K and 760 torr of O_2 , the most favorable conditions employed for the reaction of the alkoxy radical with O_2 relative to dissociation by carbon-carbon bond cleavage.

(iii) Position of Attack in the Reactions of OH and Cl with $CF_3CH_2CF_2CH_3$: The reaction scheme proposed to rationalize the formation of CF_2O with a

yield close to 200% in the Cl-atom initiated oxidation of CF₃CH₂CF₂CH₃ involves a series of carbon-carbon bond scission steps. It is possible, however, that of the carbonyl the absence compound, $CF_3C(O)CF_2CH_3$, from the products may reflect the low reactivity of the $-CH_2$ — site in the parent compound rather than the dominance of C-C bond scission in the CF₃CHOCF₂CH₃ radical compared to its reaction with O2. In order to examine the reactivity of the methylene group in CF₃CH₂CF₂CH₃ with respect to reaction with OH and Cl, rate constants were determined for the reaction of these species with $CF_3CH_2CCl_2F$ and $CF_3CH_2CF_3$. The $-CH_2$ groups in these compounds have similar molecular environments the methylene to group in CF₃CH₂CF₂CH₃ and the rate data should provide information on the reactivity of the $-CH_2$ group in 1,1,1,3,3-pentafluorobutane. Kinetic data from the photolysis of ozone in the presence of mixtures of CF₃CH₂CCl₂F/CF₃CH₂CF₂CH₃/H₂O and CF₃CH₂CF₃/CF₃CH₂CF₂CH₃/H₂O in air at 298 K are shown plotted in the form of eq. (I) in Figure 7. The data provide values of $k(OH + CF_3CH_2CCl_2F)/$ $k(OH + CF_3CH_2CF_2CH_3) = 0.13 \pm 0.04$ and $k(OH + CF_3CH_2CF_3)/k(OH + CF_3CH_2CF_2CH_3) =$ 0.06 ± 0.02 . Combination of the rate constant ratios with an estimate of $k_1(OH + CF_3CH_2CF_2CH_3) =$ $(5.9 \pm 0.4) \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ obtained in}$ this work at 298 K gives $k(OH + CF_3CH_2CCl_2F) =$ $(8 \pm 3) \times 10^{-16}$ cm³ molecule⁻¹ s⁻¹ and $k(OH + CF_3CH_2CF_3) = (3.5 \pm 1.5) \times 10^{-16}$ cm³ molecule⁻¹ s⁻¹ at 298 K. Agreement between the room temperature rate constant obtained for the reaction of OH with CF₃CH₂CF₃ and the values recently Hsu and DeMore reported by [38], $k = (3.4 \pm 1.3) \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ in a rel}^{-1}$



Figure 7 Concentration-time data for the reaction of OH radicals with $CF_3CH_2CCl_2F/CF_3CH_2CF_2CH_3$ and $CF_3CH_2CF_3/CF_3CH_2CF_2CH_3$ mixtures at 298 K.

ative rate study, by Garland and Nelson [39], $k = (4.15 \pm 0.33) \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1},$ using a laser photolysis-laser induced fluorescence method and by Gierczak et al. [40], k = $(3.2 \pm 0.6) \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ using a flash}$ photolysis-laser induced fluorescence technique is within the stated experimental errors. Thus, the rate constants for reaction of OH with CF₃CH₂CCl₂F or CF₃CH₂CF₃ are considerably smaller than that obtained for the overall reaction of OH with CF₃CH₂CF₂CH₃, suggesting that the major reaction channel for the reaction with CF₂CH₂CF₂CH₂ is via H-atom abstraction from the -CH₃ group. Estimates of the rate constants for reaction of OH at the $-CH_2$ and $-CH_3$ sites in $CF_3CH_2CF_2CH_3$ may be obtained using the empirical method developed by DeMore [17] for determination of rate constants for reaction with halocarbons. The results indicate that attack at the terminal methyl group is a factor of five faster than reaction at the methylene group.

Similar trends are shown by the rate constants determined for the reaction of Cl atoms with $CF_3CH_2CCl_2F$ and $CF_3CH_2CF_3$. The results from relative rate experiments with these compounds, Figure 3, give $k(Cl + CF_3CH_2CCl_2F)/k(Cl +$ $CF_3CH_2CF_2CH_3) = 0.032 \pm 0.003$ and k(Cl + $CF_3CH_2CF_3)/k(Cl + CF_3CH_2CF_2CH_3) < 0.01$ and, hence, $k(Cl + CF_3CH_2CCl_2F) = (3.5 \pm 1.5) \times 10^{-17}$ cm³ molecule⁻¹ s⁻¹ and $k(Cl + CF_3CH_2CF_3) <$ 1×10^{-17} cm³ molecule⁻¹ s⁻¹. The results presented above suggest that the products observed from the Clatom initiated oxidation of CF₃CH₂CF₂CH₃ in this study arise from Cl atom attack at the --CH₃ group of CF₂CH₂CF₂CH₂.

Møgelberg et al. [41] have recently investigated the fluorine atom initiated oxidation of $CF_3CH_2CF_3$ at 298 K and 760 torr total pressure. The major carboncontaining product formed was $CF_3C(O)CF_3$ and the yield was shown to be independent of O₂ partial pressure over the range 5–760 torr. The alkoxy radical, CF_3CHOCF_3 , produced in this system, by reactions analogous to those shown above for $CF_3CH_2CF_2CH_3$, can decompose or react with O₂:

$$CF_3CHOCF_3 \longrightarrow CF_3 + CF_3CHO$$
 (30)

$$CF_3CHOCF_3 + O_2 \longrightarrow CF_3C(O)CF_3 + HO_2$$
 (31)

The results from Møgelberg et al. [41] indicate that decomposition of the alkoxy radical is negligible and thus it is likely that ketone formation from the structurally similar $CF_3CHOCF_2CH_3$ radical will still dominate over C—C bond scission. Hence, the available experimental data from $CF_3CH_2CF_3$ and

 $CF_2CH_2CCl_2F$ provide strong evidence that the atmospheric oxidation of CF₃CH₂CF₂CH₃ will be initiated predominantly by OH radical attack at the $-CH_3$ group. Based on the results from the chlorine atom initiated oxidation of CF₃CH₂CF₃CH₃, it is expected that the molecule will be broken down under atmospheric conditions in a series of carbon-carbon bond breaking processes leading to the formation of CF₂O and CF₃ radicals with close to 100% yields. It is expected that the CF₃ radical will be quantitatively converted to CF₃O in the atmosphere by successive reactions with O₂ and NO. Under tropospheric conditions reaction with CH₄ and NO are the main sinks for the CF₃O radical leading to the formation of CF₂O [6,35]. Reaction at the methylene group in CF₃CH₂CF₂CH₃ is expected to be of negligible importance but may lead to small amounts of the fluoroketone, $CF_3C(O)CF_2CH_3$. This ketone is also likely to give rise to CF₂O via photolysis or OH radical initiated oxidation.

Radiative Forcings and Global Warming Potentials

The infrared absorption cross-section data, shown in Figure 8, were integrated over 100 cm^{-1} intervals and introduced into the NCAR model in order to provide radiative forcings and Global Warming Potentials (GWPs) to complete the results obtained for 11 other CFC replacement compounds [7,8]. Radiative forcings and GWPs have been introduced as convenient parameters to quantify the time-varying relative contribution of long-lived greenhouse gases to global warming [42]. The radiative forcing due to the perturbation introduced by adding a certain amount of greenhouse gas is defined as the net radiative flux



Figure 8 Infrared absorption cross-sections (cm² molecule⁻¹) measured between 600 and 1500 cm⁻¹ for HFC-365mfc.

change (in W/m^2) at the tropopause. The GWP of a well-mixed gas relative to a reference gas is defined as the product of the instantaneous radiative forcing associated with the emission of 1 kg of the gas and the concentration of the gas remaining in the atmosphere, integrated over a period of time, divided by the same quantity for the reference gas.

The two dimensional chemical-radiative model used in this study is an updated version of the model described by Brasseur et al. [43]. The infrared radiative transfer is treated as in the NCAR Community Climate wide band model CCM1 [44,45], which includes the thermal effects of H_2O , CO_2 , CH_4 , O_3 , N_2O , CFC-11, and CFC-12. Radiative forcings were determined for a mean cloud cover, using annually-averaged vertical concentration profiles for the greenhouse gases. Mixing ratios were calculated between 0 and 85 km using current ground-level concentrations [42] as a boundary condition for CO_2 , CH_4 , N_2O , CFC-11, and CFC-12, and set at 2.5 pptv for HFC-365mfc.

The absolute instantaneous radiative forcing values (in W/m^2) for CO₂, CFC-11 and HFC-365mfc were found to be, respectively, 0.652 (corresponding to a 10% increase in concentration, from 350 to 385 ppmv), 0.227, and 0.209 (values extrapolated to a 1 ppbv increase in concentration). Relative radiative forcings obtained for HFC-365mfc using CFC-11 and CO₂ as reference gases are reported in Table I. Finally, the Global Warming Potentials have been obtained for the time horizons corresponding to 20, 100, and 500 years of integration time using the methodology from the 1994 IPCC report [46], and are given in Table I. In this calculation, the Bern carbon cycle model was employed to estimate the persistence of carbon dioxide and an atmospheric lifetime of 50 years was used for CFC-11. The results are presented using both the calculated tropospheric lifetime of 10.8 years and an estimated overall atmospheric lifetime of 10.2 years for HFC-365mfc. Taking the rate constant for reaction of OH with $CF_3CH_2CF_2CH_3$ reported by Mellouki et al. [16] gives GWPs a factor of about 1.5 lower than those given in Table I.

To our knowledge, no other cross-section or radiative forcing data are available in the open literature for HFC-365mfc. We estimate the total uncertainty associated with the integrated cross-sections to be lower than 4% [7], whereas the error made when calculating radiative forcings and Global Warming Potentials is much more difficult to evaluate. Using the infrared spectra we have measured for several CFC replacement compounds, Pinnock et al. [47] have recently calculated the associated radiative forcings with a narrow band model. When normalized to the respective values for CFC-11, radiative forcings calculated by each of the two groups were found to be within $\pm 10\%$. The main discrepancies are thought to be due to the different resolution, concentration profiles and cloud cover used in the models. The use of an approximate model described by Pinnock et al. [47] allows one to obtain estimated instantaneous radiative forcings from known cross-sections. We have carried out the calculation for HFC-365mfc with the narrow band radiative forcings per unit cross-section they provide. The absolute forcings for a concentration change of 1 ppbv were found to be quite different (0.256 W/m² instead of 0.209 W/m²), but the value relative to CFC-11 was found to be very close (0.93 instead of 0.92), which validates the results obtained in this study.

CONCLUSION

The results obtained in this work indicate that the tropospheric lifetime of $CF_3CH_2CF_2CH_3$ with respect to removal by OH radicals is 10.8 years and that CF_2O will be the main oxidation product. Tropospheric loss

Table IInstantaneous Cloudy-Sky Radiative Forcing and Global Warming Potential Valuesfor HFC-365mfc Relative to CFC-11 and CO2

Reference Gas	Relative Radiative Forcing	Atmospheric Lifetimes of HFC-365mfc, Years	Global Warming Potential			
			20	100	500	years
CFC-11	0.92	10.8 10.2	0.47 0.45	0.21 0.20	0.18 0.17	
CO ₂	11200	10.8 10.2	2300 2210	830 790	260 250	

Note that relative radiative forcings are expressed on a molecular basis, GWPs on a mass basis.

of CF₂O is governed by uptake in cloud, rain, or ocean water followed by hydrolysis to give CO₂ and HF [5,6]. The tropospheric lifetime and an estimate of the overall atmospheric lifetime of 10.2 years for HFC-365mfc have been used with the measured infrared cross-sections to estimate the radiative forcing and Global Warming Potential associated with this compound. Calculations have shown that for all the integration times investigated, the contribution of this third generation substitute to the radiative forcing of climate is considerably lower than that associated with the release of the same mass of CFC-11. Using the value of 10.2 years for the overall atmospheric lifetime of HFC-365mfc, the infinite-time-horizon (or steady-state) Halocarbon Global Warming Potential, expressed relative to CFC-11, is 0.17; the Global Warming Potentials relative to CO₂ are 2210, 790, and 250, for integration time-horizons of 20, 100, and 500 years, respectively.

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