Fluorine-atom initiated oxidation of CF₃CF₂H (HFC-125) studied by FTIR spectroscopy: product yields and kinetic modelling

Alam S. Hasson, Christopher M. Moore and Ian W. M. Smith*

The School of Chemistry, The University of Birmingham, Edgbaston, Birmingham, UK B15 2TT

ssue

A comprehensive study has been carried out of the oxidation of CF₃CF₂H (HFC-125). Reaction was initiated by continuous photolysis of F_2 in the near-UV. The F atoms produced abstracted a hydrogen atom from CF_3CF_2H initiating oxidation in gas mixtures containing variable amounts of O_2 and made up to a total pressure of 700 Torr with N_2 . Product yields were measured as a function of time using FTIR spectroscopy. Experiments were performed at room temperature and in mixtures containing different ratios of [F₂] to [CF₃CF₂H]. The major products were COF₂, CF₃O₃CF₃ and CF₃O₃C₂F₅, consistent with C-C bond scission being the dominant loss process for CF₃CF₂O radicals and with previous studies which used chlorine atoms to initiate oxidation. Attempts to match the experimental results with predictions using the FACSIMILE chemical modelling program were moderately successful and confirmed recent results regarding the equilibrium constant for: $F + O_2(+M) = FO_2(+M)$.

Since it was realised¹ and accepted² that the release of mangases'.4-6

made chlorofluorocarbons (CFCs) has a deleterious effect on the Earth's atmosphere, there has been an intense effort to find more benign replacement compounds. Of course, the very chemical stability which originally made the CFCs so attractive for a range of industrial uses lies at the root of their environmental unsuitability. In particular, their imperviousness to attack by OH radicals means that they have unusually long lifetimes in the atmosphere.³⁻⁶ Consequently, they eventually reach the stratosphere, in amounts virtually undiminished by removal in the troposphere, and there they are broken down by UV light releasing chlorine atoms which initiate chain processes destroying ozone. In addition to their ability to destroy stratospheric ozone, the long atmospheric lifetime of the CFCs, coupled with their IR absorption spectra, means that they are particularly potent 'greenhouse

The search for replacements has focused on the hydrochlorofluorocarbons (HCFCs) and hydrofluorocarbons (HFCs). These compounds have similar, desirable, physical properties to the CFCs but the inclusion of at least one hydrogen atom in their structure means that they undergo attack by OH radicals which initiates their breakdown in the troposphere and leads to a significant reduction in atmospheric lifetimes relative to the CFCs. The investigation of the industrial manufacture and suitability of these compounds has been accompanied by a major scientific effort to understand all details of their chemical behaviour in the atmosphere. One result has been that HCFCs have been abandoned as anything other than temporary replacements for the CFCs since, although their ozone-destroying potential is less than that of the CFCs, it remains sufficiently high to cause concern chiefly because of the presence of chlorine atoms in these compounds. Present attention, both industrial and scientific, is strongly focused on the HFCs.7

Because of the increasing use and release of the HFCs there has been an intense worldwide effort over the past few years to understand their atmospheric chemistry. It is now clear⁷ that the first few steps of this chemistry parallels that of the alkanes: (i) abstraction of an H-atom by OH; (ii) addition by the resultant radical of O_2 ; and (iii) conversion of that peroxy radical to a substituted alkoxy radical by reaction with either NO or another peroxy radical. At that stage, the chemistry may start to diverge.

HFCs based on C₂H₆ have attracted a good deal of attention, especially HFC134a (CF₃CFH₂), which is being used as a replacement for CFC-12 (CF₂Cl₂) in automotive airconditioning systems⁸ and whose chemistry we will consider in a future publication. In the present paper we report the results of laboratory experiments on the oxidation of HFC-125 (CF_3CF_2H) for which the steps identified above are

$$CF_3CF_2H + OH \rightarrow CF_3CF_2 + H_2O$$
 (1)

$$CF_3CF_2 + O_2 + M \rightarrow CF_3CF_2O_2 + M$$
(2)

$$CF_3CF_2O_2 + NO(RO_2) \rightarrow CF_3CF_2O + NO_2(RO + O_2)$$

(3a,b)

The fate of the substituted alkoxy radicals formed at this stage of the oxidation of a HFC is especially interesting, from both a fundamental chemical viewpoint and from the context of atmospheric chemistry. It depends, inter alia, on whether (a) the radical still contains one or more H atoms, and (b) it is a C1 or higher substituted hydrocarbon. If at least one H atom is present, then its abstraction by O_2 , as in the case of a nonsubstituted alkoxy radical, will be important. For radicals derived from other than C1 HFCs this process will be competitive with C-C bond cleavage. Thus, although a specific widespread use has not yet been identified for HFC-125, its chemistry serves as a useful benchmark for other C₂ HFCs, because the substituted alkoxy radical derived from this compound contains no H atom, so that only C-C bond cleavage is likely:

$$CF_3CF_2O \rightarrow CF_3 + COF_2$$
 (4)

simplifying the overall chemistry.

There appear to have been only three previous laboratory investigations of the oxidation of HFC-125 under simulated atmospheric conditions. Both Edney and Driscoll⁹ and Tuazon and Atkinson¹⁰ have reported chlorine-initiated photoxidation studies of CFCs, including experiments on HFC-125. In both cases, experiments were conducted at room temperature on mixtures containing a large excess (700 and 740 Torr, respectively) of dry air. As in the present work, products were identified and their yields determined using FTIR spectroscopy. Both groups of workers determined the yield for COF_2 to be unity within experimental error. In addition, Sehested et al.¹¹ have reported the results of similar experiments in which the dependence of product yields on the ratio of [Cl₂]: [CF₃CF₂H] present in the mixture was observed. The yield of COF₂ was found to decrease from 1.0 to 0.63 as the ratio $[CF_3CF_2H]$: $[Cl_2]$ was increased from 0.013 to 1.26.

In the present experiments, the oxidation of the HFC-125 was initiated by F atoms, generated by continuous photolysis of F₂

$$F_2 + hv \to 2F \tag{5}$$

$$CF_3CF_2H + F \to CF_3CF_2 + HF$$
 (6)

The atoms therefore acted as a surrogate for OH radicals. Changes in the concentrations of reagents and products of the subsequent reactions were measured using FTIR spectroscopy employing a long optical path length to increase the sensitivity of the technique. Experiments were carried out at total pressures of 700 Torr and, in contrast to what has been done in previous studies, in the presence of varying amounts of O₂. In addition, the dependence of product yields on the concentrations of F₂ and CF₃CF₂H in the originally prepared mixture was observed. The experimental results are compared with the results of kinetic modelling which was performed using the FACSIMILE program.¹² The present study differs from those undertaken previously⁹⁻¹¹ on the oxidation of HFC-125 in that reaction is initiated by F, rather than Cl, atoms. In addition, it is somewhat more comprehensive, in that product yields were measured as a function of time, the $[CF_3CF_2H]$: $[F_2]$ ratio, and the partial pressure of O_2 included in the mixture that was photolysed.

Experimental method and procedures

The present experiments were carried out in an apparatus which has been used in previous measurements on the relative rate of F-atom reactions with alkanes and HFCs and it was described in some detail in a paper¹³ reporting that work. In brief, it consists of a FTIR spectrometer (Nicolet Magna, series 550) coupled to a large cylindrical (1.3 m long by 15 cm diameter) cell. Two continuously operating 'blacklamps' (Phillips TL40N/08, 35 W output) are mounted within the cell providing near-UV radiation, and the cell is equipped with White cell mirrors to provide a long pathlength for analysis by IR absorption. In the experiments reported here, mixtures containing between 0.75 and 1.25 Torr of F_2 and ≤ 20 mTorr of HFC-125 were usually photolysed for periods of between 25 min and 1 h, although in some cases reaction was effectively over after only 5 min. The optical path length was usually set at 22 m and the spectra were recorded by coadding 16 scans taken at a resolution of 0.25 cm⁻¹. At this resolution, each scan took 3 s, enabling a spectrum to be recorded in 48 s.

The reactor is internally coated with Teflon to minimise wall reactions and the temperature was controlled to within ± 4 K by passing water through tubing coiled around and in contact with the wall of the chamber. Gases were handled in a Pyrex manifold and, to facilitate rapid mixing, were admitted to the reaction cell via a narrow drilled tube which runs the length of the chamber. Once all the gases had been introduced, they were left for ca. 15 min in the dark to ensure complete mixing and equilibration to the temperature of the cell. During this period spectra were recorded to observe if any dark reactions occurred.

It was found that mixtures that were left for extended periods in the dark (ca. 1 h) showed no detectable loss of the HFC. However, small amounts of COF₂ («1 mTorr) did sometimes appear over the first 10 min. This was particularly evident if the chamber was not flushed out after a previous run, and it was prevented by ensuring that the cell was cleaned thoroughly between experiments. Our experiments on the oxidation of CF₃CF₂H were carried out at 298 K and at three oxygen partial pressures 10, 140 and 700 Torr. The experiments were repeated at least three times for each partial pressure of O₂ and the yields shown are the average of all such experiments.

HFC-125 was obtained from Fluorochem and was the first component admitted to the reaction vessel after de-gassing by successive pump-freeze-thaw cycles. Some experiments were also performed using CF₃H (obtained from Air Products) and it was treated in a similar manner. The F₂ was admitted as a 4.8% mixture in He (Distillers), any HF present being reduced by passage of this mixture through a trap containing NaF. O₂ (BOC Ltd.) and N₂ (BOC Ltd., 'oxygen-free') were taken directly from cylinders. As well as these gases used in the initial mixtures, it was necessary to calibrate the sensitivity of the FTIR to various product molecules, especially COF₂ which is not available commercially.

 COF_2 was made by the method of Fawcett *et al*¹⁴ by bubbling phosgene (COCl₂, 10 g) through a solution of NEt₃·3HF (32 g) and acetonitrile (CH₃CN, 50 g) heated to 40 °C and held under a mild vacuum. A cold finger immersed in solid CO₂ prevented any phosgene reaching the liquid-air trap in which the products of reaction were collected. Subsequently, the COF_2 was distilled from a trap at $-82^{\circ}C$ to remove any CO₂ and was transferred to a blackened storage bulb on the Pyrex gas line. Prior to its use, the gas was subjected to several freeze-pump-thaw cycles. Only minute quantities of CO₂ and SiF₄ were observed as impurities in the sample.

Results

A main objective of the present work was to explain quantitatively the kinetics and mechanism of the oxidation of CF₃CF₂H under a range of experimental conditions. For this purpose, the observed changes in concentration of reagents and products have been compared with predictions made by the modelling program FACSIMILE.¹² In the investigations of the oxidation of HFC-125 initiated by Cl atoms that are cited in Table 1 only final product yields were measured. Because the absorption of F_2 in the near-UV is weaker than that of Cl_2 , the photolysis rate and hence the subsequent rates of reaction are appreciably slower in the case of F-atom initi-

Table 1 Previous studies of the yield of COF_2 in the oxidation of HFC-125^a

ref.	pressure/Torr	results
Edney and Driscoll ⁹ Tuazon and Atkinson ¹⁰ Sehested <i>et al.</i> ¹¹ Wallington and Neilsen ⁷	700 740 760	yield of COF ₂ at 298 K = 1.09 ± 0.05 yield of COF ₂ at 298 K ≈ 1.0 yields depend on [Cl ₂]: [HFC-125] (see test) at 298 K, $p(Cl_2) = 897$ mTorr and p(HFC-125) = 11.8 mTorr: yield of COF ₂ = 1.00 yield of CF ₃ O ₃ CF ₃ = 0.20 yield of CF ₃ O ₃ C ₂ F ₅ = 0.06

^a Studies conducted by continuous UV photolysis of Cl₂ to generate Cl atoms with detection of products by FTIR spectroscopy.

However, in order to compare the experimental and model results, it was necessary to determine the first-order rate constant for photolysis of F_2 ($k_{p, 5}$). In experiments designed to estimate $k_{p, 5}$, F_2 was photolysed in the presence of HCl and the decrease in the concentration of HCl and the increase in the concentration of HCl and the increase in the concentration of HF were simultaneously measured. The rates of HCl loss and HF formation were found to be the same and were assumed to be twice the rate of photolysis of F_2 yielding a value of $k_{p, 5} = -d \ln[F_2]/dt$ of $3.3 \times 10^{-6} \text{ s}^{-1}$. The reaction of Cl atoms, released in the reaction of F atoms with HCl, and F_2 , is known to be extremely slow¹⁵ and was assumed not to generate additional F atoms in this system. This conclusion was supported by modelling calculations.

In our first experiments on the F-atom initiated oxidation of HFC-125, gas mixtures containing 140 Torr of O_2 and a high ratio of F_2 (1 Torr) to CF_3CF_2H (4 mTorr) were irradiated for between 20 and 50 min, with spectra recorded every few minutes to observe the loss of CF_3CF_2H and the formation of reaction products, especially COF_2 . Fig. 1 shows IR spectra from such a mixture recorded before illumination and after 45 min of photolysis, showing clearly the loss of CF_3CF_2H and the parallel increase in the concentration of

Fig. 1 An example of IR spectra recorded (a) before, and (b) after 45 min photolysis of a mixture containing 1 Torr F_2 , 4 mTorr CF_3CF_2H and 140 Torr O_2 , made up to 700 Torr total pressure with N_2 . Bands due to CF_3CF_2H , COF_2 , $CF_3O_3CF_3$ and $CF_3O_3C_2F_5$ are identified. The difference in absorbance scale in these two diagrams should be noted. The small sharp features between 1400 and 1800 cm⁻¹ are due to water which has not been cleared entirely from the path of IR analysing radiation outside the photochemical reactor. The sharp feature at 1030 cm⁻¹ is apparently due to SiF₄ impurity, the presence of which varied from experiment to experiment.

Clearly a unit yield of COF_2 for each CF_3CF_2H lost is consistent with the mechanism given above but, in addition, it is necessary to consider the fate of the CF_3 radicals, or actually

the CF_3O_2 radicals to which they will be immediately converted under our experimental conditions. In this respect it is interesting to note that the sequence of rapid reactions:

$$2CF_3CF_2O_2 \rightarrow 2CF_3CF_2O + O_2 \tag{3b}$$

$$2CF_3CF_2O \to 2CF_3 + 2COF_2 \tag{4}$$

$$2CF_3 + 2O_2 \rightarrow 2CF_3O_2 \tag{8}$$

yields overall $2CF_3CF_2O_2 + O_2 \rightarrow 2CF_3O_2 + 2COF_2$ (9) so that there is no net removal of peroxy radicals. Furthermore, as reaction proceeds, the reaction of CF_3O_2 with

0 500 1000 1500 time/s Fig. 2 Comparison of how the concentrations of HFC-125 (○), COF₂ (▲) and CF₃O₃CF₃ (■) were observed to vary with time in a typical experiment with those predicted using FACSIMILE and the rate data listed in Table 2: HFC-125 (----), COF₂ (----) and CF₃O₃CF₃ (-----). The variations shown by the upper lines, *i.e.* HFC-125 (----), COF₂ (-----) and CF₃O₃CF₃ (------), were calculated using $k_{p,5} = 2 \times 10^{-6} \text{ s}^{-1}$ rather than $k_{p,5} = 3.3 \times 10^{-6} \text{ s}^{-1}$.

HFC-125 (a) 0.5 0.4 0.3 0.2 HEC--124 0.1 COF2 absorbance 0.0 4 (b) 3 2 COF 1 C₃F₈O₂ COF COF 0 2000 1800 1600 1400 1200 1000 800 wavenumber/cm -1

Fig. 2 shows that there is a significant induction period during which both the consumption of CF_3CF_2H and the formation of the reaction products is slower than at longer times. The reason for this is discussed later. Product yields per CF_3CF_2H reacted were determined from observations at longer times where, as the lines in Fig. 3 show, the product concentrations increased linearly with loss of CF_3CF_2H . The yield of COF_2 determined in this way is 1.05 ± 0.06 . This finding is consistent with the production of COF_2 via reactions (5), (6), (2), (3b) and (4) only; which overall amounts to:

$$2F + 2CF_3CF_2H + O_2 \rightarrow 2HF + 2COF_2 + 2CF_3 \quad (7)$$

Furthermore, our finding of a unit yield of COF₂ in the

F-atom initiated oxidation of HFC-125 is in agreement with

previous reports of this quantity in the Cl-atom initiated oxi-

dation (see Table 1).



0.6



Fig. 3 Comparisons between the loss of CF_3CF_2H and increases in the concentrations of the products COF_2 (\blacktriangle), $CF_3O_3CF_3$ (\blacksquare) and $CF_3O_3C_2F_5$ (\bullet). The reaction mixture was the same as that specified in the caption to Fig. 1.

 $CF_3CF_2O_2$ and the reaction between two CF_3O_2 will become more important and yield CF_3O .

In addition to COF_2 , like others,^{7,11} we have identified $CF_3O_3CF_3$ and $CF_3O_3C_2F_5$ among the products resulting



Fig. 4 Comparison between (a) the experimental and (b) the calculated variation in the yields of COF_2 (\blacktriangle), $CF_3O_3CF_3$ (\blacksquare) and $CF_3O_3C_2F_5$ (\blacksquare) with changes in the relative concentrations of CF_3CF_2H and F_2 . In the experiments, the concentration of CF_3CF_2H was varied whilst the partial pressures of F_2 and O_2 and the total pressure were kept constant at 1, 140 and 700 Torr, respectively. The lines are polynomials fit to the data for each species and are included simply to 'guide the eye'. The yields in (b) were calculated according to the full model with the rate constants listed in Table 2.



Fig. 5 Dependence of yields of COF_2 (\blacktriangle), $CF_3O_3CF_3$ (\blacksquare) and $CF_3O_3C_2F_5$ (\bigcirc) on partial pressure of O_2 . The partial pressures of F_2 and CF_3CF_2H were 1 Torr and 4 mTorr, respectively, and the total pressure was 700 Torr.

from the oxidation of CF_3CF_2H . In order to quantify the yield of CF₃O₃CF₃, we had hoped to generate stoichiometric quantities of it from the F-atom initiated oxidation of CF₃H in our apparatus. However, it was clear that this reaction produced several different species and was not a clean source of bis(trifluoromethyl) trioxide. Consequently, we observed the two trioxides by their absorptions at 1292 and 1082 cm⁻¹ and their concentration were estimated using absorption crosssections that had been measured previously by Wallington et al.,¹⁶ in agreement with earlier measurements^{17,18} on the IR spectra of these compounds. Fig. 2 shows how the concentration of CF₃O₃CF₃ increases with time and Fig. 3 shows plots of the concentrations of CF₃O₃CF₃ and CF₃O₃C₂F₅ observed at various times after the initiation of reaction vs. the decrease in the concentration of CF₃CF₂H at the same times. As with COF_2 , after a short induction period, the yields of both these trioxides rose linearly with time and with decrease in the concentration of $\rm CF_3CF_2H,$ and yields of 0.19 ± 0.02 for CF_3O_3CF_3 and 0.18 ± 0.02 for CF_3O_3C_2F_5 could be determined. The combination of these yields with that of COF_2 gives a C atom yield of 1.97 ± 0.09 and a F atom yield of 4.68 ± 0.23 , relative to each molecule of CF₃CF₂H destroyed, suggesting that the yields of any other products must be very small. The quoted errors are single standard deviations and the calculation of the F atom yield does not include the HF product which is formed in reaction (6) and for which the F atom comes from photolysed F_2 . In contrast to Sehested et al.,¹¹ we were unable to detect CF₃OH or CF₃O₂CF₃ as products of reaction. Using absorption crosssections for CF₃OH or CF₃O₂CF₃ measured previously,^{11,16} and assuming the Beer-Lambert law, we estimate that this means that the yields of these species must be below ca. 0.5 and 0.3% under our experimental conditions.

Following the initial experiments using a large excess of F_2 over CF_3CF_2H and 140 Torr of O_2 , two further series of experiments were conducted: one in which the partial pressure of O_2 was maintained at 140 Torr but the ratio of $[CF_3CF_2H]$ to $[F_2]$ was varied, and a second where the partial pressure of O_2 was varied between 10 and 700 Torr using the same concentrations of F_2 and CF_3CF_2H .

The results of the first series of experiments are displayed in Fig. 4(a). It can be seen that as the $[CF_3CF_2H]$: $[F_2]$ ratio was increased the yield of COF_2 fell and this decrease was

Discussion

Qualitatively, the production of the trioxides, $CF_3O_3CF_3$ and $CF_3O_3C_2F_5$, and the absence of the peroxide $CF_3O_2CF_3$ in the oxidation of CF_3CF_2H is not difficult to explain and has a number of interesting implications. It seems that the CF_3O_2 radicals formed in reaction (8) may either react with CF_3CF_2O radicals to form the mixed trioxide

$$CF_{3}O_{2} + CF_{3}CF_{2}O(+M) \rightarrow CF_{3}O_{3}C_{2}F_{5}(+M)$$
 (10)

or they can be converted to CF_3O via reaction (3b) with another peroxy radical (*i.e.* CF_3O_2 or $CF_3CF_2O_2$). Since the lifetime of CF_3CF_2O radicals with respect to dissociation to $CF_3 + COF_2$ is short (see Table 2), and hence their steadystate concentration will be low, the latter loss process for CF_3O_2 is much more probable, a conclusion which is confirmed by the modelling calculations (see below). Once CF_3O_2 radicals are formed then they react with CF_3O_2 or $CF_3CF_2O_2$ to produce the observed trioxides,

$$CF_3O + CF_3O_2$$
,
 $CF_3CF_2O_2(+M) \rightarrow CF_3O_3CF_3$,
 $CF_3O_3C_2F_5(+M)$ (11a,b)

but they do not apparently associate to form the peroxide $CF_3O_2CF_3$. Reaction (11b) between CF_3O and $CF_3CF_2O_2$, as well as reaction (10) if it occurs, serve to reduce the yield of COF_2 .

Before discussing the effects on the product yields of changing the $[CF_3CF_2H]$: $[F_2]$ ratio and the partial pressure of O_2 , we consider some of the features peculiar to experiments where oxidation is initiated by F atoms, rather than Cl atoms. The second-order rate constant for the reaction of F atoms with CF₃CF₂H has been measured as 3.65×10^{-13} cm³ molecule⁻¹ s⁻¹ ¹³ and 3.5×10^{-13} cm³ molecule⁻¹ s⁻¹ ¹⁹ in two independent studies, so it must be considered well established. Under typical conditions in our experiments (*i.e.* at a maximum HFC partial pressure of 20 mTorr) the pseudo-first-order rate constants for reaction of the F atoms would be k_6 [CF₃CF₂H] ≈ 240 s⁻¹. The addition of O₂ to CF₃CF₂ would be even faster at the pressures employed in our experiments. Thus with 140 Torr of O₂ present, k_2 [O₂] $\approx 10^7$ s⁻¹.⁷

These pseudo-first-order rate constants demonstrate that the reaction of F atoms, released in the photolysis of F_2 , and the conversion to substituted peroxy radicals of any substituted alkyl radicals, created by H atom abstraction from the HFC, are very fast on the timescale of our experiments, suggesting that steady-state concentrations of most of the active species should be rapidly established. However, one factor which has received relatively little attention in the interpretation of experiments in which F atoms initiate photooxidation is the role of FO₂ created by the three-body association

$$F + O_2 + M \leftrightarrow FO_2 + M$$
 (12, -12)

The rate constant for the 'forward' reaction (12) has been measured several times in direct experiments with fair agreement.^{20,21,27-29} The latest kinetic data evaluation^{20d} accepts the results of Campuzano-Jost *et al.*²¹ They measured rate constants at temperatures between 100 and 420 K and total pressures between 1 and 1000 bar and concluded that, with $M = N_2$, the rate constant in the limit of low pressure at 300 K would be $k_{12} = 5.8 \times 10^{-33}$ cm⁶ molecule⁻² s⁻¹. Applying small corrections for 'fall-off' and for the change in temperature, we find that the second-order rate constant for reaction (12) at 295 K and a total pressure of 700 Torr is 1.25×10^{-13} cm³ molecule⁻¹ s⁻¹, so that, in a mixture containing 140 Torr of O₂, $k_{12}[O_2][M] = 5.7 \times 10^5$ s⁻¹. This value is much greater than the first-order rate constant for the reaction of F atoms with CF₃CF₂H (see above).

There has been far less agreement in the values derived for k_{-12} , the rate constant for dissociation of FO₂ [or the equilibrium constant for reaction (12)] than for k_{12} . This uncertainty appears to have been removed by the comprehensive measurements of Campuzano-Jost *et al.*²¹ Their experiments yield a value of the equilibrium constant associated with reaction (12) *i.e.* $k_{12}/k_{-12} = 3.9 \times 10^{-16}$ cm³ molecule⁻¹ ($\equiv 12.6$

 Table 2
 Reactions and rate constants used in modelling calculations

reaction	k^a /cm ³ molecule ⁻¹ s ⁻¹ or s ⁻¹	ref.
$F_{+} + hv \rightarrow 2F$	3.3×10^{-6}	this work
$F_2 + nv \rightarrow 21$ F + CF CF H \rightarrow HF + CF CF	3.5×10^{-13}	13
$1 + \text{Cl}_3\text{Cl}_2\text{II} \rightarrow \text{III}_1 + \text{Cl}_3\text{Cl}_2$	3.05×10^{-13}	19
$F + O_2 \rightarrow FO_2$	1.25×10^{-13}	20(c), 21
$FO_2 \rightarrow F + O_2$	280	20(c), 21
$CF_2CF_2 + O_2 \rightarrow CF_2CF_2O_2$	1.1×10^{-11}	b
$2CF_2CF_2O_2 \rightarrow 2CF_2CF_2O_2 + O_2$	2.1×10^{-12}	11
$CF_{2}CF_{2}O \rightarrow CF_{2} + COF_{2}$	2×10^{4}	c
$CF_3 + O_2 \rightarrow CF_3O_2$	8.0×10^{-12}	20
$2CF_3O_2 \rightarrow 2CF_3O_2 + O_2$	1.8×10^{-12}	23
5 2 5 2	1.2×10^{-12}	24
$CF_2O_2 + C_2F_5O_2 \rightarrow CF_3O + C_2F_5O + O_2$	2.0×10^{-12}	d
$2CF_3O \rightarrow CF_3OOCF_3$	4.2×10^{-12}	25
$CF_3O + CF_3O_2 \rightarrow CF_3O_3CF_3$	2.5×10^{-11}	e
$CF_{3}O + CF_{3}CF_{2}O_{2} \rightarrow CF_{3}O_{3}CF_{2}CF_{3}$	2.5×10^{-11}	e
$CF_3CF_2O + CF_3O_2 \rightarrow CF_3O_3CF_2CF_3$	2.5×10^{-11}	e
$CF_3O + CF_3CF_2H \rightarrow CF_3OH + CF_3CF_2$	1.0×10^{-15}	f
$CF_{3}OH \rightarrow COF_{2} + HF$	4.0×10^{-5}	11

^{*a*} Rate constants for association and dissociation reactions are quoted for the conditions appropriate to our experiments; *i.e.* 700 Torr total pressure of O_2 - N_2 . ^{*b*} Set equal to the limiting high-pressure rate constant for reaction between CF₃ and O_2 given in ref. 20(*a*). ^{*c*} This rate constant is set equal to that for CF₃CFHO \rightarrow CF₃ + HFCO given in ref. 22. ^{*d*} Taken to be the mean of the rate constants for CF₃O₂ + CF₃O₂ and C₂F₅O₂ + C₂F₅O₂. ^{*c*} These rate constants are not known; we used values for all three reactions corresponding to that used in ref. 24 for CF₃O + CF₃CF₂O₂. ^{*f*} Set equal to the rate constant for reaction between CF₃O and CF₃CFH₂ given in ref. 26.

Because reaction (12) is much faster than that of the F atoms with CF_3CF_2H under our experimental conditions, during the early part of the photoinitiated reaction the great majority of the F atoms produced by photodissociation of F_2 react with O_2 rather than with the HFC until not only the equilibrium ratio [F]/[FO₂] is established (which will occur very rapidly), but also the steady-state concentration of F atoms, determined by the balance between the rates of photolysis of F_2 and the rate of the reaction between F atoms and HFC-125, is reached. As a result, an 'induction period' is to be expected before the rate of loss of the HFC and the rate of formation of any resultant product attain their steady values. This effect is apparent for the F-atom initiated oxidation of CF_3CF_2H in the experimental results displayed in Fig. 2.

To examine this effect and the changes in concentration of reagents and products under various experimental conditions in more detail, we employed the modelling program FACSIMILE¹² including in the mechanism the reactions listed in Table 2. Fig. 2 shows the result of a comparison between the observed concentrations of CF₃CF₂H, COF₂ and $CF_3O_3CF_3$ and those calculated using the rate constants for the elementary reactions which are given in Table 2. The agreement between these experimental results and the prediction of the model depends on the rate constants for reactions (6), (12), (-12) and the rate of photolysis of F_2 . The first three of these rate constants are well established. As the dashed line in Fig. 2 shows, the agreement between the experimental and calculated results can be improved by lowering the photolysis rate by 40% which is within the uncertainty of our determination, given the possibility of a slow reaction between Cl atoms and F_2 .

The calculations just referred to and others described below suggest that FO_2 serves simply as a temporary reservoir for F atoms. There appears to be no strong evidence that FO_2 plays any major role in the oxidative chemistry of HFC-125. In particular, we note that reactions like

$$CF_3CF_2O_2 + FO_2 \rightarrow CF_3CF_2O + FO + O_2$$
 (13)

are endothermic and therefore cannot assist in the conversion of substituted peroxy radicals to substituted alkoxy radicals

We next attempted to model the variations in relative product yields that were observed when either the $[CF_3CF_2H]$: $[F_2]$ ratio or the partial pressure of O_2 was varied. Since the primary effect of both these changes must be to alter the steady-state concentration of F atoms, we decided to begin by carrying out modelling calculations using FAC-SIMILE to investigate how the yields of products depended on the concentration of F atoms. In these preliminary calculations, rather than include reactions (5), (6) (12) and (-12) in the reaction mechanism, a steady-state concentration of F atoms was specified and then the model was run including the remainder of the reactions given in Table 2 to calculate product yields. The results demonstrated that the product yields do indeed show significant, and complex, dependences on the steady-state concentration of F atoms. As an example of these results, Fig. 6 shows how the calculated product yields vary with the concentration of F atoms when the initial concentration of CF_3CF_2H was set at 1×10^{14} molecule cm^{-3} (=3 mTorr) and the partial pressure of O₂ was 140 Torr. Over the range of the curves shown in bold in Fig. 6, the calculated product yields and their variation are similar to those found experimentally as the ratio $[CF_3CF_2H]$: $[F_2]$ was changed. However, it should be noted that this range of F atom concentrations is much larger than the range of $[CF_3CF_2H]$: $[F_2]$ ratios covered in our experiments.

We then carried out full model calculations with the rate constants for reactions (6), (12) and (-12) set to their well established literature values and with $k_{p, 5}$ given the value esti-



Fig. 6 Calculated dependence of COF_2 (\blacktriangle), $CF_3O_3CF_3$ (\blacksquare) and $CF_3O_3C_2F_5$ (\bullet) yields on the steady-state concentration of F atoms

mated from our experiments on F_2 -HCl mixtures (see above). Fig. 4(b) shows the results in a plot of product yields vs. [CF₃CF₂H]: [F₂]. Although there are significant discrepancies between the experimental [see Fig. 4(a)] and model results, the model goes some way to explaining the observed variations in product yields. The effect of changing the steadystate concentration of F atoms leads, of course, to changes in the concentrations of peroxy and alkoxy radicals and it is this which leads to the variation in product yields. Although the Cl-atom initiated reaction system will differ in details, it seems likely that the explanation for the variation in product yields found by Sehested *et al.*^{7,11} must be very similar.

Finally we performed model calculations on mixtures containing different partial pressures of O_2 to see whether such calculations could explain the experimental results displayed earlier in Fig. 5. Here the calculations were even less successful in describing the variation of observed product yields with experimental conditions. The model indicated that the relative yields of COF_2 and the two trioxides do depend on the concentration of O_2 present, but neither the form of the variation nor its absolute magnitude were reproduced. A possible reason is the occurrence of slow but significant reactions involving F, FO and FO₂ but in the absence of any firm data regarding these reactions²⁹ we made no further attempts to match the calculated results to those found experimentally.

Summary and Conclusions

We have carried out the first thorough examination of the F-atom initiated oxidation of HFC-125 (CF₃CF₂H). Under laboratory conditions, the main products are COF₂, CF₃O₃CF₃ and CF₃O₃C₂F₅. It is clear that the main, and probably only, loss process for the CF₃CF₂O radicals formed in this oxidation is scission to COF₂ + CF₃. These CF₃CF₂O radicals are formed in our experiments either by reaction between two CF₃CF₂O₂ radicals or by reaction of CF₃CF₂O₂ with CF₃O₂. In the atmosphere, the oxidation of HFC-125 is initiated by its reaction with OH radicals for which the rate constant is given by $4.9 \times 10^{-13} \exp(-1655/T)$,^{20c} yielding a lifetime of approximately 20 years. Consequently, any HFC-125 released into the atmosphere will

disperse widely. CF₃CF₂O radicals will then be formed by the reactions of CF₃CF₂O₂ radicals either with other peroxy radicals or with NO. It seems certain that the overwhelming fate of CF₃CF₂O radicals in the atmosphere will be to fragment to $COF_2 + CF_3$.

Although the formation of the trioxides, CF₃O₃CF₃ and CF₃O₃C₂F₅, will be unimportant in the atmosphere, our inability to model how the observed product yields in the oxidation of CF₃CF₂H depend on the [CF₃CF₂H]: [F₂]. ratio and on the O₂ partial pressure is disappointing. It demonstrates that our knowledge of some of the secondary chemistry in this system is still less than complete.

We thank SERC and NERC for support of our work under the programme in Laboratory Measurements for Atmospheric Chemistry. A.H. and C.M.M. are also grateful to the same bodies for the award of research studentships. We thank Professor J. A. Kerr for showing us the latest IUPAC kinetic data evaluation [ref. 20(c)] prior to publication.

References

- F. S. Rowland and M. J. Molina, Nature (London), 1974, 249, 810. 1
- F. S. Rowland and M. J. Molina, Chem. Eng. News, 1994, 72, 8.
- D. J. Weubbles, J. Geophys. Res., 1983, 88, 1433. 3
- Scientific Assessment of Stratospheric Ozone, 1989, vol II; World 4 Meteorological Organization, Global Ozone Research and Monitoring Project, report no. 20.
- 5 R. P. Wayne, Chemistry of Atmospheres, Clarendon Press, Oxford, 2nd edn., 1991.
- A. R. Ravishankara and E. R. Lovejoy, J. Chem. Soc., Faraday 6 Trans., 1994, 90, 2159.
- T. J. Wallington and O. J. Nielsen, in Progress and Problems in 7 Atmospheric Chemistry, ed. J. R. Barker, World Scientific, Singapore, 1995, ch. 15.
- B. Sukornick, Int. J. Thermophys., 1982, 10, 553. 8
- 9 E. O. Edney and D. J. Driscoll, Int. J. Chem. Kinet., 1992, 24, 1067.
- 10 E. C. Tuazon and R. Atkinson, J. Atmos. Chem., 1993, 16, 301.
- J. Sehested, T. Ellerman, O. J. Nielsen, T. J. Wallington and 11 M. D. Hurley, Int. J. Chem. Kinet., 1993, 25, 701.
- 12 FACSIMILE program; UKAEA Harwell Laboratory, 1987.

- C. M. Moore and I. W. M. Smith, J. Chem. Soc., Faraday Trans., 13 1995. 91. 3014.
- F. S. Fawcett, C. W. Tullock and D. D. Coffmen, J. Am. Chem. 14 Soc., 1962, 84, 4275.
- C. M. Moore, I. W. M. Smith and D. W. A. Stewart, Int. J. Chem. Kinet., 1994, 26, 813.
- T. J. Wallington, J. Sehested, M. A. Dearth and M. D. Hurley, J. 16 Photochem. Photobiol. A: Chem., 1993, 70, 5.
- L. R. Anderson and W. B. Fox, J. Am. Chem. Soc., 1967, 89, 4313. 17 P. G. Thompson, J. Am. Chem. Soc., 1967, 89, 4316. 18
- 19
- T. J. Wallington, M. D. Hurley, J. Shi, M. M. Maricq, J. Sehested, O. J. Nielsen and T. Ellermann, Int. J. Chem. Kinet., 1993, 25, 651.
- 20 (a) R. Atkinson, D. L. Baulch, R. A. Cox, R. F. Hampson, J. A. Kerr and J. Troe, J. Phys. Chem. Ref. Data, 1989, 18, 881; (b) R. Atkinson, D. L. Baulch, R. A. Cox, R. F. Hampson, J. A. Kerr and J. Troe, J. Phys. Chem. Ref. Data, 1992, 21, 1125; (c) R. Atkinson, D. L. Baulch, R. A. Cox, R. F. Hampson, J. A. Kerr and J. Troe, J. Phys. Chem. Ref. Data, 1997, 26, 521; (d) W. B. Demore, S. P. Sander, D. M. Golden, R. F. Hampson, M. J. Kurylo, C. J. Howard, A. R. Ravishankara, C. E. Kolb and M. J. Molina, Chemical Kinetics and Photochemical Data for Use in Stratospheric Modeling Evaluation Number 11, NASA JPL-Publication 94-26, 1994.
- 21 P. Campuzano-Jost, A. Croce de Cobos, H. Hippler, M. Siefke and J. Troe, J. Chem. Phys., 1995, 102, 5317.
- M. M. Maricq and J. S. Szente, J. Phys. Chem., 1992, 96, 10862. 22
- 23 O. J. Nielsen, T. Ellerman, J. Sehested, E. Bartkiewicz, T. J. Wallington and M. D. Hurley, Int. J. Chem. Kinet., 1992, 24, 1009.
- 24 P. Biggs, C. E. Canosa-Mas, J.-M. Fracheboud, C. J. Percival, R. P. Wayne and D. E. Shallcross, J. Chem. Soc., Faraday Trans., 1997, 93, 379.
- (a) R. C. Kennedy and J. B. Levy, J. Phys. Chem., 1972, 76, 3480; 25 (b) L. Batt and R. Walsh, Int. J. Chem. Kinet., 1982, 14, 933.
- 26 J. Sehested and T. J. Wallington, Environ. Sci. Technol., 1993, 27, 146.
- 27 P. Pagsberg, E. Ratajczak, A. Sillesen and J. T. Jodkowski, Chem. Phys. Lett., 1987, 141, 88.
- J. L. Lyman and R. Holland, J. Phys. Chem., 1988, 92, 7232. 28
- 29 T. Ellerman, J. Sehested, O. J. Nielsen, P. Pagsberg and T. J. Wallington, Chem. Phys. Lett., 1994, 218, 287.

Paper 7/02105D; Received 26th March, 1997