

Mechanism of Atmospheric Oxidation of 1,1,1,2-Tetrafluoroethane (HFC 134a)

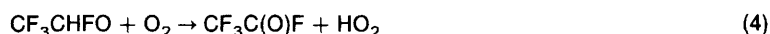
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The chlorine-initiated photooxidation of hydrofluorocarbon 134a ($\text{CF}_3\text{CH}_2\text{F}$) has been studied in the temperature range 235–318 K and at 1 atm total pressure using UV absorption. Trifluoroacetyl fluoride [$\text{CF}_3\text{C}(\text{O})\text{F}$] and formyl fluoride [$\text{HC}(\text{O})\text{F}$] were observed as the major products. IR analysis of the reaction mixture also showed carbonyl fluoride [$\text{C}(\text{O})\text{F}_2$] as a product. By measurement of the yields of $\text{HC}(\text{O})\text{F}$ from the photooxidation as a function of $[\text{O}_2]$ and temperature, the rate of the unimolecular decomposition of the oxy radical, CF_3CHFO , reaction (5), was determined relative to its reaction with O_2 , reaction (4):



The results were treated using both an arithmetic derivation and numerical integration with a detailed reaction scheme. Inclusion of other recently published kinetic data leads to the following recommended rate expression for reaction (5) at 1 atm

$$k_5 = 7.4 \times 10^{11} \exp[(-4720 \pm 220)/T] \text{ s}^{-1}$$

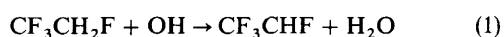
The errors are 1σ .

The observation of enhanced product yields in the present work is attributed to the reaction of the CF_3O radical with HFC 134a leading to further peroxy radical formation. The results have been incorporated into a 2D atmospheric model to assess the environmental implications of HFC 134a release in the troposphere.

It is now widely accepted that chlorofluorocarbons (CFCs) are directly responsible for the increasing levels of stratospheric chlorine observed over the past decade.¹ This has in turn led to large losses of stratospheric ozone, particularly over the polar regions (see, *e.g.* ref. 2). Hydrochlorofluorocarbons (HCFCs) and hydrofluorocarbons (HFCs) have been proposed as replacements for CFCs. These compounds contain one or more carbon–hydrogen bonds and are therefore susceptible to attack by the hydroxy radical in the troposphere leading to shorter atmospheric lifetimes.³ These shorter lifetimes, coupled with reduced chlorine substitution, lead to a lower release of chlorine in the stratosphere and hence a lower ozone-depletion potential.

In order to assess the environmental impact of HCFC and HFC release it is necessary to quantify the nature and yield of the products from atmospheric oxidation. Although the reaction of the hydroxy radical with these compounds has been the subject of several studies,^{4–6} the detailed mechanistic and kinetic pathways are somewhat uncertain.

HFC 134a ($\text{CF}_3\text{CH}_2\text{F}$) is a proposed replacement for dichlorodifluoromethane (CFC-12) which is widely used as a refrigerant and in air-conditioning systems. In the troposphere OH-initiated oxidation of HFC 134a leads to the formation of the peroxy radical CF_3CHFO_2 via the following reactions

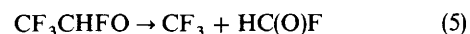
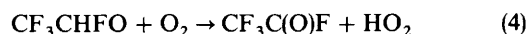


The reaction of CF_3CHFO_2 with NO [reaction (3)] has been found to be rapid^{7,8} and is expected to be a major loss reaction for the peroxy radical for most situations in the tropo-

sphere



Subsequently, CF_3CHFO radicals formed in reaction (3) may either react with O_2 [reaction (4)] or undergo unimolecular decomposition [reaction (5)]



The primary product distribution from the oxidation of HFC 134a therefore depends on the relative rates of reactions (4) and (5).

We have recently measured the UV spectra and absorption cross-sections, σ , for $\text{CF}_3\text{C}(\text{O})\text{F}$ and $\text{HC}(\text{O})\text{F}$ ^{9,10} and in the present work we have used this information to determine the yields of these products in the chlorine photosensitised oxidation of HFC 134a by UV spectroscopy. Measurement of the yields as a function of $[\text{O}_2]$ and temperature gave information on the reaction mechanism and allowed a determination of the rate constant ratio k_4/k_5 in the temperature range 235–318 K. During the course of this work a number of other studies of the photooxidation of HFC 134a have been carried out and the combination of these results has greatly aided in the understanding of the complex reaction mechanism and determination of the kinetic parameters.

Wallington *et al.*¹¹ studied the chlorine-initiated photooxidation of HFC 134a over the temperature range 261–353 K and at pressures of 15–5650 Torr using product analysis with FTIR. An expression for k_4/k_5 of $1.58 \times 10^{-25} \exp(3600/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ was reported at 2 atm and a strong pressure dependence below 1 atm was found due to fall-off in the

rate of the unimolecular reaction (5). Tuazon and Atkinson¹² have also studied the photooxidation using FTIR and their branching ratio of $k_4/k_5 = 3.2 \times 10^{-25} \exp(3510/T)$ over the range 273–320 K and 1 atm pressure is in excellent agreement. Edney and Driscoll¹³ have reported a similar study at room temperature with results that are broadly consistent.

Maricq and Szente¹⁴ have recently reported a flash photolysis UV absorption kinetics study of HFC 134a photooxidation. Diode array spectroscopy was used to obtain time-resolved spectroscopic information of the radicals CF_3CHFO and CF_3CHFO_2 . They determined the rate of the unimolecular decomposition of the CF_3CHFO radical, $k_5 = 3.7 \times 10^7 \exp(-2200/T) \text{ s}^{-1}$ over the temperature range 210–372 K and at 250 Torr, from the time dependence of growth and decay of an absorption assigned to CF_3CHFO .

Zellner *et al.*¹⁵ studied the pulsed laser photolysis of HFC 134a- Cl_2 - NO - O_2 mixtures with time-resolved measurement of $[\text{OH}]$ and $[\text{NO}_2]$ using optical methods. By simultaneous fitting to the NO_2 and OH profiles, they were able to determine values for k_2 , k_4 and k_5 of $(1.7 \pm 0.6) \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, $(2.7 \pm 0.6) \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and $(1.8 \pm 0.4) \times 10^4 \text{ s}^{-1}$, respectively, at 295 K and 38 Torr total pressure. An absolute uncertainty of a factor of two was reported for the individual values of k_4 and k_5 , but the ratio k_4/k_5 was well determined.

There is considerable uncertainty about the fate of the CF_3 radical produced in reaction (5) and its effect on the kinetics and products in the system. Under the conditions employed in this work, CF_3 is likely to form CF_3O_2 radicals by the addition of O_2 . The self- and cross-reactions of this peroxy radical lead to CF_3O .^{16,17} Good evidence has also been reported¹⁸ for the formation of trioxide species such as $\text{CF}_3\text{O}_3\text{CF}_3$, formed in the reaction of CF_3O with CF_3O_2 , although these substances are unlikely to be formed in the atmosphere in view of the low radical concentrations. Sehested and Wallington found evidence that CF_3O reacts with CF_3CHFO_2 to form a trioxide which is less stable than $\text{CF}_3\text{O}_3\text{CF}_3$.¹⁹

Recent studies have also shown that the rate constant for the reaction of the CF_3O radical in H-atom abstraction from hydrocarbons is rapid, with room-temperature rate coefficients similar to those for OH radicals.^{20–22} Sehested and Wallington found that CF_3O reacts with HFC 134a to form CF_3OH which decomposes to give COF_2 and HF.¹⁹ It seems likely that CF_3OH formation is the fate of CF_3O in the troposphere.

In the present work the relative importance of the thermal decomposition of CF_3CHFO compared to its reaction with O_2 has been computed using a 2D atmospheric model.²³ The fate of the product $\text{CF}_3\text{C(O)F}$ in the atmosphere is also discussed.

Experimental

The dual-beam diode array spectroscopy system used in this study has been described in detail previously.²⁴ A 1 m long jacketed quartz cell connected to a standard greaseless vacuum system was used as the reaction vessel. The cell was thermostatted at 235–318 K using flowing ethanol, and evacuated dual-window assemblies prevented frosting of the optical faces at low temperatures. Four interchangeable photolysis lamps were mounted adjacent and parallel to the cell. In the present study Philips TL/09 lamps of spectral output in the range 300–400 nm were used.

The source of UV for absorption measurements was a deuterium lamp (30W, Hamamatsu L 1636) collimated output from which was passed through a beam splitter (Oriental Scientific, model 78150) producing two beams (reference and

sample) which were collected in optical fibre couplers (Oriental Scientific model 77800) either directly (reference) or after passage longitudinally through the cell (sample). These two beams were then resolved and imaged by a 275 mm Czerny-Turner spectrograph, at a spectral resolution of 1.2 nm, separately onto two 512 channel unintensified silicon diode arrays (Reticon). The spectrograph and detector were controlled by a microcomputer (Dell 316SX) and software packages (Spectroscopy Instruments Ltd.) were used for linearisation of the wavelength scale, for background subtraction and averaging of the data and for calculation of the absorbance using the reference spectrum to correct for changes in the source lamp intensity. Despite this correction, however, the main limitation in absorbance measurements was baseline drift, attributed to inhomogeneities in the source output affecting the reference and sample beams differently. This limited the precision of measurements to ± 0.0005 absorbance units.

$\text{CF}_3\text{CH}_2\text{F}$ (99.8%) was obtained from ICI Chemicals and Polymers Ltd. and $\text{CF}_3\text{C(O)F}$ (97%) was obtained from Fluorochem. Both samples were purified by trap-to-trap distillation prior to use. Research grade samples of Cl_2 (5% in N_2), O_2 and N_2 obtained from BOC were used without further purification.

Formyl fluoride was prepared by the reaction of formic acid with benzoyl chloride using dry KHF_2 at 333 K.²⁵ The formyl fluoride was first purified by passing through a trap at 255 K to remove benzoyl chloride vapours and then trapped at 78 K. Several successive distillations of the formyl fluoride were carried out.

Results

Reference UV absorption spectra of pure samples of $\text{CF}_3\text{C(O)F}$ and HC(O)F were recorded over a range of conditions, prior to the photooxidation study.^{9,10} Example spectra are shown in Fig. 1. The absorption cross-section for $\text{CF}_3\text{C(O)F}$ was $13.8 \times 10^{-20} \text{ cm}^2 \text{ molecule}^{-1}$ at the maximum, 214 nm, and was found to have a small temperature dependence.⁹ For HC(O)F the cross-section at 230 nm was $6.85 \times 10^{-20} \text{ cm}^2 \text{ molecule}^{-1}$, using a resolution of 1.2 nm (FWHM), in good agreement with the results of Giddings and Innes.²⁶ The absorption cross-section was found to be independent of temperature in the range 233–318 K. IR spectra of the two main products were also recorded, in order to confirm their purity.

For the photooxidation study, mixtures of $\text{CF}_3\text{CH}_2\text{F}$ (8–12 Torr), Cl_2 , (1 Torr, 5% in N_2) and O_2 (20–730 Torr) were made up to a total pressure of 760 Torr using N_2 (17–731 Torr) and pre-mixed in the dark for several hours. Irradiation in the wavelength range 300–400 nm was then used to drive the Cl-atom-initiated photooxidation of the hydrofluorocarbon and at regular intervals prior to and during this photolysis, UV spectra of the reaction mixture were recorded. Fig. 2 shows three sequential spectra taken following 111, 171 and 243 s of irradiation. As can be seen from these spectra, there is a build-up of absorption around 230 nm, attributable to product formation and a reduction of absorption around 300 nm, attributable to chlorine consumption, with increasing irradiation time.

Spectral stripping routines were applied to the sequential spectra for the identification and quantification of products formed during the photooxidation. Reference spectra reported above were used, allowing for the temperature dependence of the $\text{CF}_3\text{C(O)F}$ spectrum. However, owing to the very weak UV absorption of HFC 134a in the wavelength range used in this study, consumption of the hydrofluorocarbon could not be monitored. Yields of the two main

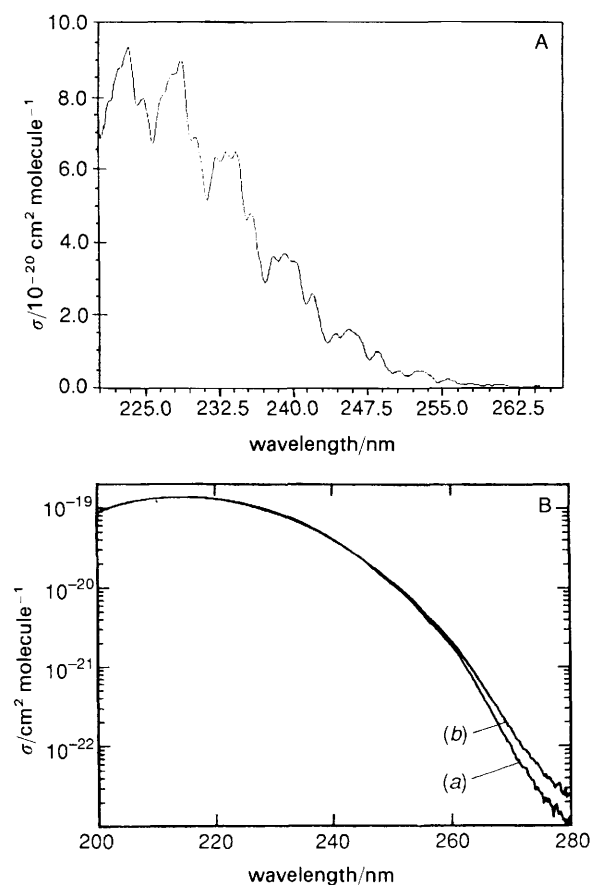


Fig. 1 Reference UV absorption spectra of, A, HC(O)F and, B, CF₃C(O)F at (a) 238 and (b) 293 K

products were therefore expressed in terms of the molecular chlorine consumed, given that the experimental conditions were arranged such that chlorine atoms were converted stoichiometrically into CF₃CHFO₂ radicals. Chlorine cross-sections were taken from the current NASA evaluation.⁵ A graph of product formation against chlorine consumption gave the 'chlorine based' yield as the gradient, and the small non-zero intercept, where present, was attributed to differential baseline shifting of the sample and reference beams and neglected. Errors on individual yields were taken from these graphs and combined with a $\pm 5\%$ uncertainty in the cross-sections. Typically, this resulted in a total error in the yield of

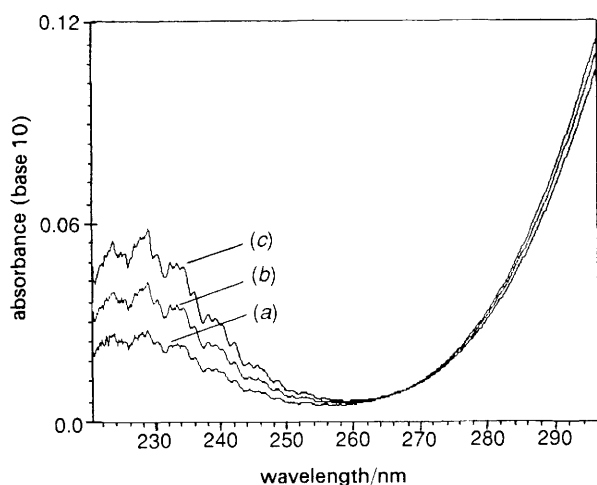


Fig. 2 Sequential UV absorption spectra of a photolysed HFC 134a-Cl₂-O₂-N₂ mixture at (a) 111, (b) 171 and (c) 243 s

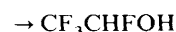
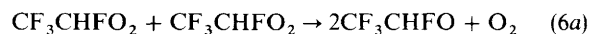
$\pm 8\%$. Following spectral stripping of Cl₂, HC(O)F and CF₃C(O)F, the baseline of UV absorption showed no additional significant absorbance.

The photooxidation study was carried out at four experimental temperatures in the range 235–318 K, and at a range of oxygen partial pressures. This range of oxygen pressures used at each experimental temperature was chosen such that comparable and therefore relatively easily measurable concentrations of the two main products were obtained. Chlorine based yields of HC(O)F and CF₃C(O)F obtained are shown in Table 1. Not all spectra were analysed for the CF₃C(O)F yield, however, since this quantity proved to be both difficult to ascertain and of limited use in extracting branching ratios. The problem is discussed further below.

In addition to the UV yield analysis, qualitative experiments to determine the composition of the reaction mixture following photolysis were carried out using IR spectroscopy. A spectrum of a typical photolysed mixture of HFC 134a, Cl₂, O₂ and N₂ is shown in Fig. 3. In addition to the major products, absorptions attributable to COF₂, HF and SiF₄ were observed.

Discussion

In the photooxidation study, the Cl-atom-initiated formation of peroxy radicals, CF₃CHFO₂, in the absence of NO, leads to the self-reaction



This reaction provides a convenient way of studying the reaction of the oxy radical in the absence of chain processes initiated by the presence of NO in the system. Oxy radicals formed in the non-terminating step (6a) then either react further with O₂ [reaction (4)] or unimolecularly decompose [reaction (5)]. The final product distribution reflects this branching. The basic mechanism for the photooxidation, in the absence of NO, is illustrated diagrammatically in Fig. 4. Table 2 shows the full mechanism, which is similar to that

Table 1 Yields of products from the photooxidation of HFC 134a

T/K	[O ₂]/10 ¹⁸ molecule cm ⁻³	yield ^a	
		HC(O)F	CF ₃ C(O)F
293	5.98	2.48	1.35
	9.89	1.96	1.87
	19.3	1.35	1.65
	24.0	1.15	1.85
235	0.822	0.98	— ^b
	2.06	0.75	1.42
	3.25	0.60	1.26
	4.11	0.59	1.34
	4.77	0.60	— ^b
	6.11	0.36	1.57
273	5.71	1.54	2.13
	10.59	1.07	1.67
	14.27	0.725	1.82
	17.73	0.754	1.75
318	9.78	3.78	— ^b
	12.20	4.50	2.26
	17.80	3.12	— ^b
	22.20	3.00	1.44

^a Product yields are expressed in terms of the amount of Cl₂ consumed. ^b Not analysed, see text for details.

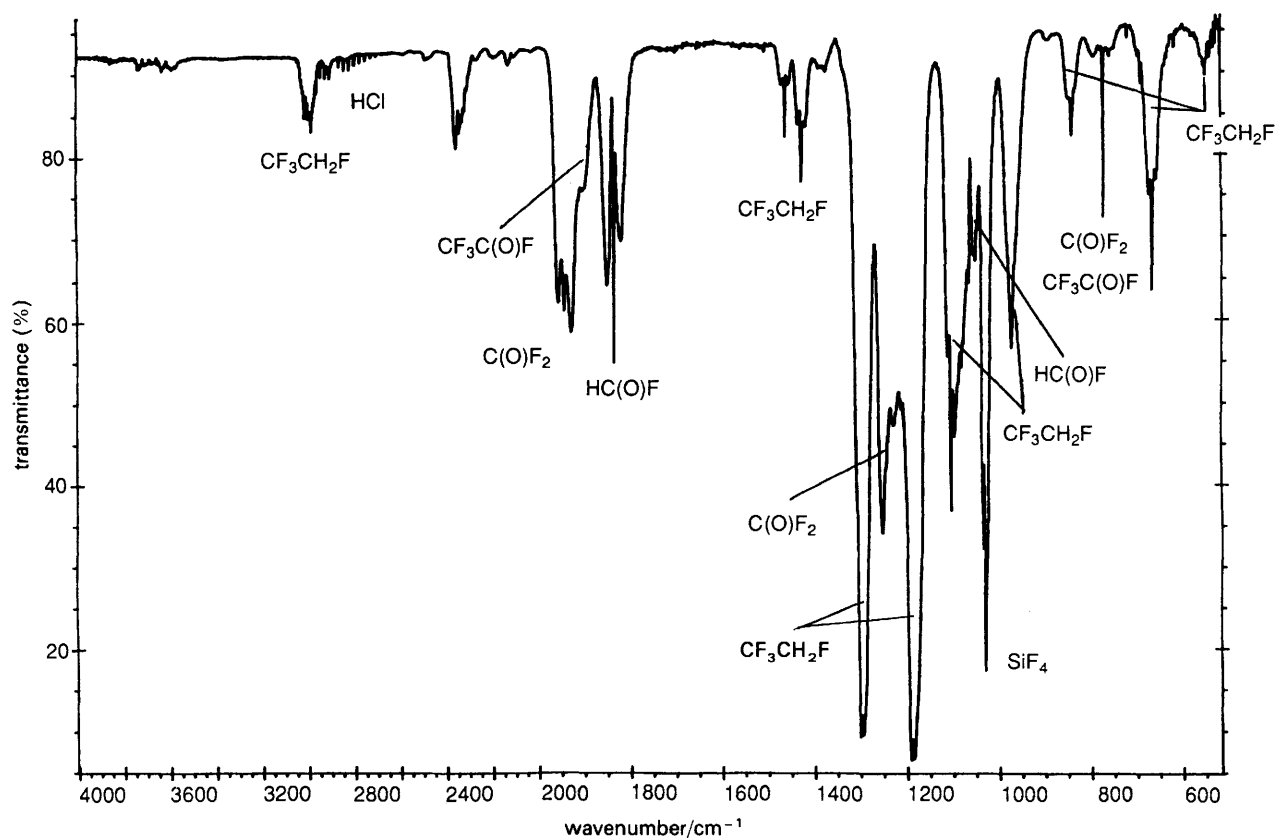


Fig. 3 IR spectrum of a photolysed HFC 134a-Cl₂-O₂-N₂ mixture

presented by Wallington and co-workers.^{11,19} Analysis of the measured product yields to obtain the CF₃CHFO rate constant ratio k_4/k_5 was carried out using two separate techniques. These methods are discussed individually below.

Arithmetic Derivation of k_4/k_5

The branching ratio for the non-terminating channel of the CF₃CHFO₂ radical self-reaction is defined as $\alpha = k_{6a}/(k_{6a} + k_{6b})$. Similarly, the branching ratio for the CF₃CHFO radical reaction with oxygen is defined as β . β therefore

depends on oxygen concentration

$$\beta = k_4[\text{O}_2]/(k_4[\text{O}_2] + k_5)$$

Both of these branching ratios affect the observed product distribution. A preliminary analysis of the product data can be undertaken by arithmetically expressing the yields. Thus, for a nominal photodissociation of x chlorine molecules in the presence of excess of HFC and oxygen, $2x$ CF₃CHFO₂ are produced.



Table 2 Full mechanism for the photooxidation of HFC 134a in the absence of NO^a

reaction	A	E/R	reaction
Cl ₂ + $h\nu$ → 2Cl	—	—	fitted
Cl + CF ₃ CH ₂ F → HCl + CF ₃ CHF	1 × 10 ¹²	1958	(2)
CF ₃ CHF + O ₂ → CF ₃ CHFO ₂			(6a)
2CF ₃ CHFO ₂ → 2CF ₃ CHFO + O ₂	$\alpha 6.7 \times 10^{-13b}$	-700	(6b)
→ CF ₃ CHFOH + CF ₃ COF + O ₂	$(1 - \alpha) 6.7 \times 10^{-13b}$	-700	(4)
CF ₃ CHFO + O ₂ → CF ₃ COF + HO ₂	6.0×10^{-14}	925	fitted
CF ₃ CHFO → CF ₃ + HC(O)F			(7)
HO ₂ + CF ₃ CHFO ₂ → CF ₃ CHFO ₂ H + O ₂	5.7×10^{-13}	-700	(9)
HO ₂ + HO ₂ → H ₂ O ₂ + O ₂			(10)
CF ₃ + O ₂ → CF ₃ O ₂			(11)
CF ₃ O ₂ + CF ₃ O ₂ → 2CF ₃ O + O ₂	1.2×10^{-13}	-800	(12)
CF ₃ O ₂ + HO ₂ → CF ₃ O ₂ H + O ₂	5.7×10^{-13}	-700	(13)
CF ₃ O ₂ + CF ₃ CHFO ₂ → CF ₃ O + CF ₃ CHFO + O ₂	$\alpha 7.6 \times 10^{-13}$	-700	(14)
→ CF ₃ OH + CF ₃ COF + O ₂	$(1 - \alpha) 7.6 \times 10^{-13}$	-700	(15)
CF ₃ O + HC(O)F → CF ₃ OH + C(O)F	1.2×10^{-12}	2030	(16)
CF ₃ O + CF ₃ O ₂ → CF ₃ O ₃ CF ₃			fitted
CF ₃ O + CF ₃ CHFO ₂ → CF ₃ CHFO ₃ CF ₃			(8)
CF ₃ O + CF ₃ CH ₂ F → CF ₃ OH + CF ₃ CHF	1.2×10^{-12}	2030	

^a Reactions of HO₂ with peroxy radicals are assumed to lead to stable hydroperoxides, with rate coefficients equal to that for the CH₃O₂ + HO₂ reaction.²⁶ ^b Temperature dependence of CF₃CHFO₂ branching ratio, $(1 - \alpha) = 3.0 \times 10^{-3} \exp(1200/T)$.

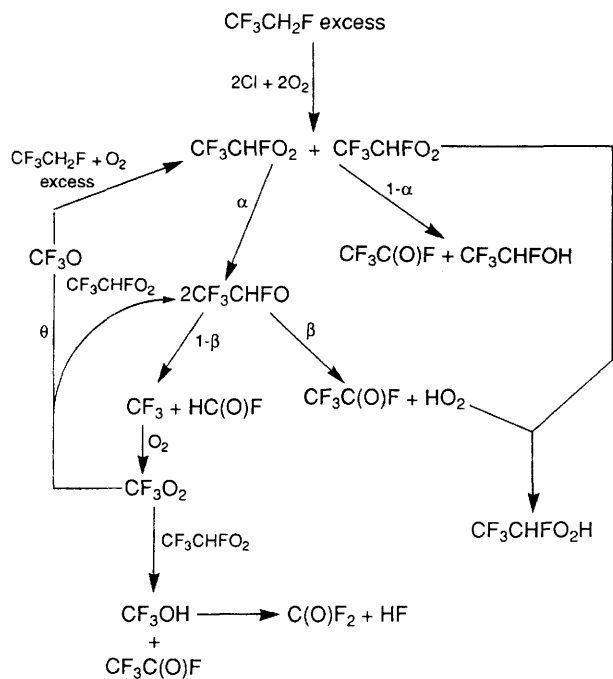
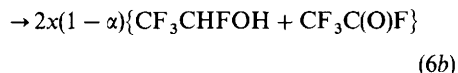
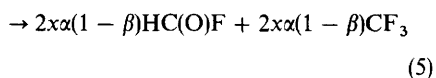
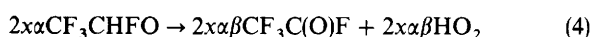


Fig. 4 Photooxidation mechanism for HFC 134a in the absence of NO

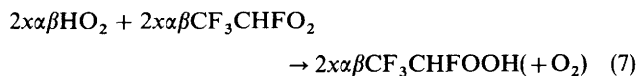
Similarly, in terms of α and β , the reaction of the peroxy radical can be expressed



For the oxy radical:



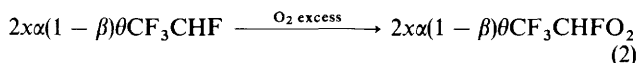
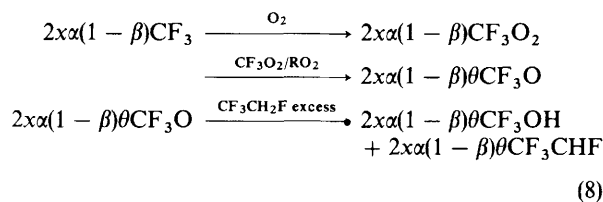
Considering the secondary chemistry, HO_2 radicals are known to react rapidly with RO_2 radicals,²⁷ usually somewhat faster than the RO_2 self-reaction, and the most probable fate of HO_2 generated in reaction (4) is therefore the cross-reaction with the 'parent' RO_2 species. Thus



In the scheme described above, the formation of HO_2 can therefore be assumed to give a further consumption of $x\alpha\beta$ photodissociated chlorine molecules.

For CF_3 radicals, the chemistry is somewhat more complex. The radicals are likely to combine rapidly with oxygen to form CF_3O_2 radicals, which then undergo self- and cross-reactions with all other RO_2 type radicals present. A number of these reactions are expected to give rise to CF_3O and, as has been recently shown,²⁰⁻²² these species react analogously to Cl atoms in hydrogen abstraction from hydrocarbons. Thus, in the excess of HFC 134a used in these experiments, the CF_3O radicals regenerate CF_3CHFO_2 radicals via reactions (8) and (2), in this case without any concomitant Cl_2 consumption. The chemistry of the CF_3 radical is therefore simplified for the purposes of this model. It is assumed that, apart from the regeneration of CF_3CHFO_2 ,

no other effect on the measured product distribution arises:



A further term, θ , is therefore defined here as the fractional efficiency of production of CF_3O radicals from CF_3 .

Sehested and Wallington¹⁹ have shown that CF_3O radicals react with HFC 134a in this photooxidation and assign an IR absorption feature to CF_3OH . The CF_3OH is observed to decay slowly in the dark, giving C(O)F_2 and HF. These products were also identified in the IR spectrum of the photolysed mixture from this study see Fig. 3. Furthermore, the observation of SiF_4 in this study presumably arises from the heterogeneous reaction of HF on the quartz cell walls.

A chain reaction is therefore taking place following the initiation of reaction by dissociation of chlorine, whereby both products $\text{CF}_3\text{C(O)F}$ and HC(O)F are formed and CF_3CHFO_2 is regenerated. However, since only a fractional regeneration of the peroxy radical takes place, the chain length of this process is limited. The total amount of CF_3CHFO_2 reacting, $t(\text{RO}_2)$, following initiation by dissociation of a nominal number, n , of Cl_2 molecules can therefore be expressed as the sum of a geometric series of the form a, ar, ar^2, ar^3, \dots , where r is the fractional regeneration of CF_3CHFO_2 and convergence is defined by $r < 1$. This sum is given by $t(\text{RO}_2) = a/(1-r)$. The total yield of a given product, $y(\text{prod})$, can then be expressed as a fraction, f , of this total RO_2 reacting, divided by the nominal chlorine concentration considered to initiate reaction. Thus

$$y(\text{prod}) = f[t(\text{RO}_2)]/n$$

where f and $t(\text{RO}_2)$ are defined in terms of α and β . Solving in this way for the yield of the HC(O)F leads to

$$\text{HC(O)F yield} = [2\alpha(1-\beta)]/[1-\alpha\theta-\alpha\beta(1+\theta)]$$

Substituting for β in terms of k_4/k_5 then gives the following linear relationship

$$1/y[\text{HC(O)F}] = [(1+\alpha)/2\alpha][\text{O}_2](k_4/k_5) + [(1-\alpha\theta)/2\alpha]$$

Plots of $1/y[\text{HC(O)F}]$ vs. $[\text{O}_2]$ for data at each experimental temperature are presented in Fig. 5, and show reasonable linearity. Fitted parameters for these plots are shown in Table 3. Using values of α from the work of Wallington *et al.*¹¹ values of θ and k_4/k_5 have been calculated and are also shown in the table. k_4/k_5 is shown in Arrhenius form in Fig. 6. There is an indication of curvature in the Arrhenius plot, but an unweighted fit to the k_4/k_5 data gives

$$k_4/k_5 = 1.18 \times 10^{-24} \exp(2860 \pm 380)/T \text{ cm}^3 \text{ molecule}^{-1}$$

The errors are 1σ .

Table 3 Parameters obtained from plots of $[\text{HC(O)F}]^{-1}$ vs. $[\text{O}_2]$

T/K	intercept	gradient ^a	α^b	θ	k_4/k_5^a
235	0.697	28.3	0.50	0.606	18.0
273	0.312	6.30	0.76	0.692	5.44
293	0.252	2.56	0.82	0.716	2.31
318	0.165	0.778	0.87	0.819	0.724

^a Units $10^{-20} \text{ cm}^3 \text{ molecule}^{-1}$. ^b Calculated from Wallington *et al.*¹¹

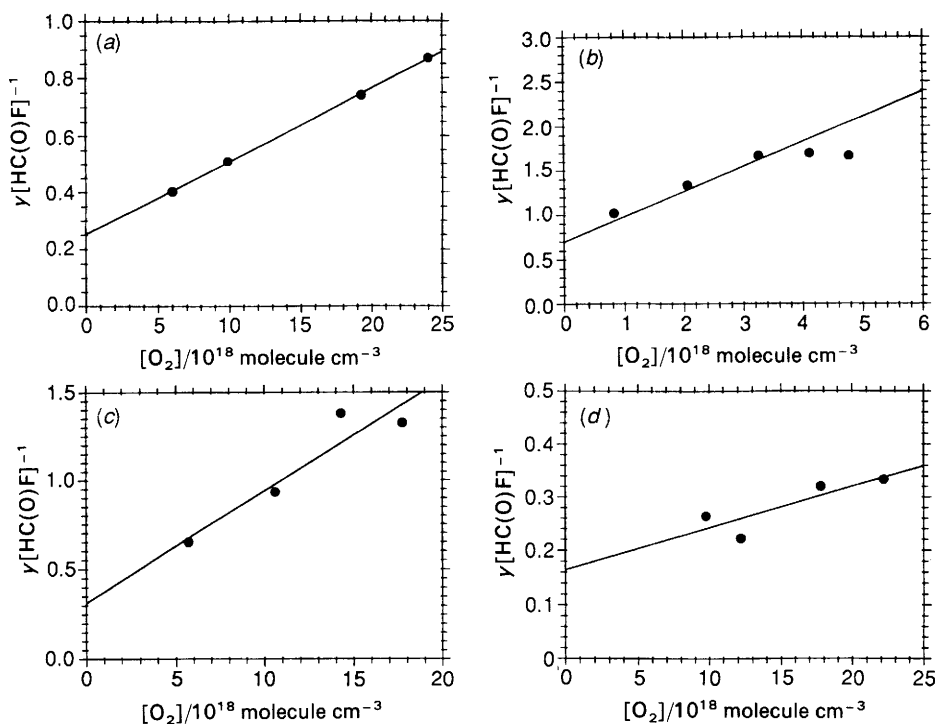


Fig. 5 HC(O)F yield⁻¹ vs. [O₂] at (a) 293, (b) 235, (c) 273 and (d) 318 K

θ increases almost linearly with temperature. The efficiency of regeneration of RO₂ radicals from CF₃ is therefore enhanced at higher temperatures. Thus, given that an excess of HFC 134a and oxygen was always present in these experiments, this can be attributed to an increased conversion of CF₃ into CF₃O radicals at higher temperatures, presumably resulting from both an increased rate of the CF₃O₂ self-reaction relative to CF₃O₂ + RO₂ and a higher branching ratio for CF₃O formation in the CF₃O₂ + RO₂ cross-reactions.

A similar approach was taken to try to quantify the CF₃C(O)F yield in terms of α and β . However, unlike HC(O)F, this compound is formed in small amounts in a number of different channels in the photooxidation of HFC 134a. The sensitivity of the yield to changes in α and β is consequently reduced. Furthermore, because the apparent experimental yields of CF₃C(O)F could be erroneous because of the presence of similar absorbing species, as discussed below, no meaningful estimates of branching ratios could be produced from this yield.

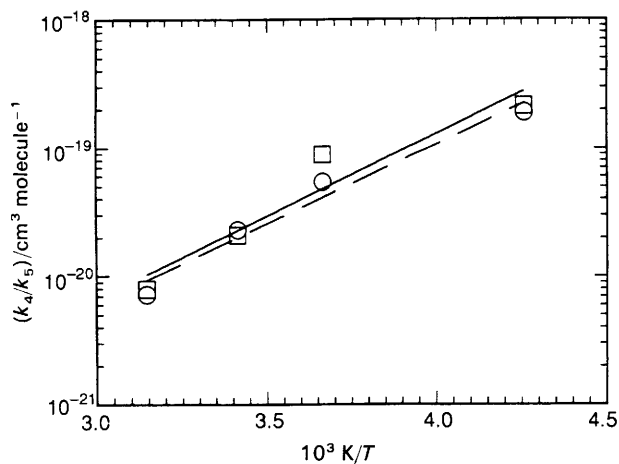


Fig. 6 k_4/k_5 deduced from arithmetic analysis (○) and computer simulation (□) of the product yields expressed in Arrhenius form

In conclusion, the preliminary analysis of yields to give estimates of the branching ratio for the CF₃CHFO radical reaction provides a useful indication of the likely chemistry involved in the HFC 134a photooxidation. The observed yields of HC(O)F confirm the presence of a chain reaction regenerating CF₃CHFO₂ without chlorine consumption.

Kinetic Modelling

In order to provide more exact kinetic parameters for the chlorine-initiated photooxidation of HFC 134a, in particular the branching ratio for the reactions of the CF₃CHFO radical, a computer simulation of the experimental system was carried out using numerical integration. The kinetic model used was based on the reaction mechanism shown in Table 2, together with the source references for the rate coefficients.

In order to define the efficiency of regeneration of CF₃CHFO₂ radicals, θ , the degradation of the CF₃ radical produced in reaction (4) is elaborated in some detail. The degradation chemistry is in accordance with the product analysis work of Sehested and Wallington¹⁹ and the discovery in the present work of enhanced product yields attributed to secondary attack on HFC 134a by the CF₃O radical formed from CF₃O₂. The rate coefficients for the self- and cross-reactions of the peroxy radicals CF₃O₂ and CF₃CHFO₂ are taken from the recent direct kinetic studies of Maricq and Szente¹⁶ and from Nielsen *et al.*¹⁷ The temperature dependence of the branching ratio for the formation of radical (CF₃CHFO) and molecular products [CF₃C(O)F + CF₃CFHOH] from the CF₃CHFO₂ self-reaction is taken from the work of Wallington *et al.*¹¹ The same branching ratio was assumed for the cross-reaction of CF₃O₂ and CF₃CHFO₂.

The model also contained the newly discovered reaction of CF₃O with peroxy radicals^{16,18} to form stable trioxides, CF₃O₃R (R = CF₃ and CF₃CHF). Rate coefficients for the formation and decomposition of the trioxides were taken from Sehested and Wallington.¹⁹ The temperature dependence of the decomposition of CF₃O₃CHF₂ was based on

the 295 K value of $k = 2.7 \times 10^{-3} \text{ s}^{-1}$ and an assumed A factor of 10^{15} s^{-1} ; this gave an activation energy of 99 kJ mol⁻¹.

Preliminary results from Sidebottom²⁰ and Chen *et al.*²¹ using a relative rate technique, and Zellner *et al.*²² using a flash photolysis-LIF method, have shown that the reactivity of CF₃O in H-abstraction from hydrocarbons is comparable to that for OH radicals. Sehested and Wallington¹⁹ have shown that the primary product of the reaction of CF₃O with HFC 134a is CF₃OH which decomposes heterogeneously to C(O)F₂ and HF. The rate coefficient for the reaction of CF₃O with HFC 134a is based on the 295 K value of $k = (1.1 \pm 0.7) \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ determined by these workers, and an assumed A factor of $1 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

The rate coefficient for the reaction of Cl atoms with HFC 134a at 298 K, $k = 1.4 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, is well established.^{28,29} The temperature dependence is based on an assumed A factor of $1.2 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. The secondary removal of HC(O)F by reaction with Cl and CF₃O was also included in the reaction scheme. The rate coefficients for the reaction of CF₃O with HC(O)F were assumed to be the same as for CF₃O with HFC 134a. The rate coefficient for Cl + HC(O)F at 295 K has been determined by Wallington *et al.*,¹¹ $k = 2.0 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. The temperature dependence is based on an assumed A factor of $1.0 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. Using these rate coefficients, the calculated secondary loss of HC(O)F was very small at the extent of reaction of HFC 134a used in the experiments. This was in accordance with the observations.

The expression for the temperature dependence of the rate coefficient for the reaction of CF₃CHFO with O₂ is based on the room-temperature value, determined by Zellner *et al.*,¹⁵ $k_4 = 2.7 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, and an A factor of $6.0 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, equal to that recommended for the C₂H₅O + O₂ reaction.⁶

The unknown rate coefficient, k_5 (unimolecular decomposition of CF₃CHFO) and R_{Cl_2} (the rate of Cl₂ photolysis) were obtained by fitting computer-generated concentration-time data for Cl₂, HC(O)F, CF₃C(O)F and other products, to experimental data obtained in 16 experiments covering a range of temperatures and O₂ partial pressures. The kinetic equations were integrated using the FACSIMILE program,³⁰ which contained an optimization routine for fitting unknown parameters to experimental data, using a non-linear least-squares criterion.

In exploratory experiments it was found that the computed yields of CF₃C(O)F were always substantially smaller than the experimentally determined yields, when values of k_5 and R_{Cl_2} were adjusted to fit the HC(O)F and Cl₂ concentrations. This observation was consistent with results from the arithmetic analysis of yields and was therefore attributed to an experimental overestimation of the CF₃C(O)F yield rather than a problem with the analyses. Such an erroneous observation could arise as a result of further UV absorptions underlying the smooth CF₃C(O)F spectrum. A number of candidates for these products exist, of which hydroperoxides (CF₃CHFOOH, CF₃OOH, H₂O₂) showing broad-band absorption in the UV region and trioxides (CF₃O₃CF₃, CF₃O₃CHFCF₃), for which no UV spectra have been reported, are strong possibilities. Interestingly, adding the modelled hydroperoxide products to the modelled CF₃C(O)F yield significantly improved the fit to the experimental data, as shown in Fig. 7. However, because of this uncertainty, only HC(O)F and Cl₂ experimental data were used to determine R_{Cl_2} and k_5 .

The effect of varying the branching ratio for the cross-reaction of CF₃O₂ and CF₃CHFO₂ was also tested since the amount of the molecular channel in this reaction influences the fraction of CF₃ radicals forming CF₃O, and hence the regeneration of CF₃CHFO₂, *i.e.* the regeneration efficiency θ . As expected it was found that the value of k_5 needed to fit the

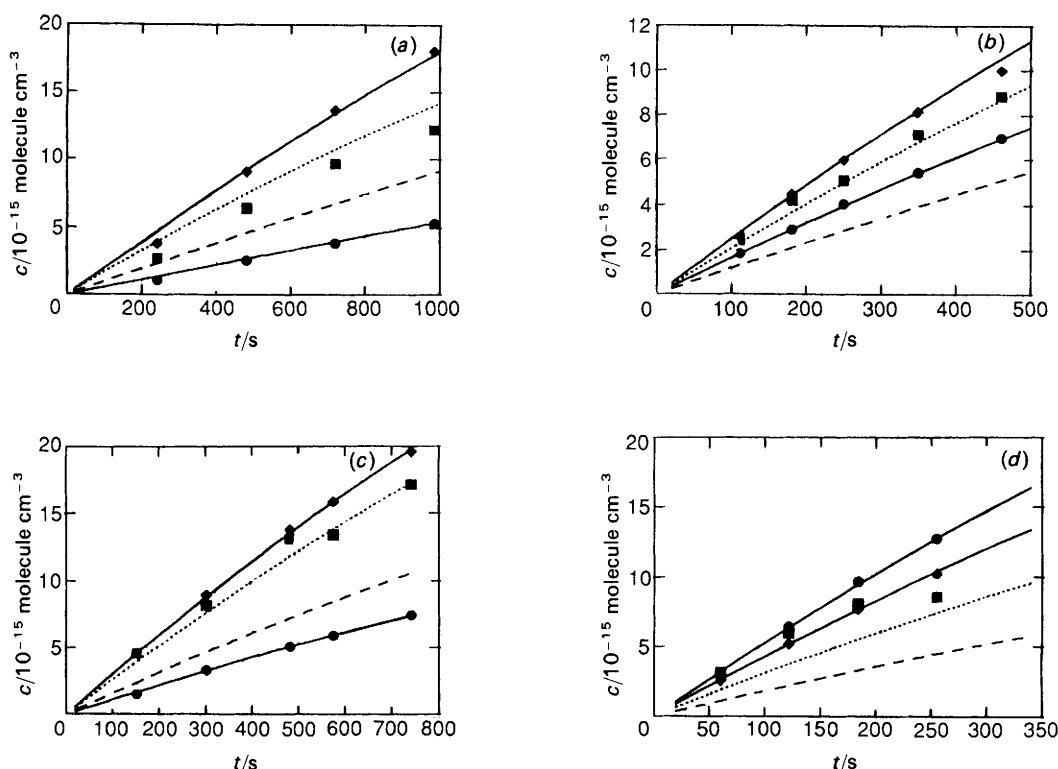


Fig. 7 Computed (—) and experimental (●, HC(O)F; ■, CF₃C(O)F and ◆, Cl₂) concentration-time profiles from HFC 134a photooxidation. Computed CF₃C(O)F (---), (a) 235 K, 100 Torr; (b) 293 K, 589 Torr; (c) 273 K, 299 Torr; (d) 318 K, 729 Torr. Computed CF₃C(O)F + hydroperoxides (see text for details) (- · -).

Table 4 Fitted values of R_{Cl_2} , k_5 and fraction, θ , of CF_3 radicals recycled in the photooxidation of HFC 134a^a

T/K	O ₂ /Torr	$k_5/10^{-3} \text{ s}^{-1}$	$R_{\text{Cl}_2}/10^4 \text{ s}^{-1}$	θ
235	148.6	6.69	3.01	0.37
	100.0	5.33	2.46	0.39
	79.0	5.41	2.41	0.40
	50.0	4.64	2.45	0.42
		5.52 ± 0.85^b		0.40 ± 0.02^b
273	761.3	24.0	4.16	0.56
	501.0	23.7	4.31	0.50
	403.0	22.8	3.82	0.51
	299.1	20.5	4.45	0.52
		22.8 ± 1.6^b		0.52 ± 0.02^b
293	726.5	96.1	5.34	0.61
	584.1	102	5.26	0.62
	300.0	125	4.76	0.66
	181.3	165	4.52	0.67
		122 ± 31.3^b		0.64 ± 0.03^b
318	729.0	340	7.66	0.72
	586.0	281	7.72	0.72
	400.0	679	7.57	0.73
	322.0	342	7.40	0.74
		411 ± 181^b		0.73 ± 0.01^b

^a The errors are 1σ . ^b Average values.

HC(O)F yields increased as the branching ratio for formation of molecular products from this reaction increased. θ and hence k_5 were also dependent on the relative values of the rate constants for the CF_3O_2 and the CF_3O reactions, *e.g.* hydroperoxide and trioxide formation.

Fig. 7 illustrates some of the computed and experimental concentration-time curves. Good fits to the experimental data for HC(O)F and Cl_2 were obtained in all experiments and the values of R_{Cl_2} and k_5 were well and independently determined, except at 318 K and low O_2 where the correlation coefficient for the fitted parameters reached 0.88. Table 4 summarizes the fitted values obtained at four temperatures for R_{Cl_2} and k_5 , together with the values of θ , obtained from the ratio of the calculated yields of CF_3OH from reactions (8), (14) and (15) and HC(O)F from reaction (5). The uncertainties are 1σ values obtained from averaging four experiments at each temperature.

The values of k_4/k_5 obtained from the simulation are plotted in Fig. 6, together with the data from the arithmetic analysis. The agreement between the values of the ratios obtained from the two methods is good, and both data sets indicate possible curvature in the Arrhenius plot. The unweighted fit to the ratio k_4/k_5 from the simulation gives

$$k_4/k_5 = 9.37 \times 10^{-25} \exp(2960 \pm 620/T) \text{ cm}^3 \text{ molecule}^{-1}$$

and a fit to results obtained from both analyses gives

$$k_4/k_5 = 1.05 \times 10^{-24} \exp(2910 \pm 310/T) \text{ cm}^3 \text{ molecule}^{-1}$$

The errors are 1σ .

Discussion of Kinetic Parameters

Expressions for the temperature dependence of the relative rate of the decomposition of CF_3CHFO compared to the reaction with O_2 have been reported by Wallington *et al.*¹¹ and by Tuazon and Atkinson¹² from data in the range 261–353 K and 273–320 K, respectively. In order to compare results for the unimolecular decomposition, k_5 was calculated in each case using the expression $k_4 = 6.0 \times 10^{-14} \exp(-925/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ as used for the reference reaction in this study. Fig. 8 shows an Arrhenius plot of the

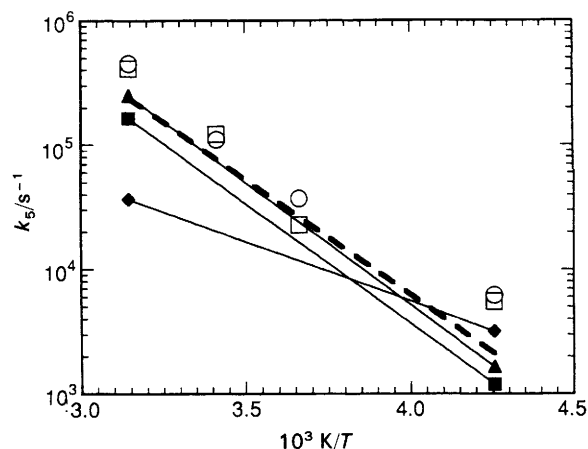


Fig. 8 Arrhenius plot for the CF_3CHFO decomposition reaction. \circ , Arithmetic analysis; \square , kinetic modelling. Fitted values delimited by \blacktriangle , Wallington *et al.*¹¹ \blacksquare , Turazon and Atkinson;¹² \blacklozenge , Maricq and Sente.¹⁴ The dashed line is the recommended fit (see text for details).

data from these sources, together with data from the present work using both the arithmetic approach and the computer simulations. Over the temperature range in which the data overlap, the value of k_5 from the present study appears to be significantly greater than that obtained by Wallington *et al.*¹¹ which is, in turn, larger than the value of Tuazon and Atkinson,¹² both determined at pressures ≥ 1 atm.

The determination of Tuazon and Atkinson¹² is based on measurements of $\text{CF}_3\text{C(O)F}$ formation, assuming that this product is produced only in reactions (4) and (6a). Other potential sources of this product exist, however, *e.g.* the $\text{HO}_2 + \text{CF}_3\text{CHFO}_2$ reaction, which could lead to an underestimation of the value of k_5 relative to k_4 . Wallington *et al.*¹¹ also used the $\text{CF}_3\text{C(O)F}$ yields to determine k_4/k_5 ; these results could be similarly affected. HC(O)F yields were also used and indeed a decrease of *ca.* 20% in the ratio k_4/k_5 was reported in this case implying a higher value of k_5 .

In both studies, a reasonably complete carbon balance among the measured products was reported, particularly at high $[\text{O}_2]$. However, in neither study was the fate of HO_2 formed in reaction (4) considered, whereas in the present work, substantial yields of CF_3CHFOOH and CF_3OOH were predicted by the simulations using the full mechanism. Heterogeneous decomposition of the hydroperoxide CF_3CHFOOH could provide another source of $\text{CF}_3\text{C(O)F}$ which is included in the carbon balance.

In the present work, only the HC(O)F yields were used in the extraction of kinetic parameters. This product has a unique source in reaction (5) and analysis of the yields using two independent techniques was used to determine k_4/k_5 . Nevertheless, an overestimation of k_5 cannot be ruled out in this work, in view of the sensitivity of k_5 to the regeneration factor, θ . In the temperature range over which these studies overlap, the temperature dependence of k_5 from the three relative rate studies is in good agreement. However, at the lowest temperature (235 K) in the present work, the value of k_5 obtained is a factor of three higher than that predicted by linear extrapolation of the Arrhenius expressions based on all data from $T > 261$ K. Furthermore, both Wallington *et al.*¹¹ and Tuazon and Atkinson¹² have shown that the ratio k_4/k_5 is pressure dependent, presumably owing to unimolecular fall-off in reaction (5) at pressure below 1 atm at room temperature. Although the results of Wallington *et al.*¹¹ would be consistent with a high-pressure limit value of k_5 up to a factor of 2 higher than the 1 atm pressure value, it seems unlikely that fall-off effects could account for the apparent

curvature in the Arrhenius plot implied by the 235 K results in the present study. An alternative explanation for this curvature is non-Arrhenius behaviour of the reference rate coefficient, k_4 , a possibility which cannot be discounted since no determinations of the temperature dependence of $\text{CF}_3\text{CHFO} + \text{O}_2$ kinetics have been reported.

Direct measurements of k_5 have been reported by Maricq and Szente¹⁴ and Zellner *et al.*¹⁵ Maricq and Szente¹⁴ used a flash photolysis time-resolved UV spectroscopic study of the CF_3CFHO_2 self-reaction over the temperature range 211–372 K. The production and loss of the CF_3CFHO radical was monitored directly from the time dependence of an absorption feature centred near 270 nm, assigned to CF_3CFHO . Rate constants were derived by fitting a mechanism similar to that used in the present work, which is based on the work of Wallington *et al.*¹¹ The expression derived for k_5 for a total pressure of 230 Torr was $k_5 = (3.7 \pm 0.7) \times 10^7 \exp[-(2200 \pm 150)/T] \text{ s}^{-1}$. These data are shown in Fig. 8. The pressure dependence obtained by Wallington *et al.*¹¹ indicates that the value of k_5 at 230 Torr would be about a factor of two lower than the high-pressure limit value. However, even allowing for this effect it can be seen that the room temperature value, corrected for the pressure dependence, is a factor of three lower than that from the relative rate determinations, and that the temperature dependence of k_5 from the direct determinations is much less pronounced. As pointed out by Maricq and Szente,¹⁴ their reaction conditions would be expected to lead to values of A_5 and E_5 lower than the high-pressure limit values. However, if fall-off effects are used to account for their reported values, they would have to be even larger than those needed to account for the results of the present study at 235 K, which already seem inconsistent with the pressure dependence observed by Wallington *et al.*¹¹ Maricq and Szente¹⁴ also noticed that their data for CF_3CHFO decomposition were not consistent with the branching ratio for the CF_3CHFO_2 self-reaction, α , extrapolated to low temperatures, indicating some mechanistic complications at low temperature.

Zellner *et al.*¹⁵ obtained a value of k_5 at 298 K and 230 Torr of $(1.8 \pm 0.4) \times 10^4 \text{ s}^{-1}$ from the time dependence of OH and NO_2 formation in the pulsed photolysis of Cl_2 -HFC 134a- NO - O_2 mixtures. Using the pressure dependence of Wallington *et al.*¹¹ this corresponds to a value of *ca.* $8 \times 10^4 \text{ s}^{-1}$ at 760 Torr, in better agreement with the relative rate studies than that of Maricq and Szente.¹⁴ However, at present, both the direct determinations and the relative rate studies show considerable uncertainty and the reasons for these discrepancies are not apparent.

Table 5 shows the Arrhenius parameters for reaction (5) obtained from the various temperature-dependent studies. All values except those of Maricq and Szente¹⁴ are close to the high-pressure limit according to the data of Wallington *et al.*¹¹ Nevertheless, the A factors are all significantly lower than the typical value of 10^{13} – 10^{14} s^{-1} expected for a radical decomposition at the high-pressure limit.³¹ This suggests that

Table 5 Arrhenius parameters for the reaction $\text{CF}_3\text{CHFO} \rightarrow \text{CF}_3 + \text{HC(O)F}^a$

$A/10^{-11} \text{ s}^{-1}$	$(E/R)/\text{K}$	$k_{293}/10^{-4} \text{ s}^{-1}$	reference
16.7	4820	12.0	this work (arithmetic)
180	5570	9.98	this work (modelling)
3.8	4525	7.5	Wallington <i>et al.</i> ¹¹
1.9	4435	5.1	Tuazon and Atkinson ¹²
0.00037	2200	2.0	Maricq and Szente ¹⁴
7.4	4720	7.5 ± 2.4	recommended

^a All results, except those of Maricq and Szente, are calculated relative to $k_4 = 6.0 \times 10^{-14} \exp(-925/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

the reaction may not be as close to the high-pressure limit as the data of Wallington *et al.*¹¹ indicate. Further experimental investigation of the pressure dependence is clearly needed to establish if this is the case.

For the purposes of calculating the rate of CF_3CFHO decomposition at atmospheric pressure the expression in Table 5 is recommended. This is based on the mean of the experimental values at 293 K and the E/R values from Wallington *et al.*,¹¹ Tuazon and Atkinson¹² and the present work, excluding the data at 235 K. The temperature dependences obtained from the present work if the 235 K data are included, and from the lower pressure data of Maricq and Szente,¹⁴ both lead to unrealistically low A factors and are therefore not included in the evaluation.

Errors

Errors in individual Arrhenius expressions in this work have been quoted, at the 1σ level solely for the temperature dependence (E/R) of the returned k_4/k_5 or the k_5 value from the analysis. This is in accordance with other recent published work^{11,12} on this reaction and reflects the fact that although the relative rate k_4/k_5 is well established, the pre-exponential factor and hence the absolute values of k_4 and k_5 are not. Furthermore, because of the limited number of data points obtained in this study, a full statistical analysis of errors is inappropriate. The error given in the final recommendation for k_5 has been obtained using the procedure adopted by the NASA panel for chemical data evaluation.⁵ This method uses the error in the ambient temperature value of k_5 [$f(293)$] and that in the temperature dependence ($\Delta E/R$) to determine the approximate 1σ errors over the entire temperature range. The errors are obtained by multiplying or dividing the value of k_5 at any given temperature, T , by $f(T)$. Thus

$$f(T) = f(293) \exp \left[\frac{\Delta E}{R} \left(\frac{1}{T} - \frac{1}{293} \right) \right]$$

Adopting this procedure, the percentage errors in k_5 for this study are $\pm 30\%$ at ambient temperature, rising to $\pm 56\%$ at 235 K and $\pm 38\%$ at 318 K. The average errors in the recommended k_5 value are $\pm 40\%$ across the entire temperature range.

Atmospheric Modelling

There is considerable interest in the relative rate of production of $\text{CF}_3\text{C(O)F}$ and HC(O)F in the atmospheric oxidation of HFC 134a. Neither of these compounds will be significantly photolysed in the troposphere^{6,9} and their major fate is likely to be physical removal in the aqueous phase. Hydrolysis of $\text{CF}_3\text{C(O)F}$ leads to $\text{CF}_3\text{C(O)OH}$, trifluoroacetic acid (TFA), which is the subject of some environmental concern.⁴ TFA is also likely to be physically removed in rain water³² and the source region of $\text{CF}_3\text{C(O)F}$ will therefore determine the atmospheric distribution of $\text{CF}_3\text{C(O)OH}$ produced from HFC 134a photooxidation. A 2D model²³ was used to calculate the latitude–height distribution of the OH-induced oxidation of HFC 134a. Coupled with a knowledge of the temperature and pressure dependence of the relative rate of formation of $\text{CF}_3\text{C(O)F}$ and HC(O)F , the distribution of the source term of these two products in the atmosphere was computed.

The model²³ is a classical zonally averaged Eulerian model. It extends horizontally from 90° S to 90° N in 19 discrete latitude boxes and from ground level vertically up to 60 km in 17 levels with a resolution of 3.5 km. The model includes a representation of tropospheric photochemistry in order to produce a seasonally varying OH concentration

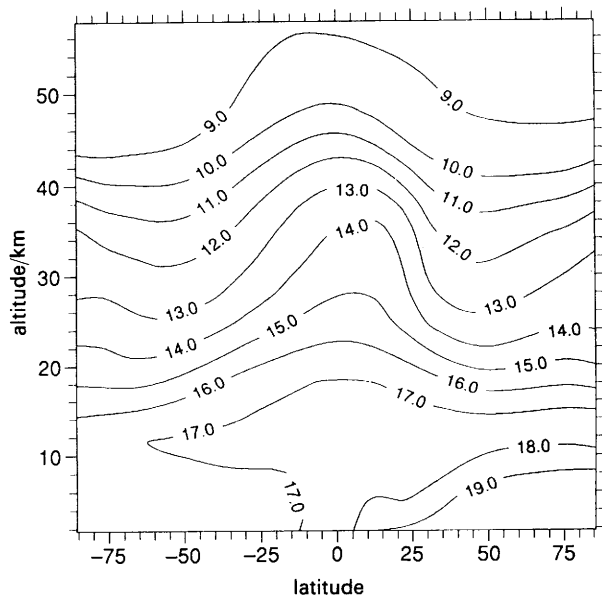


Fig. 9 Modelled atmospheric abundance of HFC 134a in ppt after photochemical loss by the hydroxy radical

field. In the model HFC 134a was released mainly between latitudes 33 and 62° N at ground level at a fixed rate of 29.5 kt year⁻¹ i.e. 10% by volume of the 1986 CFC 11 emission rates. The calculated tropospheric lifetime of HFC 134a in the model due to loss by the hydroxyl radical, using a value for $k(\text{OH} + \text{HFC 134a})$ of $8.4 \times 10^{-13} \exp - 1535/T$, was 12 years. This is somewhat shorter than the value of 15 years calculated by Prather *et al.*,³ the differences probably arising from the higher hydroxy group concentrations in the present model.

Fig. 9 shows the distribution of HFC 134a in ppt following a 40 year integration with photochemical destruction by the hydroxy radical. The even global distribution reflects the relatively long tropospheric lifetime (12–15 years) of this hydrofluorocarbon. Fig. 10 shows the logarithm of the annual average destruction rate of HFC 134a in molecule $\text{cm}^{-3} \text{s}^{-1}$ due to loss by the OH radical. The major loss (ca.

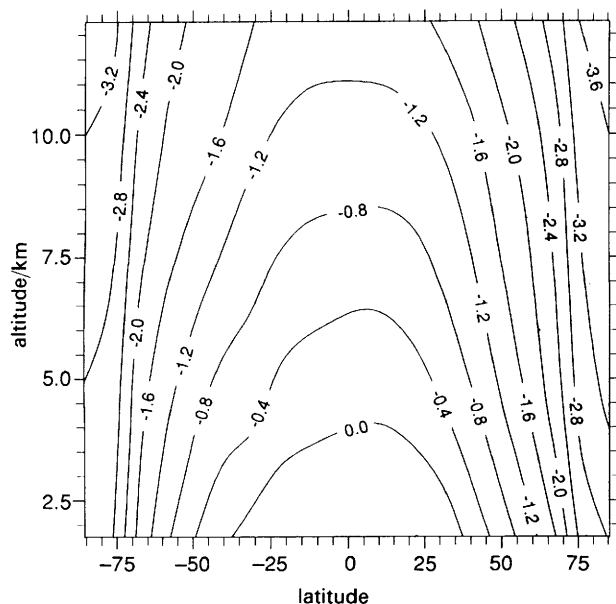


Fig. 10 Logarithm (base 10) of the modelled annual average destruction rate of HFC 134a (molecule $\text{cm}^{-3} \text{s}^{-1}$)

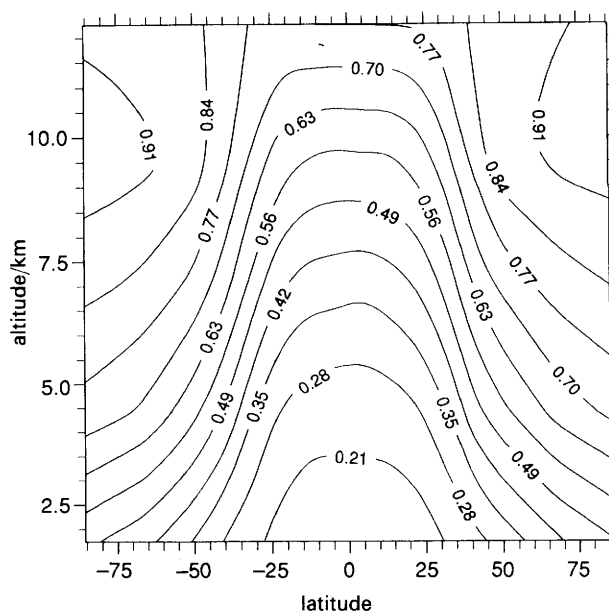


Fig. 11 Modelled fraction of $\text{CF}_3\text{C}(\text{O})\text{F}$ formed from the CF_3CHFO radical in the atmosphere

1 molecule $\text{cm}^{-3} \text{s}^{-1}$) occurs in the tropical lower troposphere from 40° S to 40° N corresponding to both high OH fields and high concentration of the hydrofluorocarbon source. Following the destruction of HFC 134a the oxy radical, CF_3CHFO , formed may either react with molecular oxygen to form $\text{CF}_3\text{C}(\text{O})\text{F}$ and HO_2 , reaction (4) or undergo unimolecular decomposition to CF_3 and $\text{HC}(\text{O})\text{F}$, reaction (5)

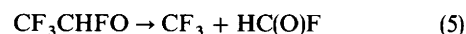


Fig. 11 shows the fraction of $\text{CF}_3\text{C}(\text{O})\text{F}$ formed in the troposphere from the degradation of the CF_3CHFO radical using the recommended parameters for k_4 and k_5 from Table 5 and the pressure dependence of the ratio k_4/k_5 from Wallington *et*

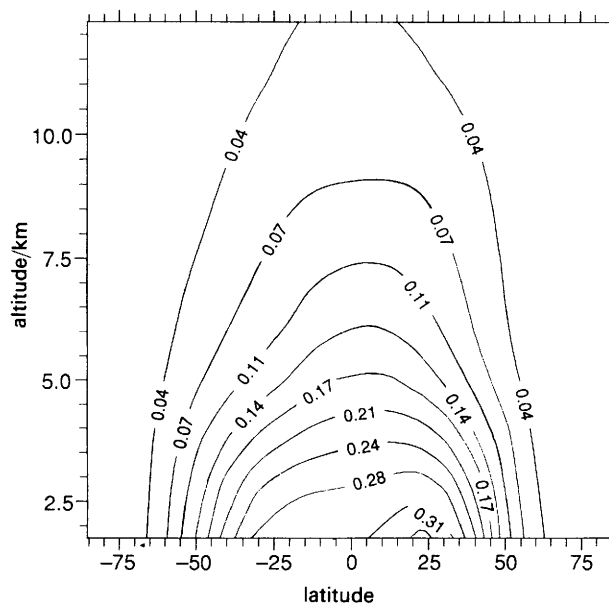


Fig. 12 Annual average production rate of $\text{CF}_3\text{C}(\text{O})\text{F}$ (molecule $\text{cm}^{-3} \text{s}^{-1}$) formed from the photooxidation of HFC 134a

al.¹¹ assuming the same pressure dependence at low temperatures. The fraction of CF₃C(O)F produced increases with altitude (lower temperatures and decreasing pressure both favour this channel, the temperature effect being dominant), from a value of 20% at ground level to ca. 80% at the tropopause. However, the maximum loss of HFC 134a occurs in the tropical lower troposphere (Fig. 10) and the rate of CF₃C(O)F formation is a maximum in this region because the destruction rate of HFC 134a falls off more rapidly with altitude. Fig. 12 shows the computed rate of CF₃C(O)F production from HFC 134a degradation. Preliminary results by DeBruyn *et al.*³³ suggest that efficient removal of CF₃C(O)F by hydrolysis in cloud water to form CF₃C(O)OH occurs with a lifetime of ca. 1 month. Most of the hydrolysis will occur in the tropical lower troposphere and hence the hydrolysis product, CF₃C(O)OH, will be formed in this region.

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