

TROPOSPHERIC DEGRADATION CHEMISTRY OF HCFC-123 (CF₃CHCl₂): A PROPOSED REPLACEMENT CHLOROFLUOROCARBON

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Abstract—HCFC-123 has been proposed as a replacement for some of the fully halogenated chlorofluorocarbons and other chlorinated hydrocarbons, which are being phased out under the Montreal Protocol. This paper reports laboratory studies which were undertaken to determine kinetic and mechanistic parameters of reactions involved in the atmospheric degradation of HCFC-123 and the use of these parameters in a 2D global model of the troposphere to evaluate the yields of products formed in the degradation.

The experimental studies have made use of the laser flash photolysis technique with time-resolved ultra-violet absorption spectroscopy for the kinetic measurements and broad-band ultra-violet absorption spectroscopy for product characterization. Rate coefficients have been determined for the self-reaction of CF₃CCl₂O₂ as $(3.6\pm0.5)\times10^{-12}$ cm³ mol⁻¹s⁻¹ and for its reactions with HO₂ and NO as $(1.9\pm0.7)\times10^{-12}$ cm³ mol⁻¹s⁻¹ and $(1.5-2.0)\times10^{-11}$ cm³ mol⁻¹s⁻¹, respectively, at room temperature. Kinetic data have also been obtained for the reaction of CF₃CCl₂O₂ with C₂H₅O₂ and two channels have been identified; CF₃CCl₂O₂ + C₂H₅O₂ → CF₃CCl₂O₂ + C₂H₅O₂ → CF₃CCl₂O₂ + C₂H₅O₂ → CF₃CCl₂O₂ + C₂H₅O₃ → CF₃CCl₂O₂ + C₂H₅O₃ → CF₃CCl₂O₁ + C₃CH₃O₁ + CH₃CHO + O₂, $k = (3.6\pm0.5)\times10^{-12}$ cm³ mol⁻¹s⁻¹. Studies undertaken using the Cl-initiated oxidation of HCFC-123 suggest that trifluoroacetyl chloride, CF₃COCl, is the major product of the gas-phase degradation.

The kinetic and mechanistic data have been used to formulate a chemical module of the degradation of HCFC-123 in the troposphere. The module has been incorporated into a 2D model of the global troposphere so that the potential atmospheric impact of using HCFC-123 can be assessed.

Key word index: HCFC-123, tropospheric chemistry, kinetics, mechanisms, numerical modelling.

1. INTRODUCTION

Major depletions of ozone over Antarctica each spring and significant losses of ozone over the Arctic have been observed in recent years (WMO 1990a, 1992). It is now accepted that the elevated concentrations of chlorine-containing species present, not only in the Antarctic stratosphere (Anderson *et al.*, 1989), but also in the Arctic (Brune *et al.*, 1990) are implicated in the ozone losses. As a result of these observations and of the studies undertaken in the laboratory, the Montreal Protocol on "Substances that Deplete the Ozone Layer" has been implemented to control and phase-out the production of the fully halogenated chlorofluorocarbons (CFCs).

A number of compounds which have similar properties to the CFCs has been identified by the chemical manufacturers as potential *in kind* replacements. HCFC-123 is being considered as a substitute for CFC-11 in foam-blowing applications, for CFC-113 in metal and electronic cleaning (Fischer *et al.*, 1991) and as a potential halon replacement (Todd and Associates, 1991).

An initial assessment of the atmospheric fate of HCFC-123 and the other replacement compounds was made for the chemical manufacturers (AFEAS, Alternative Fluorocarbon Environmental Acceptability Study, in WMO (1990b)). The assessment indicated that the proposed replacements would either cause no or reduced ozone loss and would make a smaller direct contribution to global warming. Solomon and Albritton (1992) have, however, suggested that the chlorine released from the HCFCs in the stratosphere could cause comparable losses of stratospheric ozone to those calculated for the fully halogenated CFCs in the short term.

The mechanisms of the subsequent degradation of the replacement compounds in the atmosphere were derived, in the absence of experimental data, from those of simple organic and related halogenated organic compounds (WMO, 1990b). Although substantial progress has been made in this area (WMO, 1992), there is still a need to confirm and quantify the pathways and products so that the full environmental impact of using these compounds can be made.

HCFC-123, like other HCFCs and HFCs, contains hydrogen. It is the presence of hydrogen in the molecule that makes it susceptible to attack by OH (1) in the troposphere, a reaction not available to the fully halogenated CFCs.

$$CF_3CHCl_2 + OH \rightarrow CF_3CCl_2 + H_2O.$$
 (1)

There have been a number of determinations of the rate coefficient for reaction of OH with HCFC-123 (Howard and Evenson, 1976; Clyne and Holt, 1979; Watson *et al.*, 1979; Liu *et al.*, 1990; Brown *et al.*, 1990; Gierczak *et al.*, 1991). These are in reasonable agreement and the latest IUPAC evaluation (Atkinson *et al.*, 1992) recommends the rate expression for reaction (1) as $k(T) \neq 5.5 \times 10^{-13} \exp(-815/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, implying an atmospheric residence time of 1.7 yr (WMO, 1992).

The main radical species formed in the subsequent chemistry is a peroxy radical, $CF_3CCl_2O_2$. The fate of the peroxy radical depends on the ambient concentrations of HO₂, NO and NO₂ and on the rate parameters associated with the reactions of $CF_3CCl_2O_2$ with these compounds (reactions (2)–(4)).

$$CF_3CCl_2O_2 + HO_2 \rightarrow CF_3CCl_2OOH + O_2$$
 (2)

 $CF_3CCl_2O_2 + NO_2 + M \rightarrow CF_3CCl_2O_2NO_2 + M$ (3)

$$CF_3CCl_2O_2 + NO \rightarrow CF_3CCl_2O + NO_2.$$
 (4)

The reactions with $HO_2(2)$ and $NO_2(3)$ lead to the formation of reservoir species—hydroperoxides and nitrates—from which the active radicals can be regenerated by thermal decomposition or photolysis.

$$CF_{3}CCl_{2}O_{2}NO_{2} + M \rightarrow CF_{3}CCl_{2}O_{2} + NO_{2} + M$$
(5)

$$CF_3CCl_2OOH + h\nu \rightarrow CF_3CCl_2O + OH.$$
 (6)

The reaction with NO, equation (4), will, in the main, form a halogenated oxy radical, CF_3CCl_2O . The stable products derived from this radical will depend on whether C-C or C-Cl bond fission occurs (Cox and Lesclaux, 1990; Atkinson, 1990).

$$CF_3CCl_2O \rightarrow CF_3 + COCl_2$$
 (7a)

$$\rightarrow$$
 CF₃COCl+Cl. (7b)

The formation of CF₃COCl in the degradation of HCFC-123 is important since the uptake of CF₃COCl into the aqueous phase and its subsequent hydrolysis will lead to the formation of trifluoroacetic acid, CF₃COOH.

$$CF_3COCl_{(g)} \rightarrow CF_3COCl_{(aq)}$$
 (8)

$$CF_3COCl_{(aq)} + H_2O \rightarrow CF_3COOH_{(aq)} + HCl_{(aq)}.$$
 (9)

The production of CF_3COOH has been of concern since it could have possible effects on vegetation. The compound monofluoroacetic acid (CH_2FCOOH) is known to be toxic to all cells since, on activation to fluoroacetyl coenzyme-A, inhibition of the citric acid (Krebs) cycle can occur (Peters, 1957).

Edney et al. (1991) have studied the Cl-atom initiated degradation of HCFC-123 in the gas-phase using FT-IR spectroscopy. Quantitative conversion of HCFC-123 into CF₃COCl was observed. This has also been observed by Meller et al. (1991) and Tuazon and Atkinson (1993) using a similar approach. Jemi-Alade et al. (1991) have used the flash photolysis technique with time-resolved absorption spectroscopy to study the photolysis of $Cl_2/HCFC-123/O_2$ mixtures. The production of $CF_3CCl_2O_2$ was observed and the UV absorption spectrum of $CF_3CCl_2O_2$ was derived. Jemi-Alade *et al.* could not derive any kinetic data from the transient waveforms recorded because a catalytic chain appeared to be set-up under their experimental conditions. The formation of a stable UV-absorbing product was observed at long reaction times and this was identified as CF_3COCl . Au these studies imply that CF_3CCl_2O radicals undergo mainly C–Cl bond fission equation (7b) to give CF_3COCl and Cl as products.

A different approach has been adopted in this work in an attempt to derive kinetic data on the reactions of CF₃CCl₂O₂. CF₃CCl₂O₂ radicals were generated following the laser flash photolysis of CF₃CCl₃/O₂ mixtures at 193 nm with either CH₃OH or C₂H₆ added to scavenge the Cl atoms produced in the initial photolysis and in the subsequent chemistry. The radicals produced following the laser flash were detected at specific wavelengths using time-resolved UV absorption spectroscopy. Broad-band UV absorption spectroscopy with diode array detection was used to characterize and study the stable products formed in the gas-phase degradation of HCFC-123 during the constant photolysis of Cl₂/HCFC-123/O₂/N₂ mixtures. The kinetic and mechanistic data obtained for the processes involved in the degradation of HCFC-123 were collated to produce a reaction mechanism of the degradation of HCFC-123 for use in Harwell's 2D tropospheric chemistry model.

2. EXPERIMENTAL

2.1. Laser flash photolysis apparatus

The laser flash photolysis-UV absorption apparatus used in this work has been described previously by Murrells *et al.* (1991). It consists of a cylindrical silica reaction vessel, 30 cm in length with internal white optics, which was irradiated through one side by 193 nm radiation from a pulsed ArF excimer laser (Lambda Physik, LPX 205i). The reaction gases, which were premixed, were flowed slowly through the reaction cell with a typical residence time of 5 s. The repetition rate of the laser was set so that each gas mixture was exposed to only one flash during its residence in the cell.

Radical species and stable products formed in the reactions were detected using ultra-violet absorption spectroscopy. Broad-band UV radiation from a high brightness deuterium lamp (Hamamatsu, L2196) was focused into the cell and then into a monochromator for spectral dispersion and detection by a photomultiplier tube (EMI 9783B). The use of internal multipass reflection optics in the reaction vessel increases the effective optical absorption pathlength and thereby enhances the overall sensitivity. The optical pathlength was determined to be 85 ± 5 cm, as described by Murrells et al. (1991). A storage oscilloscope (Hitachi VC6020) was used to capture transient absorption profiles produced following the laser pulse before they were transferred to a microcomputer for data storage and analysis. The microcomputer also provided the timing pulses to trigger the laser and storage oscilloscope.

 $CF_3CCl_2O_2$ radicals were produced by the 193 nm photolysis of CF_3CCl_3 (Aldrich, 99%) in the presence of oxygen (BOC, Breathing Grade). Nitrogen (Air Products, High Purity) was added to bring the total pressure to one atmosphere. All experiments were conducted at room temperature.

$$CF_3CCl_3 + h\nu (\lambda = 193 \text{ nm}) \rightarrow CF_3CCl_2 + Cl.$$
 (10)

To avoid complications with the Cl atom produced in the initial photolysis, either ethane (C_2H_6 , BOC, 99% purity) or methanol (CH₃OH, Fisons, AR grade) was added to scavenge the Cl atoms. The reactions of ethane and methanol with Cl atoms lead to the formation of $C_2H_5O_2$ and HO₂, respectively. These peroxy radicals can be used to calibrate the absorption spectrum of CF₃CCl₂O₂ as the UV absorption spectra of C₂H₅O₂ and HO₂ have been extensively characterized (Crowley et al., 1991; Lightfoot et al., 1992; Wallington et al., 1992).

$$Cl + C_2H_6 \rightarrow C_2H_5 + HCl$$
(11)

$$C_2H_5 + O_2 + M \rightarrow C_2H_5O_2 + M$$
 (12)

$$Cl + CH_3OH \rightarrow CH_2OH + HCl$$
 (13)

$$CH_2OH + O_2 \rightarrow HCHO + HO_2.$$
(14)



Fig. 1a. The initial absorptions obtained at different wavelengths following the laser flash photolysis of CF₃CCl₃/CH₃OH/O₂/N₂ or CF₃CCl₃/C₂H₆/O₂/N₂ mixtures at 193 nm.



Fig. 1b. The UV absorption spectrum of $CF_3CCl_2O_2$ obtained from the deconvolution of the composite absorption spectra shown in Fig. 1a.

2.2. Multichannel UV absorption spectroscopy

Product studies were carried out using UV absorption spectroscopy with multichannel diode array detection. UV radiation from a deuterium lamp was passed into a white cell (Infrared Associates, pathlength = 320 cm) before entering a monochromator (B+M Spectronik 50) for spectral dispersion. A diode array camera (Reticon) was positioned in the focal plane of the monochromator. A Tracor Northern 1710 controller was used to initialize the camera, set the exposure and acquisition time and to retrieve transmission spectra recorded by the camera.

Static photolysis experiments were conducted on reaction mixtures containing Cl2/HCFC-123/O2/N2, which were prepared in situ by addition of the individual gases in turn. The sample of HCFC-123 (ICI, 96.7% purity, with CF₃CCl₃ as the main impurity) was degassed prior to use but was not further purified. The other reagents (Cl_2 diluted in N_2 (BOC) Special Gases), N2 (Air Products, High Purity)) were used as received except O₂ (BOC, Breathing Grade), which was passed through a molecular sieve trap to remove hydrocarbons. Typical reagent concentrations were CF_3CHCl_2 , (2.5-50.0) × 10¹⁶ mol cm⁻³; Cl_2 , (1.3-28.0) × 10¹⁶ mol cm⁻³; O_2 , 2.3 × 10¹⁸ mol cm⁻³, N_2 , 1.0 × 10¹⁹ mol cm⁻³. The concentrations of gases were determined from pressure measurements using a capacitance monometer (Baratron, model 222BA). More accurate determinations of the concentrations of Cl₂ and HCFC-123 were made using the ultra-violet absorption by these molecules at 300 nm (Seery and Britton, 1964) and 220 nm (WMO, 1990b), respectively. The reaction mixture was allowed to stand for 30 min before photolysis at 370 nm using two blacklights was started (Phillips, TLD 32 W).

Transmission spectra covering the region 219-302 nm were recorded prior to photolysis and at specific times after photolysis had been initiated. The transmission spectra, $I_1(\lambda)$, were converted into absorption spectra, $a(\lambda)$, by reference to a transmission spectrum recorded with the cell evacuated $I_0(\lambda)$, using the relationship:

$$a(\lambda) = \log_{10} \left[I_0(\lambda) / I_t(\lambda) \right]. \tag{I}$$

Photolysis of Cl_2 occurred and the attack on HCFC-123 by Cl atoms produced the same peroxy radical, $CF_3CCl_2O_2$, as observed in the laser experiment.

3. RESULTS

3.1. UV absorption spectrum of $CF_3CCl_2O_2$

Transient decay traces were recorded at specific wavelengths between 220 and 290 nm following the 193 nm photolysis of CF₃CCl₃/CH₃OH/O₂/N₂ or CF₃CCl₃/C₂H₆/O₂/N₂ mixtures. The other experimental parameters, such as reactant flow rates, residence time, were maintained at the same value for each of the wavelengths used. Traces were recorded periodically at 250 nm to ensure that the experimental parameters had not changed significantly. The transient absorptions recorded were composed of contributions from CF₃CCl₂O₂ and either HO₂ or C₂H₅O₂, together with absorptions due to products.

The initial absorptions were determined at each wavelength for the two reaction systems (Fig. 1a). It was assumed that the photolysis of CF_3CCl_3 only had one channel (10), or, if additional channels existed,

they were either minor or did not influence the chemistry under study. Thus, for each $CF_3CCl_2O_2$ radical formed by the laser pulse, an equivalent concentration of HO_2 or $C_2H_5O_2$ was produced. The initial composite absorption spectrum at each wavelength was given by the Beer-Lambert law as:

$$a_0(\lambda) = \{\sigma_\lambda(\mathrm{HO}_2) + \sigma_\lambda(\mathrm{CF}_3\mathrm{CCl}_2\mathrm{O}_2)\}c_r l \qquad (\mathrm{II})$$

for the $CF_3CCl_3/CH_3OH/O_2/N_2$ photolysis system, and

$$a_0(\lambda) = \{\sigma_\lambda(C_2H_5O_2) + \sigma_\lambda(CF_3CCl_2O_2)\}c'_r l \quad (III)$$

for the CF₃CCl₃/C₂H₆/O₂/N₂ photolysis system. In equations (II) and (III), *l* is the optical absorption pathlength, c_r and c'_r are the concentration of radicals produced in the initial pulse, and $\sigma_{\lambda}(HO_2)$ and $\sigma_{\lambda}(C_2H_5O_2)$ are, respectively, the UV absorption cross-sections of HO₂ and C₂H₅O₂ at the wavelength, λ .

The unknown parameters in equations (II) and (III) were the absorption coefficients of $CF_3CCl_2O_2$ and the initial radical concentrations. The absorption cross-sections for HO_2 and $C_2H_5O_2$ were taken from Crowley et al. (1991) and Lightfoot et al. (1992), respectively. A nonlinear least-squares method was used to analyse the initial absorption obtained at each wavelength and to derive the individual contributions to the total absorptions. The cross-sections obtained for $CF_3CCl_2O_2$ are given in Table 1 and are shown graphically in Fig. 1b. The cross-sections have an uncertainty of $\pm 10\%$ which represents the uncertainties in the cross-sections for HO₂ and C₂H₅O₂ and the extrapolation to the initial absorbances. The cross-sections were found to be in excellent agreement with those determined by Jemi-Alade et al. (1991), providing support for the assumption that the photolysis of CF₃CCl₃ gave only CF₃CCl₂ and Cl.

$$CF_3CCl_3 + hv(\lambda = 193 \text{ nm}) \rightarrow CF_3CCl_2 + Cl.$$
 (10)

The shape of the absorption spectrum obtained at long times after the initial laser pulse (100 ms), showed that a new absorber was being formed in the $CF_3CCl_3/CH_3OH/O_2/N_2$ photolysis system. The absorption spectrum of this absorber maximized near

Table 1. UV Absorption cross-section for CF₃CCl₂O₂

Wavelength λ (nm)	UV absorption cross-section σ (10 ⁻²⁰ cm ² mol ⁻¹)		
220	191*	216†	
230	230	223	
240	214	206	
250	179	181	
260	147	160	
270	110	116	
280	53	63	
290	25	29	

*This work, uncertainties are $\pm 10\%$.

†Data taken from Jemi-Alade et al. (1991).

255 nm and was identified as CF_3COCI from the results of the broad-band spectroscopic studies (Section 3.3).

3.2. Kinetics of the self-reaction of $CF_3CCl_2O_2$ and of its reactions with HO_2 , $C_2H_5O_2$ and NO

Using the absorption cross-sections and initial radical concentrations determined in Section 3.1 above, the complete transient decays were analysed to extract kinetic and mechanistic data on the reactions of $CF_3CCl_2O_2$ radicals. Given the complexity of the chemistry occurring, the decay traces were modelled with an assumed reaction scheme. The time evolution of the different radical concentrations and absorptions were then obtained by numerical integration of the reaction scheme using the FACSIMILE program (Curtis and Sweetenham, 1988). This program contains a nonlinear least-squares facility so that given parameters can be optimized to give the best fit to the experimental data.

The reaction scheme used is shown in Table 2. The reactions (2, 7b, 10, 11, 16-21, see Table 2 for identity of reactions) were used to simulate the data recorded using the CF₃CCl₃/C₂H₆/O₂/N₂ chemical system, whilst reactions (11, 17a, 17b, 18a, 18b, 20 and 21) were omitted and reactions (13) and (14) were added for the CF₃CCl₃/CH₃OH/O₂/N₂ chemical system. To avoid potential correlation between the parameters being optimized, the decay traces obtained at different wavelengths using the same reagent conditions were analysed simultaneously. The UV absorption cross-sections determined by Rattigan et al. (1993) were used for CF₃COCl. Absorptions due to CH₃CHO (Calvert and Pitts, 1967) and H₂O₂ (Vaghjiani and Ravishankara, 1989) were included. The UV absorption spectra of C₂H₅OOH and CF₃CCl₂OOH were assumed to have the same wavelength dependence as that of CH₃OOH (Vaghjiani and Ravishankara, 1989). The absorptions by the hydroperoxide species were found to be very small and had little effect on the values of the rate parameters obtained even if these absorptions were omitted.

The rate parameters given in Table 3 were obtained from the analysis of the two sets of transient decay traces. Rate coefficients could be determined for both the terminating and non-terminating reactions involving CF₃CCl₂O₂ since those reactions which form CF₃CCl₂O (16 and 17a) will lead to the regeneration of HO₂ and C₂H₅O₂ via reactions (7b, 13 and 14) and (7b, 11 and 12), respectively. The experimental traces and the simulated curves obtained using the optimized kinetic parameters are shown in Fig. 2 for the CF₃CCl₃/CH₃OH/O₂/N₂ chemical system. The errors include the uncertainties calculated by the numerical optimization procedure and the uncertainties in the UV absorption cross-sections derived for CF₃CCl₂O₂.

In a separate experiment, NO was added to the $CF_3CCl_3/CH_3OH/O_2/N_2$ photolysis system so that

Reaction number	Reactio	n	Rate constant at 298 K $k/cm^3 mol^{-1} s^{-1}$	Note
(10)	$CF_3CCl_3 + hv$	$\rightarrow CF_3CCl_2 + Cl$	Initiation reaction	
(15)	$CF_3CCl_2 + O_2$	$\rightarrow CF_3CCl_2O_2$	Assumed instantaneous	
(11)	$Cl + C_2H_6$	→ C ₂ H ₃ +HCl	5.7×10^{-11}	1
(12)	$C_2H_3+O_2$	$\rightarrow C_2 H_3 O_2$	Assumed instantaneous	
(13)	CI+CH ₃ OH	→ CH ₂ OH	5.7×10^{-11}	1
(14)	$CH_2OH + O_2$	\rightarrow HCHO + HO ₂	Assumed instantaneous	
(16)	$CF_3CCl_2O_2 + CF_3CCl_2O_2$	$\rightarrow CF_3CCl_2O_2 + CF_3CCl_2O + O_2$	$(3.6 \pm 0.5) \times 10^{-12}$	This work
(7b)	CF ₃ CCl ₂ O	$\rightarrow CF_3COCI + CI$	Assumed instantaneous	
(17a)	$CF_3CCl_2O_2 + C_2H_5O_2$	$\rightarrow CF_3CCl_2O + C_2H_5O + O_2$	$(9^{+9}_{-5}) \times 10^{-13}$	This work
(17b)		\rightarrow CF ₃ CCl ₂ OH + CH ₃ CHO + O ₂	$(3.6\pm0.5)\times10^{-12}$	This work
(18a)	$C_{2}H_{5}O_{2}+C_{2}H_{5}O_{2}$	$\rightarrow C_2H_5O+C_2H_5O+O_2$	3.48×10^{-14}	2
(18b)		$\rightarrow C_2H_5OH + CH_3CHO + O_2$	2.32×10^{-14}	2
(2)	$CF_3CCl_2O_2 + HO_2$	$\rightarrow CF_3CCl_2OOH + O_2$	$(1.9 \pm 0.7) \times 10^{-12}$	This work
(19)	$HO_2 + HO_2$	\rightarrow H ₂ O ₂ +O ₂	2.8×10^{-12} [M = air]	2
(20)	$C_2H_5O_2 + HO_2$	$\rightarrow C_2 H_5 OOH + O_2$	5.8×10^{-12}	2
(21)	$C_2H_3O+O_2$	$\rightarrow CH_3CHO + HO_2$	8.0×10^{-15}	1
(4)	$CF_3CCl_2O_2 + NO$	$\rightarrow CF_3CCl_2O + NO_2$	1.8×10^{-11}	This work

Table 2. Chemical scheme used to analyse transient absorption traces recorded following the 193 nm laser photolysis of CF₃CCl₃/CH₃OH/O₂/N₂ or CF₃CCl₃/C₂H₆/O₂/NO/N₂ mixtures

Notes 1. Kinetic data taken from DeMore et al. (1990).

2. Kinetic data taken from Atkinson et al. (1992).

Table. 3. Summary of kinetics results obtained for the reactions of CF₃CCl₂O₂

Reaction		Rate constant at 298 K $k/\text{cm}^3 \text{mol}^{-1} \text{s}^{-1}$
$CF_{3}CCl_{2}O_{2}+CF_{3}CCl_{2}O_{2}$ $CF_{3}CCl_{2}O_{2}+HO_{2}$ $CF_{3}CCl_{2}O_{2}+NO$ $CF_{3}CCl_{2}O_{2}+C_{2}H_{3}O_{2}$	$\rightarrow CF_3CCl_2O + CF_3CCl_2O + O_2$ $\rightarrow CF_3CCl_2OOH + O_2$ $\rightarrow CF_3CCl_2O + NO_2$ $\rightarrow CF_3CCl_2O + C_2H_3O + O_2$ $\rightarrow CF_3CCl_2OH + CH_3CHO + O_2$	$(3.6 \pm 0.5) \times 10^{-12}$ (1.9 \pm 0.7) × 10 ⁻¹² (1.5 - 2.0) × 10 ⁻¹¹ (9 ⁺ 9) × 10 ⁻¹³ (3.6 ± 0.5) × 10 ⁻¹²



Fig. 2. Transient decay traces recorded from 230 to 270 nm following the 193 nm laser photolysis of mixtures containing CF₃CCl₃, CH₃OH, O₂ and N₂.

the rate constant for reaction (4) could be evaluated. Transient decay traces were recorded at 270 nm, where $CF_3CCl_2O_2$ is the dominant absorber in the initial stages of the decay. Complications due to the formation of NOCl (DeMore *et al.*, 1990), NO₂ (De-More *et al.*, 1990) and organic nitrates and peroxynitrates (see references in Atkinson *et al.*, 1989, or DeMore *et al.*, 1990, for HO₂NO₂ or CH₃O₂NO₂ as examples) which absorb in this region prevented a complete analysis of the decay traces. However, an enhanced loss of $CF_3CCl_2O_2$ was observed compared to the traces recorded at 270 nm with no NO added. A preliminary value for the rate constant of reaction (4) was obtained from an analysis of the initial slope of the radical absorption.

CF₃CCl₂O₂ + NO → CF₃CCl₂O + NO₂ (4)

$$k(298 \text{ K}) = (1.5-2.0) \times 10^{-11} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}.$$

The magnitude of this rate constant is in good agreement with the rate coefficients determined for the fully halogenated methylperoxy radicals, CF_3O_2 , CF_2ClO_2 , $CFCl_2O_2$ and CCl_3O_2 (Atkinson *et al.*, 1989).

3.3. Broad-band UV absorption studies

The pre-photolysis spectrum consisted of absorptions due to HCFC-123 at the short wavelength end of the observation region (WMO, 1990b) and Cl_2 at



Fig. 3(a-b). The deconvolution of the composite spectrum recorded after 120 s (a) and 6315 s (b) of continuous photolysis at 370 nm of mixtures containing Cl₂, HCFC-123, O₂ and N₂. Presented are (a) the prephotolysis spectrum containing HCFC-123 and Cl₂, (b) the composite absorption spectrum, (c) the residual absorption spectrum after Cl₂ has been removed and (d) a scaled UV absorption spectrum of CF₃COCl (shown as boxes) recorded by Rattigan *et al.* (1993).

the longer wavelengths (Seery and Britton, 1964) (spectra labelled a in Figs 3a and 3b). The absorption at the long wavelength end of the region under study appeared to remain relatively constant under photolysis. However, the growth of an absorber at shorter wavelengths, with a maximum absorption near 255 nm, was clearly seen (Figs 3a and 3b). At reaction times longer than 3600 s, the absorption at 255 nm remained constant. At the short wavelength end of the observation region, there was initially a slight decrease in the total absorption followed by a subsequent growth.

The contribution of Cl_2 to the composite spectra was removed on the basis that no net loss of Cl_2 had occurred. This would be expected from the reaction sequence (22, 23, 15, 16, 7b) as the Cl atom lost in the initial attack on the HCFC-123 (23) is regenerated in the decomposition of CF_3CCl_2O (reaction 7b)

$$Cl_2 + hv (\lambda = 370 \text{ nm}) \rightarrow Cl + Cl$$
 (22)

$$Cl + CF_3CHCl_2 \rightarrow CF_3CCl_2 + HCl$$
 (23)

$$CF_3CCl_2 + O_2 + M \rightarrow CF_3CCl_2O_2 + M$$
 (15)

$$CF_{3}CCl_{2}O_{2} + CF_{3}CCl_{2}O_{2} \rightarrow CF_{3}CCl_{2}O + CF_{3}CCl_{2}O + O_{2}$$
(16)

$$CF_3CCl_2O \rightarrow CF_3COCl + Cl$$
 (7b)

$$Cl + Cl + M \rightarrow Cl_2 + M$$
 (25)

net: $2CF_3CHCl_2 + O_2 \rightarrow 2CF_3COCl + 2HCl.$

The residual absorption spectra obtained by subtracting the spectrum of Cl_2 recorded prior to photolysis are also shown in Figs 3a and 3b. The excellent agreement between the residual absorption spectra and the spectrum of CF₃COCl, recorded by Rattigan *et al.* (1991), shown as boxes in these figures, confirmed that CF₃COCl was the major UV absorbing product formed in this reaction system.

The absorption due to CF_3COCl reached a maximum value and the absorption did not change with time (after ≈ 2000 s) during the constant photolysis at 370 nm (Fig. 4). This would suggest that CF_3COCl does not react with Cl atoms. The concentration of CF_3COCl was determined from the absorption spectra recorded at long reaction times using the absorption cross-sections of Rattigan *et al.* (1991) and compared with the initial amount of HCFC-123 present.

Initial [HCFC-123] /10 ¹⁶ mol cm ⁻³	Final yield of CF ₃ COCI /10 ¹⁶ mol cm ⁻³ % Yield		
4.6	5.4	117	
13.0	13.3	102	
22.0	23.1	105	

The yields of CF_3COCl determined above were greater than 100%, but as the uncertainty of the cross-section of HCFC-123 at 220 nm is of the order



Fig. 4. The growth of the absorption of CF₃COCl at 255 nm during the constant photolysis of Cl₂/HCFC-123/O₂/N₂ mixtures.

Table 4. Photolysis studies on CF₃COCl Run 1: [CF₃COCl] at start of 253.7 nm photolysis $= 2.3 \times 10^{17}$ mol cm⁻³.

Time (in s) after photolysis	$\Delta CF_3 COCI$ /10 ¹⁷ mol cm ⁻³	ΔCl_2 /10 ¹⁷ mol cm ⁻³
130	-0.01	+0.04
640	-0.2	+0.3
1210	-0.5	+0.5
1870	-0.7	+0.7
2470	-0.9	+0.9
3620	-1.2	+1.2
4510	-1.4	+1.4
5470	-1.6	+1.5

Run 2: [CF₃COCI] at start of 253.7 nm photolysis $= 5.5 \times 10^{16}$ mol cm⁻³.

Time (in s) after photolysis	$\Delta CF_3 COCl$ /10 ¹⁷ mol cm ⁻³	$\frac{\Delta \text{Cl}_2}{10^{17} \text{ mol cm}^{-3}}$
100	-0.03	+ 0.08
190	0.08	+0.2
400	-0.3	+0.4
700	-0.6	+0.7
1000	-0.9	+1.1
1300	-1.2	+1.3
1600	-1.4	+1.5
1900	-1.7	+ 1.8
2502	-2.1	+ 2.1
3165	-2.6	+ 2.6
4062	-3.1	+ 3.0

of 20% (WMO, 1990b), the data were consistent with complete conversion of HCFC-123 into CF₃COCl. The results confirmed those obtained in the FT-IR studies of Edney *et al.* (1991), Meller *et al.* (1991) and Tuazon and Atkinson (1993). The results of the three studies indicated quantitative conversion of HCFC-123 into CF₃COCl (reaction (7b)) and suggested that

the decomposition of CF_3CCl_2O to form CF_3 and $COCl_2$ (reaction (7a)) was minor or did not occur under the experimental conditions used.

$$CF_3CCl_2O \rightarrow CF_3 + COCl_2$$
 (7a)

$$\rightarrow CF_3COCl + Cl.$$
 (7b)

3.4. Photolysis of CF_3COCl at 253.7 nm using in situ generation of CF_3COCl

HCFC-123 was quantitatively converted into CF_3COCl using Cl-initiated photo-oxidation of $HCFC-123/O_2/N_2$ mixtures at 370 nm as described above. The blacklight photolysis was stopped and photolysis at 253.7 nm using bare quartz fluorescent tubes was started. The absorption centred at 255 nm decreased whilst the absorptions at 300 and 200 nm increased. The absorption at 300 nm was similar in shape to that of Cl_2 . The changes in absorption at 255 and 300 nm were converted into changes in the concentrations of CF_3COCl and Cl_2 , respectively.

The results indicated that Cl_2 was formed at the same rate as CF_3COCl was being lost (Table 4). However, the expected rate of increase of Cl_2 should have been one-half of the rate at which CF_3COCl was photolysed from the reaction stoichiometry, which was observed by Rattigan *et al.* (1991) when CF_3COCl was used directly rather than being generated *in situ*.

$$CF_3COCl + hv (\lambda = 253.7 \text{ nm}) \rightarrow CF_3CO + Cl (26a)$$

 $\delta[\text{Cl}_2] = -0.5\Delta[\text{CF}_3\text{COCl}].$

$$\rightarrow CF_3 + COCI (26b)$$

$$COCI+M \rightarrow CO+CI+M \quad (2/)$$

$$CI + CI + M \rightarrow CI_2 + M \qquad (25)$$

After the photolysis at 370 nm was stopped and prior to the commencement of photolysis at 253.7 nm, the reaction mixture contains CF₃COCl, HCl, O₂ and N_2 . The only other source of chlorine in the system is therefore HCl, formed when Cl atoms reacted with HCFC-123. CF₃O radicals have been observed to abstract H from CH₄ (Zellner, personal communication) and it may be expected that they could abstract H or Cl from HCl. Meller et al. (1991) have studied the photolysis of CF₃COCl at 253.7 nm using FT-IR spectroscopy. CF₃O radicals could be formed in the 253.7 nm photolysis of CF₃COCl from either CF₃ or CF₃CO. CF₃CO radicals would be expected to add O₂ to give the peroxy radical, CF₃COO₂. By analogy with the reactions of CH₃COO₂, CF₃COO₂ radicals will give CF₃CO₂ and then CF₃ radicals following the thermal decomposition of CF₃CO₂. CF₃ radicals will add O_2 to give the corresponding peroxy radical, CF_3O_2 , and by a similar set of mutual reactions, the oxy radical, CF₃O, will be formed. If abstraction of H from HCl by CF₃O dominates, the observed yield of Cl_2 is explained.

4. ATMOSPHERIC MODELLING STUDIES

In order to assess the relative importance of the different reaction pathways which occur during the degradation of HCFC-123 in the atmosphere, numerical modelling studies were undertaken using a 2D global tropospheric chemistry model.

4.1. Description of model

The model used in this study is a two-dimensional, latitudinally averaged Eulerian grid model (Hough, 1989, 1991), with a domain which extends from pole to pole and from the Earth's surface to an altitude of 24 km. Within this domain, the model is divided into 288 grid cells (24 in the horizontal direction by 12 in the vertical). The model simulates the transfer of material between cells and the chemical transformations which occur within each cell. The model transport has been described by Hough (1989) and validated for a number of tracer species such as ⁸⁵Kr and CFC-11. Apart from the constrained transport and temperature fields, the model is driven completely by the emissions, chemistry, deposition processes and upper boundary conditions. The concentrations of all chemical species are determined as solutions to the differential equations which define the model transport and chemistry. The chemical scheme used in the model, together with a description of the emissions used and comparisons of the results with available measurements are described by Hough (1991).

The model used in the present study contains a correction to the water vapour concentration in the lowest model layers where the predicted concentrations were found to be too high (Johnson, 1992). The water vapour pattern in the lowest few layers has been changed to agree with observed values for the global abundance of water vapour.

The model includes both dry and wet deposition to the surface. Dry deposition is parameterized in the usual manner, using dry deposition velocities (Sehmel, 1980; Chamberlain, 1986). The parameterization used to represent wet deposition is of particular importance in this study. Wet deposition is parameterized as a function of the local liquid water content, the rainfall rate and the solubility of each species concerned as represented by its Henry's law coefficient (Hough, 1991). The algorithm used in the model represents washout in the following manner. In each grid cell, (i), the fraction of a gas-phase species taken up into the aqueous phase is governed by its Henry's law coefficient and the liquid water content present in the cell. This material is then transported into the next lowest altitude cell, (i-1), at the local rainfall rate. As the lower cell, (i-1), is at a higher temperature than that of the cell, (i), from which the material was derived, the droplet is assumed to evaporate immediately. The uptake of gas-phase species in the lower cell, (i-1), is once again determined by its Henry's law coefficient and the liquid water content present in the cell. Transport down to the next lower cell, (i-2), occurs and a cascade of material is set-up from higher altitudes to lower altitudes. Eventually, the material reaches the lowest altitude cell where it is lost from the model domain by wet deposition to the ground.

4.2. Studies using the model

A gas-phase degradation scheme for HCFC-123 has been formulated (Table 5) which is shown schematically in Fig. 5.

The loss processes included for HCFC-123 were reaction with hydroxyl radicals and removal out of the top of the model domain. The OH rate coefficients used were taken from the latest IUPAC evaluation (Atkinson et al., 1992). The coefficient used to describe the loss process out of the top of the model domain was derived by estimating the concentration gradient which existed between the highest altitude cell in the model (at 23 km) and the next cell centered at 25 km. The gradients were based on those observed for CFC-11 and CFC-12 at 24 km. As the major loss process for CFC-11 and CFC-12 at these altitudes is photolysis, the gradients were modified for HCFC-123 by comparing the relative position and magnitude of the UV absorption spectra of the CFCs with HCFC-123 (DeMore et al., 1992).

The scheme formulated for the degradation of HCFC-123 used experimental data on rate coefficients, branching ratios, UV absorption cross-sections and quantum yields where these were available. For those processes for which no experimental data were available, the parameters needed were based on those of related compounds (CFCl₂O₂, CF₂ClO₂ and CF₃O₂). The sources for the parameters used are indicated in the notes attached to the scheme. The

Table 5. Degradation scheme used for HCFC-123 in the Harwell 2D global tropospheric chemistry model

Reaction		Rate expression	Ref.
Thermal reactions			
$OH + CF_3CHCl_2(+O_2)$	$\rightarrow CF_3CCl_2O_2 + H_2O$	$5.5 \times 10^{-13} \exp(-815/T)$	1
$CF_3CCl_2O_2 + HO_2$	$\rightarrow CF_3CCl_2OOH + O_2$	$1.3 \times 10^{-13} \exp[790/T]^*$	This work
CF ₃ CCl ₂ OOH+OH	$\rightarrow CF_3CCl_2O_2 + H_2O$	Set equal to that for CH ₃ OOH [†]	2
$CF_3CCl_2O_2 + NO$	$\rightarrow CF_3COCl + Cl + NO_2$	$1.8 \times 10^{-11} (T/300)^{-1.2}$	1
$CF_3CCl_2O_2 + NO_2(+M)$	$\rightarrow CF_3CCl_2O_2NO_2(+M)$	Set equal to that for CF_3O_2 §	1
$CF_3CCl_2O_2NO_2(+M)$	$\rightarrow CF_3CCl_2O_2 + NO_2(+M)$	Set equal to that for $CF_2CIO_2NO_2$	1
$CF_3O_2 + HO_2$	$\rightarrow CF_3OOH + O_2$	Assumed to be the same as that for CF ₃ CCl ₂ O	2 This work
CF ₃ OOH+OH	$\rightarrow CF_3O_2 + H_2O$	Set equal to that for CH ₃ OOH [†]	2
$CF_{3}O_{2} + NO$	$\rightarrow COF_2 + HF + NO_2$	$1.6 \times 10^{-11} (T/300)^{-1.2}$	1
$CF_3O_2 + NO_2(+M)$	$\rightarrow CF_3O_2NO_2(+M)$	p and T dependent§	1
$CF_3O_2NO_2(+M)$	$\rightarrow CF_3O_2 + NO_2(+M)$	Set equal to that for $CF_2ClO_2NO_2$	1
$Cl + CH_4(+O_2)$	\rightarrow CH ₃ O ₂ + HCl	$9.6 \times 10^{-12} \exp(-1350/T)$	1
OH+HCl	\rightarrow H ₂ O + Cl	$2.4 \times 10^{-12} \exp(-330/T)$	1
Photolysis processes			
$CF_{3}COCl + hv(+O_{2})$	\rightarrow CF ₃ O ₂ + CO + Cl	Calculated from absorption cross-sections**	3
CF ₃ CCl ₂ OOH + hv	$\rightarrow CF_{3}COCl + Cl + OH$	Assumed to be the same as for CH ₂ OOH ⁺⁺	4
CF ₃ OOH + hv	→ COF, + HF + OH	Assumed to be the same as for CH ₃ OOH ⁺⁺	4
$CF_3CCl_2O_2NO_2 + hv$	$\rightarrow CF_1CCl_2O_2 + NO_2$	Assumed to be the same as that for	
	5	HO2NO2tt	1
$CF_3O_2NO_2 + hv$	$\rightarrow CF_3O_2 + NO_2$	Assumed to be the same as that for	
	5 N · · 2	HO ₂ NO ₂ ‡‡	1

*The temperature dependence of the rate coefficient expression for the reaction of $CF_3CCl_2O_2 + HO_2$ is assumed to be the same as that recommended for $CH_3O_2 + HO_2$ by Lightfoot *et al.* (5). The A-factor has been calculated to give the value of the rate constant derived in this work at 298 K, i.e. 1.9×10^{-12} cm³ mol⁻¹ s⁻¹.

The rate constant is taken to be 70% of the overall rate constant for the reaction of OH with CH₃OOH. The branching ratio for the abstraction of the hydroperoxide hydrogen is 0.7 (2). $k(OH + CH_3OOH \rightarrow CH_3O_2 + H_2O) = 2.7 \times 10^{-1}$ $\exp(200/T)$ cm³ mol⁻¹ s⁻¹.

 \ddagger Room temperature rate coefficient for the reaction, CF₃CCl₂O₂ + NO, taken from this work. The temperature dependence is assumed to be as that for the reaction between $CF_3O_2 + NO$. The decomposition of CF_3CCl_2O assumed instan-

taneous: $CF_3CCl_2O \rightarrow CF_3COCl + Cl.$ $\$k_0 = 2.7 \times 10^{-29} (T/300)^{-5.0} [M] \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}, k_{\infty} = 9.0 \times 10^{-12} (T/300)^{-0.7} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1} \text{ and } F_c = \exp(-T/416) (3).$ $\|k_0 = 5.6 \times 10^{-4} \exp(-9310/T) [M] \text{ s}^{-1}, k_\infty = 1.0 \times 10^{16} \exp(-11,880/T) \text{ s}^{-1}, \text{ and } F_c = 0.4 (1).$ ${}^{\circ}\text{CF}_3\text{O}$ is assumed to be converted rapidly into COF₂ with the additional F being converted to HF.

**The photolysis rate of CF₃COCl is calculated in situ from the ultra-violet absorption cross-sections (4) given as averages over the same 500 cm⁻¹ intervals as used for the solar irradiation spectrum presented in the WMO report number 16. Atmospheric Ozone 1985 (6). The quantum yields are taken to be unity and independent of wavelength. The products of the initial photolysis are assumed to be converted rapidly into those shown.

the photolysis rate of CH₃OOH is calculated in situ from the ultra-violet absorption cross-sections (5) and quantum yields. The quantum yield is assumed to be unity.

 \ddagger The photolysis rate of HO₂NO₂ is calcuated *in situ* from the ultra-violet absorption cross-sections (2) and quantum yields. The quantum yield is assumed to be unity.

References: (1) Atkinson et al. (IUPAC, 1992); (2) DeMore et al. (NASA, 1990); (3) Rattigan et al. (1993); (4) Vaghjiani and Ravishankara (1989); (5) Lightfoot et al. (1992); (6) WMO Report Number 16 (1986).

degradation scheme was incorporated into the 2D global tropospheric chemistry model.

Some of the compounds produced in the degradation (e.g. COF₂, HF) have no loss process within the model domain. COF₂ is only lost by transport out of the top of the model domain and it is eventually photolysed in the upper stratosphere. The possibility exists for scavenging by droplets but recent measurements of the sticking coefficients show that this is not an efficient process (Hanson and Ravishankara, 1991). However, there is the possibility of dry deposition occurring for COF₂ but no deposition data exist to quantify the rate of this process. This process, which may occur on the timescale of months, was not specifically included in the modelling studies carried out.

The present emission rates of CFC-11, -12, -113, -114 and -115 are 0.360, 0.465, 0.165, 0.015 and 0.010 Tg yr⁻¹, respectively [Table 8.1 in WMO, 1992] whilst that for HCFC-22 is given as 0.140 Tg yr^{-1} in the same table. In this study, the emission rate of HCFC-123 was fixed at 0.1 Tg yr^{-1} , in recognition that the production of HCFC-123 is likely to be smaller than that of the CFCs. The emissions of HCFC-123 were given the same latitudinal distribution as that used previously for the CFCs. The distribution, derived by Hough (1991), was based on the emission profile proposed for a compound of industrial or man-made origin.

Washout or wet deposition was included for the hydroperoxides (CF₃CCl₂OOH and CF₃OOH) and peroxynitrates (CF₃CCl₂O₂NO₂ and CF₃O₂NO₂) formed in the degradation of HCFC-123, as well as for CF₃COCl, CF₃COOH and HCl. In these simulations, the uptake of CF_3COCI into the aqueous phase and



Fig. 5. The degradation pathways available for HCFC-123 in the troposphere.

its subsequent hydrolysis is the only source of CF_3COOH . The wet deposition processes are characterized by the local liquid water content, the rainfall rate and the solubility of each species concerned as represented by its Henry's law coefficient. The Henry's law coefficients for the hydroperoxides and the peroxynitrates were set to the values recommended by Wine and Chameides (1990). For the hydroperoxides, these values were assumed to be equal to those of CF_3OOH . The effective Henry's law coefficients for CF_3COOH and HCl for uptake by cloudwater were set to the preferred values given, respectively, by Wine and Chameides (1990) and DeMore *et al.* (1992).

The uptake of CF₃COCl and its subsequent hydrolysis in the aqueous phase to CF₃COOH is more difficult to treat as the model currently does not have an explicit formulation of liquid-phase chemistry. In this case, CF₃COCl is assumed to be irreversibly hydrolysed to give CF₃COOH and HCl. The liquidphase concentration of CF₃COOH is set equal to the liquid phase concentration of CF₃COCl which would have been derived from the gas-phase abundance of CF₃COCl present in the cell. The uptake and hydrolysis of CF₃COCl in water increases the overall solubility of CF₃COCl. The AFEAS review (WMO, 1990b) implied that the effective Henry's law coefficient for CF₃COCl was greater than 10 M atm⁻¹ (Wine and Chameides, 1990). The magnitude of the coefficient has recently been shown to be about a factor of 10 too large by Worsnop et al. (1992), which suggests an effective Henry's law coefficient for CF_3COCl of 1 M atm⁻¹. Calculations have been undertaken using both values (1 and 10 M atm⁻¹).

Table 6 gives the inventory present in the model domain for HCFC-123 and the major compounds formed during the degradation of HCFC-123 after 2 yr model simulation (i.e. at January 1985) with washout (Henry's law coefficient for CF₃COCl= 1 Matm^{-1}) and stratospheric loss included. Table 6 also indicates the partitioning of chlorine and fluorine present in HCFC-123 amongst the various products formed in the degradation. The inventory has been weighted by the number of halogen atoms present in each compound relative to that of the original HCFC-123. It can be seen that apart from unreacted HCFC-123, the major gas-phase products are CF₃COCl (1.2% of the chlorine originally present in HCFC-123), the hydrogen halides (HF-6.1% of the fluorine originally present, HCl-2.7% [Cl]) and COF_2 (12.2% [F]). Minor products (<0.5%) are the hydroperoxides and peroxynitrates. The radical species have low abundances. Wet deposition of HCl (45.4% [Cl]) and CF₃COOH (27.2% [F]) to the ground represents the major fate of HCFC-123. The formation of significant concentrations of COF₂ and HF indicates that photolysis of CF₃COCl can compete with uptake into the aqueous phase.

The calculations undertaken using a Henry's law coefficient of 10 M atm⁻¹ for CF₃COCl give results which are qualitatively and quantitatively similar (less than 1% change in the inventories) to the results presented in Table 6 for a value of 1 M atm⁻¹. This

Process	Model inventory	Weighted inventory [Cl]	(% [Cl])	Weighted inventory [F]	(%[F])
(1) HCEC 102	1.01109	2 (2 109	(100.0)	2.02109	(100.0)
(1) HCFC-123 emitted	1.31×10^{5}	2.62×10^{-5}	(100.0)	3.92 × 10 ²	(100.0)
(2) Gas-phase inventory:					
Unreacted CF ₃ CHCl ₂	6.61 × 10°	1.32×10^{9}	(50.5)	1.98×10^{9}	(50.5)
Other species —CF ₃ COCl	3.19×10^{7}	3.19×10^{7}	(1.2)	9.57 × 10 ⁷	(2.4)
HCl	7.09×10^{7}	7.09×10^{7}	(2.7)		
-CF,COOH	1.86×10^{7}	<u> </u>		5.57 × 107	(1.4)
-COF,	2.36×10^{8}			4.72×10^{8}	(12.0)
—HF	2.36×10^{8}		_	2.36×10^{8}	(6.0)
(3) Transport loss to region above model domain:					、
CF ₃ CHCl ₂	5.40 × 10 ⁶	1.08×10^{7}	(0.4)	1.62×10^{7}	(0.4)
-CF ₃ COCI	9.12 × 10 ⁴	1.82×10^{5}	<u> </u>	2.74×10^{6}	´
-HCI	1.06×10^{6}	2.12×10^{6}	(0.1)		
(4) Washout:					
-CF,CCl,OOH	4.70 × 10 ⁵	9.40 × 10 ⁵		1.41 × 10 ⁶	
-CF,CCl ₂ O ₂ NO ₂	3.84×10^{3}	7.68×10^{3}		1.15×10^{4}	
CF ₃ COCl	4.44×10^{6}	4.44×10^{6}	(0.2)	1.33×10^{7}	(0.3)
-CF-COOH	3.50×10^{8}		<u> </u>	1.05×10^{9}	(26.8)
HCl	1.17 × 10 ⁹	1.17 × 10 ⁹	(44.9)	_	()
Total (inventory + losses)		2.62 × 10 ⁹	(99.9)	3.92 × 10 ⁹	(100.0)

Table 6. Budget analysis for HCFC-123 (CF₃CHCl₂) after 2 yr model simulation with gas-phase chemistry, washout and transport out of model included (position at January 1985)

The units of the model inventory and weighted inventories are those of moles. The weighted inventories are related to the model inventory by the number of Cl or F atoms in each molecule.

Percentages are of total emitted CF₃CHCl₂ over the 2-year period $[2 \times 0.1 \text{ Tg} = 1.31 \times 10^9 \text{ mol}]$.

suggests that uptake of CF_3COCI in the model domain is limited by the amount of liquid water present in the grid cell.

The budget analysis, when combined with all the fluxes leading to net loss of a given compound, can be used to estimate the lifetime of that compound (see Table 7). The lifetime of the compounds formed in the degradation of HCFC-123 are shorter than that of the parent. Once the calculations have been taken past 3 or 4 lifetimes of the longest-lived product (25 d for HCl), the relative yields of the products do not change. The only effect of extending the simulation is to achieve greater conversion of the parent compound into products.

A more detailed analysis of the distribution of the intermediate and stable compounds was undertaken. HCFC-123 shows a strong gradient with both altitude and latitude (Fig. 6a), reflecting the comparatively short atmospheric lifetime of this particular HCFC (1.7 yr). It is mainly emitted in the Northern Hemisphere. The chlorine present in HCFC-123 is converted into CF₃COCl and HCl in the gas-phase. The majority of CF₃COCl (60.4%) is lost to precipitation and rainout. As indicated above, photolysis represents a significant loss process for CF₃COCl (38.6%) and this leads to the formation of CF_3O_2 and ultimately COF_2 and HF. The distribution of CF_3COCI (Fig. 6b), CF₃COOH (Fig. 6c), HCl (Fig. 6d), COF₂ and HF are complex, reflecting the different factors affecting both their sources, reactions and loss processes. The competition between photolysis (leading to HF and COF₂) and uptake (leading to CF₃COOH and

Table	7.	Representative	atmospheric	lifetimes	for	species
		formed in deg	radation of H	ICFC-123	5	

Species	Lifetime	Major loss process
HCFC-123	1.7 yrs	Reaction with OH
CF ₃ CCl ₂ O ₂	70 s ์	Reaction with NO
CF ₃ CCl ₂ OOH	25 h	Reaction with OH
CF ₃ CCl ₂ O ₂ NO ₂	36 min	Thermal decomposition
CF ₃ COCI	15 d	Washout
CF ₃ O ₂	140 s	Reaction with NO
CF.OOH	26 h	Reaction with OH
CF ₁ O ₂ NO ₂	3 h	Thermal decomposition
CI	2 s	Reaction with CH ₄
HCI	25 d	Washout
HF		Washout
COF ₂	—	Transport to stratosphere

HCl) depends critically on the intensity of solar radiation and the local water vapour content.

A number of the short-lived species formed in the degradation of HCFC-123, e.g. $CF_3CCl_2O_2$, CF_3CCl_2OOH , CF_3O_2 and CF_3OOH have maxima in their abundances which depend on season. Thus in January, there is a Southern Hemisphere maximum moving to the Northern Hemisphere in July, reflecting the shift in the maxima of OH and HO₂. The peroxynitrates, $CF_3CCl_2O_2NO_2$ and $CF_3O_2NO_2$, the stabilities of which are strongly temperature-dependent, have peak abundances in the colder regions of the atmosphere, i.e. the upper troposphere and lower stratosphere.

In summary, the major products of the degradation of HCFC-123 are CF₃COCl, HCl, CF₃COOH, COF₂ and HF.

5. DISCUSSION AND ATMOSPHERIC IMPLICATIONS

The rate coefficients reported in this paper represent the first determinations of these parameters. The rate coefficient for the self-reaction of $CF_3CCl_2O_2$ is significantly faster than that for the self-reaction of $C_2H_5O_2$ (Lightfoot *et al.*, 1992) but comparable to that reported for $ClCH_2CH_2O_2$ (Dagaut *et al.*, 1988). The reaction of $CF_3CCl_2O_2$ with HO₂ appears to be slower than the corresponding reaction of $C_2H_5O_2$ with HO₂ (Lightfoot *et al.*, 1992). The database on the self-reactions of substituted peroxy radicals and of



their reactions with HO₂ is limited and no conclusions should be inferred as to the general trend in the reactivity of halogen-substituted peroxy radicals. The rate coefficient derived for reaction of $CF_3CCl_2O_2$ with NO is comparable to the values reported for other fully and partially halogenated peroxy radicals (Atkinson et al., 1992; Wallington and Nielson, 1991).

The rate coefficient data derived in this work, when combined with typical atmospheric abundances of HO₂, NO and NO₂, suggest that the major loss process for $CF_3CCl_2O_2$ is by reaction with NO. The oxy



Fig. 6b.

radical formed in this reaction (4), CF_3CCl_2O undergoes C-Cl rather than C-C bond fission as the major gas-phase product observed in the degradation of HCFC-123 was CF_3COCl .

$$CF_3CCl_2O \to CF_3 + COCl_2 \tag{7a}$$

$$\rightarrow CF_3COCl + Cl.$$
 (7b)

The aqueous-phase uptake of CF_3COCl and its conversion into CF_3COOH is expected to be the major loss process for CF_3COCl in the troposphere (WMO 1990b). The parameterization used to model the uptake by the aqueous phase indicates that this process will lead to a tropospheric residence time for CF_3COCl of 15 d.

CF3COOH JULY 1984 (X 1E15)





Fig. 6(a)-(d). Contour plots for HCFC-123, CF₃COCl, CF₃COOH and HCl at July 1984 (after 18 months simulation) and January 1985 (24 months simulation). The calculations assume an annual emission rate of 0.1 Tg yr⁻¹ with the same latitudinal dependence of the emissions as for the fully halogenated chlorofluorocarbons. Abundances are given in units of parts per 10¹² for HCFC-123 (a) and in units of parts per 10¹⁵ of CF₃COCl (b), CF₃COOH (c) and HCl (d).

The other significant loss process for CF₃COCl is photolysis. The UV absorption spectrum recorded by Rattigan *et al.* (1991) has been used to calculate the photolysis of CF₃COCl in the atmosphere. The calculations of Rattigan *et al.* (1991) suggest an upper tropospheric lifetime of 86 days (also confirmed by our modelling studies) with respect to loss by photolysis.

Uptake into the aqueous phase is therefore the major loss process in the lower atmosphere but photolysis of GF_3COCl will be a minor but significant loss process in the upper troposphere and lower stratosphere. The final products formed in the degradation of HCFC-123 depend on which of these two processes occurs. If CF_3COCl is taken up into the aqueous phase, CF_3COOH is the major product, which will eventually be rained out. On the other hand, if CF_3COCl is photolysed, then the end-products of HCFC-123 degradation are COF_2 , HF and HCl.

Although kinetic and mechanistic data, particularly as a function of temperature, are still lacking on specific processes, it is clear that substantial progress has been made in our understanding of the tropospheric degradation processes of HCFC-123. Quantitative predictions on the impact of using HCFC-123 can now be made with some confidence.

Note added in press-T. J. Wallington, T. Ellerman and O. J. Nielsen (Research in Chemical Intermediates, in press) have recently undertaken a study of the pulse radiolysis of SF₆/HCFC-123 and SF₆/HCFC-123/O₂ mixtures with ultra-violet absorption detection of the radical species formed (CF₃CCl₂ and CF₃CCl₂O₂). Wallington et al. derived an ultra-violet absorption spectrum for CF3CCl2O2 which is in excellent agreement, both in shape and magnitude, with that derived in this work and have obtained a rate coefficient for the self-reaction of CF₃CCl₂O₂, k[CF₃CCl₂O₂+CF₃CCl₂O₂ \rightarrow CF₃CCl₂O + CF₃CCl₂O + O₂]=(3.33±0.53) × 10⁻¹² cm³ mol⁻¹s⁻¹, which is almost equal to the value determined in this work, i.e. $k = (3.6 \pm 0.5) \times 10^{-12} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$.

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