Kinetics of the self-reaction of CF_2 radical and its reaction with H_2 , O_2 , CH_4 and C_2H_4 over the temperature range 295–873 K

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Laser flash photolysis, coupled with time-resolved UV absorption detection, has been used to measure rate coefficients for the self-reaction of CF_2 :

$$CF_2 + CF_2 \rightarrow C_2F_4$$

(1)

and its reaction with the molecular species H_2 , O_2 , CH_4 and C_2H_4 over the temperature range 295-873 K. The CF_2 radicals were produced by the 193 nm laser photolysis of C_2F_4 . At room temperature, values of $k_1 = (4.01 \pm 0.51) \times 10^{-14}$ cm³ molecule⁻¹ s⁻¹ were obtained for the rate coefficient of reaction (1) and $\sigma_{249} = (1.61 \pm 0.21) \times 10^{-17}$ cm² molecule⁻¹ for the absorption cross-section of CF_2 at 249 nm, where the spectral resolution was 0.5 nm (FWHM). The value of k_1 is in good agreement with previous room-temperature measurements, but the value of σ_{249} is almost a factor of two lower, reflecting the lower spectral resolution used in this study. The absorption cross-section, σ_{249} , was found to decrease with increasing temperature, whereas the rate coefficient, k_1 , exhibits a positive temperature dependence. The temperature dependence of k_1 at 760 Torr N₂, when combined with earlier shock-tube determinations at 1200 and 1400 K, could be fitted to a modified Arrhenius expression:

$$k_1 = (1.39 + 0.20) \times 10^{-19} T^2 \exp[(347 + 56)/T] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

for the temperature range 295–1400 K. The uncertainties refer to random error in the parameters at the 95% confidence level. Systematic errors are estimated to be $\pm 10\%$. However, the variation of k_1 with pressure at 873 K indicated that the reaction had not quite reached its high-pressure limit at 760 Torr, so this expression can only be regarded as an empirical expression for the temperature dependence at atmospheric pressure. At lower temperatures, k_1 had clearly reached its high-pressure limiting value at 760 Torr. No evidence could be found at any temperature for products other than C_2F_4 , implying that recombination is the only channel occurring.

No reaction was observed between CF₂ and any of the molecular reagents studied at temperatures up to 873 K. Upper limits were derived for the rate coefficient of CF₂ with each reagent at several temperatures. At 873 K, the values are (in units of cm³ molecule⁻¹ s⁻¹) < 5 × 10⁻¹⁹ for H₂, <3 × 10⁻¹⁷ for O₂, <4 × 10⁻¹⁹ for CH₄ and <2 × 10⁻¹⁶ for C₂H₄.

Experiments performed using the 193 nm photolysis of C_3F_6 as a source of CF_2 suggested another reactive and absorbing species is generated in rather higher yield than CF_2 , at variance with earlier studies. The results could be rationalised by assuming the species to be C_2F_3 which reacts with CF_2 with a rate coefficient estimated to be ca. 2×10^{-13} cm³ molecule⁻¹ s⁻¹ at 295 K.

The implications of the very low reactivity of CF_2 with molecular species, compared with its reactivity with radical species, O, H and OH, are discussed in the context of the role played by the CF_2 radical in the chemistry of flame inhibition by fluorinated hydrocarbons considered as potential halon replacements.

The continuing deterioration of the Earth's ozone layer led to the adoption of the Copenhagen Amendment to the Montreal Protocol in 1992,^{1,2} the terms of which have now resulted in the phase-out of the production of halons since the beginning of 1994.³ Halons, such as CF_3Br (Halon-1301) and CF_2ClBr (Halon-1211), have found widespread use as fire-extinguishing agents, but are potent stratospheric-ozone depleting compounds because of the presence of the bromine atom in the molecule. Three classes of compounds currently being considered as 'in-kind' replacements to halons as fire inhibitors are perfluorocarbons (FCs), hydrofluorocarbons (HFCs) and hydrochlorofluorocarbons (HCFCs).

For the purpose of formulating halon substitutes which have low ozone-depletion potential, but optimum properties as fire-extinguishing agents, it is necessary to develop correctly validated kinetic and mechanistic models which can predict the efficiency of the compound as a combustion inhibitor under different flame conditions. There have been several reported attempts at modelling combustion inhibition in flames and stirred reactors by $CF_3Br^{4,5}$ and FC and HFC replacement compounds.⁶ The latter study has indicated that flame inhibition by the FC and HFC compounds may not just be a physical quenching effect but, at least partially, a chemical effect, involving the trapping of the H and OH radical chain carriers of the combustion process by their reaction with fluorinated radicals CF_3 and CF_2 . CF_2 radicals have been detected by molecular-beam-sampling mass spectrometry as intermediate products in low-pressure stoichiometric CH_4-O_2-Ar flames seeded with 1% $C_2F_6^6$ and with 1% CF_3CHFC1 (HCFC-124) and 1% CF_3CFHCF_3 (HFC-227ea).⁷ The modelling studies have stressed a lack of available kinetic data in the literature on reactions involving these radicals at elevated temperature.

 CF_2 is a particularly unreactive radical towards reaction with molecular species at room temperature. No definitive evidence has ever been found for any reaction of CF_2 with O_2 , H_2 or hydrocarbons likely to be present in flames, at temperatures below 1000 K.⁸⁻¹² Slow reaction has been reported with NO_2^{12} and the alkenes $(CH_3)_2C=C(CH_3)_2$ and $(CH_3)_2C=CH_2^{13}$ at room temperature and with Cl_2 ,^{11,14} Br_2 ,^{11,15} HBr,¹⁶ $C_2F_4^{17,18}$ and O_3^{19} at elevated temperatures. In a shock-tube study, Keating and Matula²⁰ did

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observe a slow reaction of CF_2 with O_2 at high temperatures, but with an activation energy of 111 kJ mol⁻¹ and an Arrhenius expression leading to $k = 4 \times 10^{-14}$ cm³ molecule⁻¹ s⁻¹ at 2000 K. More recently, Chowdhury has found evidence for reaction of CF_2 with O_2 when the radicals were produced translationally hot by the IR multiphoton dissociation of octafluorocyclopentene.²¹ The ground electronic state of CF_2 is a singlet X ¹A₁ state; the first excited triplet state (a ³B₁) lies *ca.* 2 eV above this. This is in contrast with CH_2 where the ground state is the triplet state and the singlet-triplet separation is only *ca.* 0.4 eV. Thus, unlike CH_2 in flames, the chemistry of CF_2 will be dominated by the ground singlet state.

Because of its low reactivity, the only reactions of CF_2 included in kinetic mechanisms of flame inhibition by halons and fluorinated hydrocarbons are those with radical species O, H, OH and CH₃.⁴⁻⁶ These reactions are rapid and seem to account for the fast consumption of CF_2 observed in flames.^{6,7} Absolute measurements of the rate coefficients of the reactions with O and H atoms are confined to room temperature or below,²²⁻²⁵ while only an estimate is available for the rate coefficient of the $CF_2 + OH$ reaction, based on the analysis of COF_2 product profiles in CH_4-O_2-Ar flames inhibited by $CF_3Br.^{26}$

In spite of the probable dominance of these CF_2 + radical reactions in flames, the low reactivity of CF_2 with molecular species needs to be verified over an extended temperature range. Even a slow reaction of CF_2 with these species at combustion temperatures, particularly with O_2 , would affect the modelling of flame inhibition by fluorocarbons because of their higher abundance in flames. The aim of this investigation was to examine for the occurrence of any reaction of CF_2 with O_2 , H_2 and the hydrocarbons CH_4 and C_2H_4 at temperatures up to 900 K and, if none was observed, to set upper limits on the values of their rate coefficients.

In the absence of any significant reaction between CF_2 and X (X = O_2 , H_2 , CH_4 or C_2H_4), the removal of CF_2 proceeds via its relatively slow self-reaction (1). This reaction has been studied by kinetic spectroscopy over a limited, low-temperature range, between 298 and 573 K, by several groups^{8,10,27} and over a high-temperature range (1150–1600 K) in a shock-tube study by Schug and Wagner.²⁸ The rate coefficient has a positive temperature dependence.

The technique employed in this study was pulsed laser photolysis with time-resolved UV absorption spectroscopy to detect CF_2 . As in all the previous investigations of the selfreaction, determination of the rate coefficient required knowledge of the absolute absorption cross-section (σ) at the detection wavelength. Agreement in the values of σ at the 249.0 nm maximum in the $\tilde{A}^{-1}B_1 \leftarrow X^{-1}A_1$ absorption bands at room temperature is quite good,^{10,27} but early studies of the self-reaction at higher temperatures^{8,10} did not consider the possible variation of σ with temperature. In this study, the temperature dependence of σ at 249 nm has been measured in order to put the measurements of the self-reaction rate coefficient on a firm absolute basis. The present study bridges the temperature gap between the low-temperature flash photolysis studies of the self-reaction and the high-temperature, shocktube study.

Experimental

The laser flash photolysis apparatus, employing time-resolved UV absorption spectroscopic detection, and experimental procedure for measurement of absolute rate coefficients have been described previously.^{29,30} The second experimental configuration referred to in a previous publication was used,³⁰ in which the pulsed laser beam was passed along the axis of a 1 m long, 25 mm id cylindrical reaction cell, in the opposite direction to the continuous spectroscopic monitoring beam from a deuterium lamp emitting broad-band UV radiation. The only difference in this study was that the silica reaction cell was housed in a temperature-regulated electrical furnace (max. 4.3 kW). A schematic of the experimental configuration is shown in Fig. 1. The resistive heating elements of the furnace were wired in such a way that they could be differentially heated so as to minimise temperature gradients along the cell. Temperature was measured at five points along the length of the cell by calibrated type-K thermocouples. Supplementary heating at the end of the cell where the gases enter and exit was provided by additional resistive heating wire. The voltages applied to the heating elements were adjusted so that the temperature along the entire length of the cell was uniform to within 3% at the highest temperature studied, 900 Κ.

The laser radiation was reflected into the cell by a 193 nm narrow-band coated reflector which transmits >90% of the monitoring beam at $\lambda > 210$ nm, allowing it to be focused onto the entrance slit of the monochromator. The inner,



Fig. 1 Schematic diagram of laser flash photolysis apparatus

Suprasil quartz window of each removable end-piece was located inside the cell, ca. 10 cm from each end, thus ensuring that the reaction volume was well inside the uniform temperature region of the cell. This defined an optical pathlength of 81 cm. The 'dead space' inside each end-piece, between the inner and outer windows, was evacuated to minimise the absorption contribution of ozone formed by photolysis of atmospheric oxygen by the 193 nm laser beam in the path of the monitoring beam.

A pre-heated gas mixture containing the CF₂ precursor and other reagents usually, but not always, diluted in nitrogen or other inert gas (Ar or He), flowed slowly through the cell with a residence time of ca. 6 s. The laser was fired at a repetition rate of one pulse every 6 s to ensure a fresh sample of gas was always being photolysed.

CF₂ radicals were generated by the 193 nm photolysis of $C_{2}F_{4}:$

$$C_2F_4 + hv \rightarrow 2CF_2$$

No evidence was found for any other photolysis products. Some experiments were performed using C_3F_6 as a source of CF_2 , but although CF_2 was produced, evidence was found for the formation of another reactive and absorbing species which interfered with the kinetic studies, as will be discussed in the Results section.

The temporal behaviour of the CF₂ concentration after the laser flash was monitored by time-resolved UV absorption spectroscopy at the sharp 249 nm peak of the $\tilde{A}^1 B_1 \leftarrow X^1 A_1$ band system shown in Fig. 2. The wavelength dependence of the absorbance signal measured immediately after the laser flash, and also shown in Fig. 2, normalised to the measurements of Sharpe *et al.*,²⁷ confirms that the species being detected is CF₂. The rather broader peak observed in this study, when compared with the spectrum of Sharpe et al., is a result of the lower resolution of the monochromator, a compromise necessary to achieve adequate signal-to-noise ratios for the kinetic experiments. The monochromator resolution, using a 0.25 mm slit width, was ca. 0.5 nm (FWHM) at the 253.7 nm Hg line.

Absorbance (A) is related to concentration by the Beer-Lambert law:

$$A = \ln(I_o/I_t) = \sigma(\lambda) l[CF_2]$$

where $\sigma(\lambda)$ is the absorption cross-section at the wavelength λ in cm² molecule⁻¹ and *l* the pathlength in cm. I_0 and I_1 are, respectively, the transmitted light intensities before the flash and at time t after the flash. In most experiments, signal vs. time profiles for 200 laser shots were accumulated to provide sufficiently well averaged profiles for kinetic analysis.

Before and after a series of experiments, the fluence of the laser beam entering the cell was measured with a calibrated laser energy meter (Molectron J50 Joulemeter) positioned at the end of the cell where the laser beam exits, with the window end-piece removed. The fluence was typically 5 mJ cm⁻², corresponding to a photon flux of ca. 5×10^{15} photons cm⁻². In order to avoid complications to the analysis of the signal decays due to significant radical concentration gradients along the length of the cell, it was important to ensure that the optical density at the laser wavelength due to the radical precursor was below ca. 0.5.30 This constrained the maximum C_2F_4 concentration which could be used to *ca.* 1.5×10^{15} cm⁻³, based on an absorption cross-section for C_2F_4 at 193 nm of 5.2×10^{-18} cm² molecule⁻¹.²⁷ The optical density due to the C_2F_4 was determined using the laser energy meter to measure the attenuation of the photolysis laser beam when the C_2F_4 was added to the main nitrogen-gas flow. This was facilitated by means of the 193 nm reflector positioned near the exit window which reflected >99% of the laser beam onto the laser energy meter, but transmitted the longer wavelength monitoring beam. The optical density of the C_2F_4 in the cell, α , is given by:

$$\alpha = \ln\{I(N_2)/I(N_2 + C_2F_4)\}$$

Here, $I(N_2)$ and $I(N_2 + C_2F_4)$ are, respectively, the relative intensities of the laser beam transmitted through the cell without and with C_2F_4 added.

Measurement of α also allowed the determination of the initial mean concentration of CF₂ in the cell produced by the

wavelength/nm

Fig. 2 UV absorption spectrum of CF₂. (•) This work, measured immediately after laser flash, normalised to data of Sharpe et al.²⁷ (--).



laser flash. This is given by the equation:

$$CF_2]_o = \Phi N_o[1 - \exp(-\alpha)]/V$$

where Φ is the quantum yield for CF₂ formation by C₂F₄ photolysis per photon absorbed and is assumed to be 2; N_o is the absolute intensity of the laser beam (i.e. number of photons) entering the cell, measured with the laser energy meter; V is the photolysis volume. The initial concentration of CF_2 generated in the experiments was typically ca. 5 × 10¹³ cm^{-3} . The determination of $[CF_2]_o$ was subject to a systematic error of ca. $\pm 10\%$. This arose mainly from uncertainty in the ratio $\Phi N_o/V$ which stems from uncertainties in the absolute laser energy meter calibration and in the photolysis volume. However, these are 'instrumental' parameters and should not change from experiment to experiment, for example, when temperature is changed. Therefore, relative changes in values of the CF₂ absorption cross-section and $CF_2 + CF_2$ rate coefficient as a function of temperature will have been determined in these experiments with a greater degree of accuracy than their absolute values.

The maximum temperature of the experiments was limited to 900 K. At higher temperatures, pyrolysis of the C_2F_4 precursor started to occur, evidenced by the build-up of a whitish polymerisation product deposited on the inner cell walls and windows.

The concentration of the reagent gases O_2 , H_2 , CH_4 and C_2H_4 in the reaction cell was derived from the cell pressure and reagent gas flow rates measured by calibrated mass-flow meters or flow controllers. The maximum concentration of each of these gases, except CH_4 , which could be added was limited either by absorption by the gas of the 193 nm laser radiation, or by thermal reaction with C_2F_4 , or by both effects.

In most of the experiments, nitrogen was used as the bath gas at atmospheric pressure, but some experiments on the $CF_2 + CF_2$ reaction were carried out at reduced pressures and/or used helium or argon as bath gas.

The gases N_2 (Air Products, oxygen free), Ar (Linde, 99.995%), He (BOC, 99.995%), H₂ (BOC, 99.99%), CH₄ (BOC, CP grade) and C₂H₄ (BOC, 99.9%) were used directly from the cylinder. O₂ (BOC breathing grade) was passed through a molecular sieve trap to remove hydrocarbons. The C₂F₄ obtained from Fluorochem Ltd. was >99% pure, but contained a trace (ppm levels) of (+)-limonene to inhibit polymerisation. This was removed in these experiments by passing the gas from the cylinder through either a sulfuric acid bubbler or a column of activated charcoal. However, the removal of the inhibitor did not affect the kinetics of the CF₂ decay at any of the temperatures investigated.

In order to examine for products of certain of the reactions investigated, some repetitive photolysis experiments were carried out in which a static mixture of the reagent gases in the cell was repeatedly photolysed by several hundred laser shots. The contents of the cell after photolysis, which may have contained accumulated reaction products, were then passed through a liquid nitrogen trap. The condensed gases collected in the trap were then allowed to warm up and were analysed by Fourier transform infra-red absorption spectroscopy (FTIR) or gas chromatography with mass spectrometric detection (GC-MS). Such product analysis was carried out to examine for products other than C_2F_4 from the CF_2 selfreaction and for COF_2 formation in the reaction of CF_2 with O_2 .

Results

Absorption spectrum and self-reaction kinetics of CF₂ at room temperature

The initial absorbance observed immediately after the laser flash, before any significant decay of the signal had occurred, was measured at several wavelengths between 247 and 251 nm and the results, normalised to the measurement of Sharpe *et al.* at 249 nm, are shown in Fig. 2.

Fig. 3(a) shows a typical decay of the absorption signal at the 249 nm peak with time after the laser flash, obtained for mixtures containing only C_2F_4 and N_2 at room temperature. The decay of the absorbance occurred fairly slowly and followed second-order kinetics, as demonstrated by the linearity of the (absorbance)⁻¹ vs. time plot displayed in Fig. 3(b). This indicates that CF_2 is removed predominately by the selfreaction (1).

Decay traces were recorded for 17 experiments in which different C_2F_4 concentrations and laser fluences were used. Each decay was analysed by a non-linear least-squares fitting procedure to determine the ratio k_1/σ_{249} , which characterises the second-order decay rate of the absorption signal, where k_1 is the rate coefficient for reaction (1) and σ_{249} is the absorption cross-section of CF₂ at 249 nm. The mean value of k_1/σ_{249} obtained was $(2.51 \pm 0.20) \times 10^3$ cm s⁻¹. The quoted error limits refer to the random error in the measurements at the 95% confidence level, and reflect the statistical error in the fits. No dependence of k_1/σ_{249} on pressure was observed over the range 35-780 Torr N2. Knowledge of the absolute concentration of CF₂ radicals generated by the laser flash enabled the individual values of k_1 and σ_{249} to be determined directly in the least-squares fitting analysis. The mean of nine measurements of σ_{249} was $(1.61 \pm 0.21) \times 10^{-17}$ cm² molecule⁻¹ leading to $k_1 = (4.01 \pm 0.51) \times 10^{-14}$ cm³ molecule⁻¹ s⁻¹ at 295 K. The error limits for σ_{249} and k_1 combine the uncertainty in the value of k_1/σ_{249} at the 95% confidence level with the $\pm 10\%$ systematic error in the measurement of $[CF_2]_0$.



Fig. 3 (a) Decay of the CF₂ absorption signal at 249 nm following the 193 nm flash photolysis of C_2F_4 -N₂ mixtures at 295 and 873 K and 760 Torr. The continuous lines are simulations using best-fit parameters assuming second-order kinetics. (b) (absorbance)⁻¹ vs. time for 249 nm signal at 295 K. The linearity of the plot indicates the decay of the signal follows second-order behaviour.

Absorbance vs. time decay traces were recorded at eight temperatures between 295 and 873 K using N₂ as the bath gas at atmospheric pressure. An example of a decay trace at 873 K is shown in Fig. 3(a). The decay rate of CF₂, as characterised by the values of k_1/σ_{249} tabulated in Table 1, increased with increasing temperature. Values of k_1 and σ_{249} were determined at each temperature and are also presented in Table 1. In the analysis of the decays at temperatures above 573 K, the contribution to removal of CF₂ of its reaction with C₂F₄ was taken into account:

$$CF_2 + C_2F_4 \rightarrow \text{cyclo-}C_3F_6 \tag{2}$$

using the Arrhenius expression for k_2 derived by Mel'nikovich and Moin.¹⁷ This gives $k_2 = 2.5 \times 10^{-16}$ cm³ molecule⁻¹ s⁻¹ at 873 K. The contribution made by reaction (2) to the total CF₂ decay rate was always less than 5% at 873 K and less than 0.5% at 573 K. The values derived for k_1 were not sensitive to the value of k_2 used in the analysis.

Fig. 4 displays the variation of σ_{249} with temperature; a steady decrease in the value of σ_{249} with increasing temperature is apparent. Fig. 5 is an Arrhenius plot of the temperature dependence of k_1 . Also shown on the plot are two shock-tube determinations of k_1 at 1200 and 1400 K by Schug and Wagner.²⁸ The temperature dependence of the rate coefficient clearly deviates from normal Arrhenius behaviour, but the combined data from this study and from Schug and Wagner can be fit quite well to the modified Arrhenius

Table 1 Summary of results for $CF_2 + CF_2$

T/K	mean (k_1/σ_{249}) /10 ³ cm s ⁻¹	mean σ_{249} /10 ⁻¹⁷ cm ²	$ mean k_1 / 10^{-14} cm^3 s^{-1} $
295 323 373 473 573 673 773 873 873 873	$\begin{array}{c} 2.51 \pm 0.20 \\ 2.80 \pm 0.21 \\ 3.31 \pm 0.22 \\ 5.58 \pm 0.58 \\ 8.76 \pm 1.02 \\ 9.99 \pm 0.84 \\ 13.9 \pm 1.0 \\ 22.5 \pm 1.3 \\ 20.2 \pm 3.1 \end{array}$	$\begin{array}{c} 1.61 \pm 0.21 \\ 1.58 \pm 0.20 \\ 1.37 \pm 0.16 \\ 1.14 \pm 0.16 \\ 1.03 \pm 0.16 \\ 0.972 \pm 0.127 \\ 0.878 \pm 0.108 \\ 0.716 \pm 0.083 \\ 0.712 \pm 0.130 \end{array}$	$\begin{array}{c} 4.01 \pm 0.51 \\ 4.42 \pm 0.55 \\ 4.54 \pm 0.55 \\ 6.40 \pm 0.92 \\ 8.78 \pm 1.35 \\ 9.70 \pm 1.27 \\ 12.1 \pm 1.5 \\ 16.1 \pm 1.9 \\ 14.3 \pm 2.6 \end{array}$
873(He)	23.1 ± 3.3	0.758 ± 0.132	17.5 ± 3.1

All data 760 Torr N2 except where stated.

The error limits for σ_{249} and k_1 combine the uncertainty in the value of k_1/σ_{249} at the 95% confidence level with the $\pm 10\%$ systematic error in the measurement of $[CF_2]_0$.



Fig. 4 Temperature dependence of the absorption cross-section for CF_2 at 249 nm. Error limits combine random errors at the 95% confidence level with a $\pm 10\%$ systematic error in the determination of $[CF_2]$.



Fig. 5 Arrhenius plot of the temperature dependence of k_1 , the rate coefficient for the CF₂ + CF₂ reaction at 760 Torr. N₂ (\Box) From Schug and Wagner,²⁸ (\blacksquare) this work, with error limits combining random errors at the 95% confidence level with a $\pm 10\%$ systematic error in the determination of [CF₂]. The curve is a non-linear least squares fit to the modified Arrhenius expression $k = AT^2 \exp(-B/T)$ of the data from this study and the data from Schug and Wagner,²⁸ over the temperature range 295–1400 K.

expression:

 $k_1 = (1.39 \pm 0.20) \times 10^{-19} T^2$

 $\times \exp[(347 \pm 56)/T]$ cm³ molecule⁻¹ s⁻¹

for the temperature range 295-1400 K, in 760 Torr N₂. The uncertainties refer to random error in the parameters at the 95% confidence level. Systematic errors are estimated to be $\pm 10\%$. It should be pointed out, however, that the variation of k_1 , with pressure at 873 K indicates that the reaction has not quite reached its high-pressure limit at this temperature and atmospheric pressure. This can be seen in Fig. 6 which shows the pressure dependence of k_1 at room temperature and 873 K. At room temperature, the rate coefficient has clearly reached its high-pressure limit at atmospheric pressure, 760 Torr, whereas at 873 K, the rate coefficient still appears to be increasing with increasing pressure at 760 Torr, i.e. it is in the 'fall-off' region. Within the uncertainty of the measurements, there does not appear to be any dependence on the nature of the bath gas. The extension of the fall-off region for a rate coefficient to higher pressures with increasing temperature is quite normal for a recombination reaction such as this, as collisional stabilisation of the recombination product by a third body becomes increasingly important. Where the highpressure limiting rate coefficient for a reaction cannot be measured experimentally because it lies at too high a pressure, it can often be calculated by RRKM theory or estimated by



Fig. 6 Pressure dependence of k_1 at 295 and 873 K. \Box , Argon, 873 K; \bigcirc , nitrogen; 873 K; \triangle , helium, 873 K; \bigcirc , nitrogen 295 K.

fitting the low-pressure data to the functional form for the variation of k with pressure proposed by Tröe,³¹ where this is warranted by the quality of the data. Such analysis has not been carried for the 873 K data. Strictly, it should be the high-pressure limiting value of k_1 at 873 K which is displayed in the Arrhenius plot of Fig. 5, rather than the value measured at 760 Torr. This means that the curvature in the Arrhenius plot of the high-pressure limiting values of k_1 is actually more pronounced than is apparent from Fig. 5 and that the temperature-dependent expression for k_1 given above can only be regarded as an empirical expression for the temperature dependence of the value of k_1 at 760 Torr.

Products of the CF₂ + CF₂ reaction at 873 K

Curvature in the Arrhenius plot of the rate coefficient for a reaction can sometimes be attributed to a change in the reaction mechanism at higher temperature. The possibility that channels other than radical recombination for the $CF_2 + CF_2$ reaction play an increasingly important role at higher temperature, contributing to the observed curvature in the Arrhenius plot of k_1 , was considered by examining for alternative products to C_2F_4 for the reaction at 873 K. Potential product channels for the reaction and their enthalpies are given below:

$$\frac{\Delta H_{298}/\text{kJ mol}^{-1}}{\text{CF}_2 + \text{CF}_2 \rightarrow \text{C}_2\text{F}_4} ; -295}$$

$$\rightarrow \text{CF}_3 + \text{CF} ; 149$$

$$\rightarrow \text{C}_2\text{F}_3 + \text{F} ; 198$$

$$\rightarrow \text{C}_2\text{F}_2 + \text{F}_2; 385}$$

$$\rightarrow \text{C}_2\text{F}_2 + 2\text{F}; 544$$

The reaction enthalpies were calculated using heats of formation taken from the JANAF Thermochemical Tables,³² except for C_2F_3 for which the heat of formation was estimated by the methods of Benson.³³

Several repetitive photolysis experiments with stable product analysis were carried out, but no evidence could be found for the formation of products such as C_2F_2 , C_2F_6 or C_4F_6 which would have been indicative of these alternative channels. It can be seen that all the channels except for recombination are considerably endothermic. The conclusion is, therefore, that the measured rate coefficients and the non-Arrhenius temperature dependence do actually refer to the CF_2 recombination reaction.

Reaction of CF_2 with H_2 , O_2 , CH_4 and C_2H_4

The reactions of CF_2 with X (X = H₂, O₂, CH₄ and C₂H₄) were studied by adding varying concentrations of X to C_2F_4 -N₂ mixtures:

$$CF_2 + X \rightarrow \text{products}$$
 (3)

In the case where $k_3[X] \ge k_1[CF_2]_0$, the decay rate of CF₂ would be much faster than measured in the absence of X and would be expected to follow first-order kinetic behaviour. In fact, this condition was never met for any of the reactions studied. None of the reagents added had any discernible effect on the rate of decay of the CF₂ absorption signal and did not modify the value of k_1/σ_{249} , concluded from second-order analysis of the data, outside its limit of uncertainty, at any of the temperatures investigated over the range 294–873 K.

Upper limits for k_3 , the rate coefficient for reaction of CF₂ with X, were derived for each reagent by considering what would be the smallest value of k_3 , for the particular concentration of reagent added, which would have led to a discernible increase in the rate of decay of CF₂. The decision as to



Fig. 7 Decay of the CF₂ absorption signal at 249 nm following the 193 nm flash photolysis of C₂F₄ in the presence of 1 atm of CH₄ at 873 K. The continuous lines are simulations; (----) assumes there is no reaction between CF₂ and CH₄, *i.e.* the decay is purely second-order due to the self-reaction; (---) assumes the rate coefficient for CF₂ + CH₄ is $k = 5 \times 10^{-19}$ cm³ molecule⁻¹ s⁻¹.

what a discernible increase in decay rate would be took into account the signal noise of the decay trace being analysed and the limits of uncertainty in the value of k_1/σ_{249} for reaction (1) at the relevant temperature. As an example, Fig. 7 shows the decay of the CF_2 absorption signal produced when C_2F_4 is photolysed in the presence of 1 atm CH₄ at 873 K. Also shown is a fit to the data assuming that the decay of CF_2 is purely second order, *i.e.* there is no reaction between CF₂ and CH₄. The fit to the experimental data is good and gives a value for k_1/σ_{249} of 2.06 \times 10⁴ cm s⁻¹ which is in good agreement with the mean value of $k_1/\sigma_{249} = (2.25 \pm 0.13) \times 10^4$ cm s^{-1} obtained for the CF₂ self-reaction in the presence of N₂ at 873 K. The lower curve is a simulation assuming that the rate coefficient for $CF_2 + CH_4$ is 5×10^{-19} cm³ molecule⁻¹ s⁻¹. A higher rate coefficient would take the simulated decay just outside the noise of the experimental decay trace. For this experiment, the lowest discernible rate coefficient for the CF₂ + CH₄ reaction is concluded to be 5×10^{-19} cm³ molecule⁻¹ s⁻¹.

Upper limits were derived in this way for each reagent at several temperature between 294 and 873 K and are summarised in Table 2. For all reagents except CH_4 , the maximum concentration which could be added was limited by two complicating factors: (1) thermal reaction between the reagent and C_2F_4 at high temperatures; (2) absorption of the 193 nm laser radiation by the reagent. The first factor was a problem for H_2 and O_2 which both showed evidence of a thermal reaction with C_2F_4 in the cell at 873 K. This led to smaller initial CF_2 radical concentrations. The problem was particularly acute for O_2 , limiting the amount which could be added to $<1 \times 10^{17}$ cm⁻³. The second factor was a problem for O_2 and C_2H_4 which both absorbed the 193 nm radiation. Oxygen has fairly strong absorption bands in the UV around 193 nm. These are the Schumann-Runge bands and are due

Table 2 Summary of upper limits for $k(CF_2 + X)$ (cm³ molecule⁻¹ s⁻¹)

T/K	H ₂	0 ₂	CH ₄	C ₂ H ₄
295	$< 5 \times 10^{-20}$	$< 1.5 \times 10^{-19}$	$< 5 \times 10^{-20}$	$< 2 \times 10^{-18}$
473 573		$< 3 \times 10^{-18}$	$< 2 \times 10^{-19}$	<2 × 10
673 873	$< 5 \times 10^{-19}$	$< 3 \times 10^{-17}$	$< 4 \times 10^{-19}$	$< 2 \times 10^{-16}$ $< 2 \times 10^{-16}$

to excitation to vibrational levels of the ${}^{3}\Sigma_{u}^{-}$ state of O₂. At room temperature, C₂H₄ absorbs more strongly than O₂ at the laser wavelength. Its absorption spectrum is continuous in this region and is due to a $\pi \to \pi^{*}$ transition. The consequences of absorption were (a) reduced yields of CF₂ radicals; (b) potential radical concentration gradients resulting from attenuation of the laser beam along the cell and (c) photolysis of the reagent and formation of other active radical species.

The photolysis of O_2 leads to formation of O atoms. The consequences of this in the experiments depended on temperature as a result of the competition of the two reactions:

$$O + O_2 + M \leftrightarrow O_3 + M \tag{4}$$

$$O + C_2 F_4 \rightarrow COF_2 + CF_2 \tag{5}$$

At lower temperatures, under the conditions employed, formation of O_3 was favoured and this interfered with the detection of CF_2 because O_3 absorbs strongly at 249 nm. At higher temperatures, O_3 is thermally unstable and the equilibrium for reaction (4) lies in favour of O atoms. Reaction with C_2F_4 was then the dominant removal process for O atoms, and while this reaction occurred rapidly, there is the possibility that some of the CF_2 may have been formed in the triplet ${}^{3}B_1$ state.³⁴

Photolysis of C_2H_4 can proceed via three channels of which two lead to formation of active radical species:

$$C_2H_4 + h\nu \rightarrow C_2H_2 + H_2 \tag{6a}$$

 $\rightarrow C_2 H_2 + 2H \tag{6b}$

$$\rightarrow C_2 H_3 + H \tag{6c}$$

H atoms will be rapidly scavenged, so the most likely radical species present will be C_2H_5 , C_2H_3 and CHF_2CF_2 :

$$\mathbf{H} + \mathbf{C}_2 \mathbf{H}_4 + \mathbf{M} \to \mathbf{C}_2 \mathbf{H}_5 + \mathbf{M} \tag{7}$$

$$H + C_2 H_4 \rightarrow C_2 H_3 + H_2 \tag{8}$$

$$H + C_2F_4 + M \rightarrow CHF_2CF_2 + M \tag{9}$$

Absorption of the laser radiation by O_2 and C_2H_4 occurred at all temperatures, but the problem became more severe at higher temperatures due to an increase in the effective absorbance of the gas, integrated over the 193 nm laser transition band width. By measuring the attenuation of the laser beam transmitted through the cell, the effective absorbance due to a particular concentration of O_2 was found to increase by over two orders of magnitude between 294 and 873 K. This is presumably due to broadening of adjacent vibrational bands on either side of the minimum near 193 nm. Although ethylene absorbed the laser radiation more strongly than O_2 at room temperature, by more than two orders of magnitude for the same concentration, the effective absorbance increased by only a factor of *ca*. 20 between 294 and 873 K.

Because these limitations were all exacerbated at higher temperatures, the lower reagent concentrations which could therefore be added meant that the upper limits for k_3 concluded were always larger at higher temperatures than at room temperature, and should not be interpreted as indicating the onset of occurrence of a reaction.

The possibility that reaction of CF_2 with O_2 was being masked by rapid regeneration of CF_2 via reactions (10) and (5) was investigated by looking for the build-up of COF_2 which would be expected to occur following the repetitive photolysis of a static $C_2F_4-O_2-N_2$ mixture in the reactor at 873 K:

$$CF_2 + O_2 \rightarrow COF_2 + O \tag{10}$$

$$O + C_2 F_4 \rightarrow COF_2 + CF_2 \tag{5}$$

However, FTIR analysis of the mixture after photolysis failed to reveal the presence of any COF_2 product, from which it is concluded that no reaction was occurring.

Photolysis of C₃F₆

Some additional experiments were carried out using C_3F_6 as the source of CF_2 in order to verify the results obtained using C_2F_4 .

While a transient absorption signal was observed at 249 nm, the kinetic behaviour of the signal was quite different from that exhibited by C_2F_4 . The observed decay rates were consistently faster than obtained with C_2F_4 and were dependent on the initial concentration of C_3F_6 . The data could be analysed assuming second-order kinetics, but the values of k_1/σ_{249} obtained were in the range (3.5–18) × 10³ cm s⁻¹ at room temperature, depending on the C_3F_6 concentration, compared with $2.5\times10^3~cm~s^{-1}$ obtained using C_2F_4 . The value of k_1/σ_{249} increased with decreasing C_3F_6 concentration. Assuming a quantum yield of unity for CF₂ formation from C₃F₆ photolysis and measurements of the laser intensity transmitted through the cell, gave values of σ_{249} between (5–8) × 10⁻¹⁸ cm² molecule⁻¹, *i.e.* a factor of 2–3 times lower than obtained using C₂F₄. Examination of the wavelength dependence of the measured absorption signals revealed that the peak at 249 nm was considerably broader than obtained using C_2F_4 , with the spectrum showing significant intensity in the wavelength region between adjacent peaks. This can be seen in Fig. 8 which shows the wavelength dependence of the absorption signal measured immediately after the laser flash normalised to the data of Sharpe et al. at 249 nm.²⁷

All these observations suggest that an additional reactive and absorbing species is produced by the photolysis of C_3F_6 . The sharp absorption bands of CF_2 appear to be superimposed on a broader, more continuous underlying spectrum of the other absorber. The combined data recorded at several different C_3F_6 concentrations could be interpreted by assuming two photolysis paths for C_3F_6 :

$$C_3F_6 + hv \rightarrow CF_2 + CFCF_3 \tag{11a}$$

$$C_3F_6 + h\nu \to C_2F_3 + CF_3 \tag{11b}$$

 CF_3 radicals do not absorb in this wavelength region of the UV. Their absorption bands occur much deeper in the vacuum UV, between 145 and 165 nm.³⁵ Reaction of $CFCF_3$ radicals with CF_2 is expected to occur slowly at room temperature. Extrapolating the Arrhenius expression reported by Buravtsev *et al.*¹⁸ to room temperature gives a rate coefficient



Fig. 8 Initial absorption spectrum produced from the 193 nm photolysis of C_3F_6 (\blacksquare) normalised to the data of Sharpe *et al.*²⁷ at 249 nm obtained from the photolysis of C_2F_4

 $k = 4 \times 10^{-15}$ cm³ molecule⁻¹ s⁻¹ for this reaction. However, if it is assumed that the additional absorbing species is C₂F₃, produced in parallel to the photolysis channel producing CF₂, then the faster decay of the composite absorption signal can be attributed to the reaction:

$$CF_2 + C_2F_3 \rightarrow \text{products}$$
 (12)

The combined absorption vs. time data recorded at five different C_3F_6 concentrations at room temperature could be modelled using a chemical scheme involving reactions (11a), (11b), (1) and (12) and the slow $CF_2 + CFCF_3$ reaction. Through a parameter optimisation procedure, using the numerical integration program FACSIMILE,³⁶ values for the following parameters were obtained which fitted the combined absorption vs. time data set: $k_{12} = 2 \times 10^{-13}$ cm³ molecule⁻¹ s⁻¹; $\sigma_{C_2F_3} = 1.6 \times 10^{-18}$ cm² molecule⁻¹; $\Phi_{CF_2} = 0.11$; where k_{12} is the rate coefficient for reaction (12), $\sigma_{C_2F_3}$ is the absorption cross-section of C_2F_3 at 249 nm and Φ_{CF_2} is the quantum yield for the CF₂ forming channel from C₃F₆ photolysis. Other reactions involving the interaction of the various fluorinated radicals have minor importance. It should be stressed, however, that this may not be a unique solution of the fitting procedure.

Reaction between CF₂ and C₃F₆ was neglected in the analysis on the basis that the apparent decay rate decreased with increasing C₃F₆ concentration. This reaction is not expected to be rapid ($k < 1 \times 10^{-18}$ cm³ molecule⁻¹ s⁻¹) by analogy with the reactions of CF₂ with C₂H₄, C₃H₆ and C₂F₄ which are all very slow at room temperature.^{12,15} Use of the Arrhenius parameters estimated for the CF₂ + C₃F₆ reaction at high temperature by Buravtsev *et al.*³⁷ to calculate the rate coefficient at 295 K also indicates that the reaction would be very slow.

Discussion

The value of k_1 derived for the CF₂ + CF₂ reaction at room temperature is in very good agreement with the other two most recent measurements reported in the literature. All the previous measurements are summarised in Table 3. The value of σ_{249} obtained in this study is almost a factor of two lower than obtained by Tyerman¹⁰ and Sharpe *et al.*,²⁷ but reflects the lower resolution of the monochromator used in the present study. The value of σ_{249} reported here is effectively an absorption cross-section for CF₂ integrated over the bandwidth of the monochromator at 249 nm.

The low value of the rate coefficient for the $CF_2 + CF_2$ reaction and its positive temperature dependence is fairly unusual for a radical recombination reaction. It has been suggested that the approach of two singlet ground-state CF_2 radicals occurs on a repulsive potential-energy curve and that for recombination to occur, the system has to pass through a transition state in which the ground-state CF_2 radicals are excited into the triplet ${}^{3}B_1$ state, corresponding to the crossing of the potential-energy curves correlating with singlet and triplet states of CF_2 .³⁸

The observation that an additional reactive and absorbing species is produced by the 193 nm photolysis of C_3F_6 is not in accord with the early work of Dalby⁸ or the more recent study of Sharpe *et al.*²⁷ Sharpe *et al.* studied the flash lamp photolysis of C_3F_6 between 185 and 209 nm. They obtained values of σ_{249} and k_1 which were indistinguishable from those of C_2F_4 when they assumed that the quantum yield for CF_2 formation $\Phi_{CF_2} = 1$. A much lower value of Φ_{CF_2} is implied in this work. Sharpe *et al.* apparently found no evidence for the formation of an additional reactive and absorbing species in their experiments. A possible explanation which can be found to reconcile this with the present results is that the C_2F_3 rad-

icals initially produced in their high intensity flash contained sufficient excess energy to dissociate to CF_2 within the duration of the flash. The photolysis of C_3F_6 merits further attention to resolve this disagreement.

The very low upper limits measured for the rate coefficients of the reactions of CF₂ with H₂, CH₄ and C₂H₄ are the lowest which have been measured for CF₂ over an extended temperature range (295-873 K). The upper limit derived for the rate coefficient of CF₂ with O₂ at 873 K, $k < 3 \times 10^{-17}$ cm³ molecule⁻¹ s⁻¹, is consistent with the upper limit value obtained recently by Hack *et al.*¹⁹ at 803 K in a flow-tube study with LIF detection of CF₂. Extrapolating the Arrhenius expression derived from the shock-tube study of Keating and Matula²⁰ leads to $k_{10} = 8 \times 10^{-18}$ cm³ molecule⁻¹ s⁻¹ at 873 K and 1×10^{-30} cm³ molecule⁻¹ s⁻¹ at 298 K, consistent with the present observations. Chowdhury reported a value of $k_{10} = 8.3 \times 10^{-13}$ cm³ molecule⁻¹ s⁻¹ by observing the rate of formation of COF₂ when CF₂ was generated by IR multiphoton dissociation of octafluorocyclopentene in the presence of O₂.²¹ This value corresponded to a translational temperature of 3650 K for CF₂ formed in their experiments.

Slow reaction has been reported for CF₂ with NO₂,¹² and the alkenes (CH₃)₂C=C(CH₃)₂ and (CH₃)₂C=CH₂¹³ at room temperature and with Cl₂,^{11,14} Br₂,^{11,15} HBr¹⁶ and C₂F₄^{17,18} at elevated temperatures. Given the lack of any observable reaction with C₂H₄ and C₃H₆,¹² alkyl substitution of the alkenes must activate them towards reaction with CF₂.

The significance of the apparent lack of reactivity of CF_2 with molecular species is to accentuate the importance of its reactions with free radical species in flames, principally H, O and OH, even though their abundance is lower. Flame modelling studies have demonstrated the important role played by these reactions in inhibited flames.^{6,7} Reaction with H and OH are believed to be the major loss processes for CF_2 in inhibited flames and are a significant source of HF. Moreover, the reactions forming HF constitute a trap for H and OH which are the chain carriers of the combustion process.

The kinetic data used in the mechanism of Westbrook⁴ and refined by Vovelle and co-workers^{6,7} for the reactions of CF_2 with O, H, OH and also CH_3 radicals are given below:

$$CF_2 + O \rightarrow FCO + F;$$

 $k = 1.7 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (13)

 $CF_2 + H \rightarrow CF + HF;$

$$k = 3.3 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$
 (14)

 $CF_2 + OH \rightarrow FCO + HF;$

$$k = 1.7 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$
 (15a)

 $CF_2 + OH \rightarrow COF_2 + H;$

$$k = 8.3 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$
 (15b)

$$CF_2 + CH_3 \rightarrow CH_2CF_2 + H;$$

$$k = 1.7 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$
 (16)

All these reactions are assumed in the models of flame inhibition to have temperature-independent rate coefficients. The $CF_2 + O$ and $CF_2 + H$ reactions are the only CF_2 + radical reactions for which direct measurements of the rate coefficient are available, and these are all at or below room temperature. The values used for the O and H reactions are based on the measurements made by Hancock *et al.*²² and Tsai and McFadden,²⁵ respectively. The values used for the OH and CH₃ reactions are only estimates based on the analysis of CF₂, COF₂ and CH₂CF₂ profiles in CH₄-O₂-Ar flames inhibited by CF₃Br.²⁶

Table 3 Summary of measurements of k_1 and σ_{249} for CF₂ + CF₂ at 298 K

	pressure /torr	$(k_1/\sigma_{249})/cm s^{-1}$	$/10^{-17} \text{ cm}^2$	$k_1/10^{-14} \text{ cm}^3 \text{ s}^{-1}$
Dalby ⁸ Tyermann ¹⁰	20-760 (Ar) 50-280 (N ₂)	1870 1222	$\begin{array}{c} 0.76 \pm 0.33 \\ 2.9 \pm 0.15 \end{array}$	1.4 ± 1.0 3.60 ± 0.33
Sharpe et al. ²⁷ this work	$\frac{20-800 (N_2)}{35-760 (N_2)}$	$1464 \\ 2510 \pm 200$	$\begin{array}{c} 2.91 \pm 0.44 \\ 1.61 \pm 0.21 \end{array}$	4.26 ± 0.64 4.01 ± 0.51

Based on the temperature-independent values for the rate coefficients for these radical reactions used in the models and the upper limits for the CF_2 + molecule reactions measured in this study, it can be concluded that the rate coefficients for reaction of CF₂ with O, H and OH are at least five orders-ofmagnitude higher than those for reaction of CF_2 with O_2 and CH₄ at temperatures below 900 K. Even at 2000 K, based on the Arrhenius expression of Keating and Matula,²⁰ the rate coefficient for reaction with O_2 will be 600 times slower than for reaction with OH. The flame measurements of Vovelle et $al.^7$ show that at the position in their flame where the CF₂ concentration is greatest (ca. 0.5 cm), the mole fractions of CH₄ and O₂ are ca. 0.03 and ca. 0.15, respectively, compared with ca. 0.01 for H and OH. This clearly indicates that reaction of CF_2 with CH_4 and O_2 (and other molecular species) will never compete with their reaction with these radical species under typical flame conditions.

Radical trapping involving formation of HF through reactions such as (14) and (15*a*) must contribute to the efficiency of fluorinated compounds as flame inhibitors through a chemical mechanism, rather than a purely physical effect. The trapping effect is expected to be sensitive to the rate and the fraction of the $CF_2 + OH$ reaction producing HF via reaction (15*a*), but no information exists in the literature on this.

Compared with CF_2 , CF_3 radicals are much more reactive towards molecular reagents. This is testified by the large body of kinetic data available on its reactions. Nevertheless, data on its reactions with species present in flames are still relatively sparse, particularly at high temperatures. Data on CF_3 reactions used in the flame inhibition models are based mainly on the estimates derived by Biordi *et al.*²⁶ from the analysis of concentration profiles in methane flames inhibited by CF_3Br and are therefore subject to uncertainty. These are for reactions of CF_3 with H, O, OH, CH_3 , CF_3 , O_2 and CH_4 . Among these, the only reactions for which direct measurement of the rate coefficients have been made are for O, H, O_2 and CF_3 and these are mainly confined to room temperature. Investigation of the radical trapping reactions involving CF_3 , such as the reaction with OH:

$$CF_3 + OH \rightarrow COF_2 + HF$$
 (17)

would certainly be beneficial to understanding the role of this radical in inhibition chemistry.

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