APPLICATIONS OF FOURIER TRANSFORM IR SPECTROSCOPY TO THE DETERMINATION OF PHOTO-OXIDATION QUANTUM YIELDS FOR HALOCARBONS

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(Received June 19, 1985; in revised form September 18, 1985)

Summary

Fourier transform IR spectroscopy has been applied to the quantitative analysis of the products from the photo-oxidation of CF_2Cl_2 and CF_3Br by molecular oxygen. $\Phi_{COF_2}^{184.9}$ for CF_2Cl_2–O_2 mixtures was measured as 1.08 ± 0.08 in good agreement with previous studies. $\Phi_{COF_2}^{184.9}$ for CF_3Br–O_2 mixtures has been measured for the first time in this work, its value being 1.02 ± 0.08.

1. Introduction

Chlorofluorocarbons and bromofluorocarbons do not occur naturally; they are manufactured presently at the rate of hundreds of kilotonnes per year with the only known sinks for the fully halogenated fluorocarbons occurring at altitudes of tens of kilometres in the atmosphere [1]. Two types of loss mechanism have been postulated in the stratosphere which are as follows. Firstly, for the chloromethanes with two or more chlorine atoms such as CF_2Cl_2, the UV cross sections are sufficiently high at 185 - 227 nm (the solar UV window) that photodissociation is the primary decomposition pathway. Secondly, for fully halogenated fluorocarbons with lower absorption cross sections such as CF_3Br, $O(^1D_2)$ atom attack is probably a significant reaction pathway in addition to photodecomposition. The subsequent fate of the released halogen atoms has been particularly well studied in the last ten years since Molina and Rowland [2] first predicted that the effect of injecting chlorofluorocarbons into the atmosphere might be to deplete the ozone layer. However, the exact mechanism by which the associated carbon-containing radical reacts in the atmosphere is poorly understood as illustrated by the following reactions. For example, the oxidation of the $\cdot CF_3$ radical to carbonyl fluoride has been suggested [3] to occur directly

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$$\dot{C}F_3 + O_2 \longrightarrow F\dot{O} + CF_2O \qquad (1)$$

or via an intermediate peroxy radical

$$\dot{C}F_3 + O_2 \xrightarrow{M} CF_3\dot{O}_2 \qquad (2)$$

There is now a considerable body of evidence to support a route involving the intermediacy of peroxy radicals in the oxidation process. For example, the formation of the $CF_2O_2^+$ fragment has been monitored mass spectrometrically by Caralp and Lesclaux [4] in the photolysis of CF_3I–O_2 mixtures and an absorption feature attributed to $CF_3\dot{O}_2$ has been measured in the pulse radiolysis of CF_3Cl–O_2 and CF_3Br–O_2 [5]. Furthermore the IR spectra of $CF_3{}^{16}\dot{O}_2$ and $CF_3{}^{18}\dot{O}_2$ have been recorded on photolysis of CF_3I in ${}^{16}O_2$- and ${}^{18}O_2$-doped argon matrices at 4.2 K [6].

The subsequent chemistry to produce carbonyl fluoride in laboratory studies is apparently dependent on the presence of halogen molecules. Thus the generally accepted, but endothermic [7], disproportionation reaction of the peroxy radicals

$$2CF_3\dot{O}_2 \longrightarrow 2CF_3\dot{O} + O_2 \qquad (3)$$

can be followed, in the presence of molecular iodine, by the following reaction [8]:

$$CF_3\dot{O} + I_2 \longrightarrow I_2F + CF_2O \qquad (4)$$

In such a system the endothermic reaction between two $CF_3\dot{O}$ radicals to produce carbonyl fluoride

$$2CF_3\dot{O} \longrightarrow 2CF_2O + F_2 \qquad (5)$$

is thought to be absent. It should be pointed out that there is no spectroscopic evidence for the existence of $CF_3\dot{O}$ under any experimental conditions although a recent calculation has predicted its expected IR spectrum [9].

For the oxidation of $\cdot CF_2Cl$ radicals, experiments by Jayanty et al. [10] and Suong and Carr, Jr., [11] are consistent with the following mechanism:

$$\dot{C}F_2Cl + O_2 \xrightarrow{M} CF_2Cl\dot{O}_2 \qquad (6)$$

$$2CF_2Cl\dot{O}_2 \longrightarrow 2CF_2Cl\dot{O} + O_2 \qquad (7)$$

$$CF_2Cl\dot{O} \longrightarrow CF_2O + Cl \qquad (8)$$

The intermediacy of $CF_2ClO\dot{O}$ and $CF_2Cl\dot{O}$ was proposed by analogy with the reported oxidation mechanism of $\cdot CF_3$ radicals but neither the peroxy nor the oxy species have been observed directly.

A recent report by Molina and Molina [12] suggests that heterogeneous reactions play an important part in the oxidation of $\dot{C}F_2Br$ radicals formed

in the photolysis of $CF_2Br_2-O_2$ mixtures in the 200 - 300 nm region. The exact nature of the processes involved was not speculated on but it could be shown that the measured quantum yield for carbonyl fluoride formation was unity within experimental error, which is a conclusion in some disagreement with an earlier study by Walton [13]. The results of the later publication were obtained by Fourier transform IR (FTIR) measurement of the ν_2 absorption of COF_2 at 1943 cm^{-1}. Accurate knowledge of the quantum yield of end product formation is an essential first step in the determination of a photochemical mechanism and to complement our studies of intermediates involved in matrix-isolated halocarbon photo-oxidation reactions, a gas phase study of the measurement of $\Phi_{COF_2}^{184.9}$ was undertaken using FTIR spectroscopy. Two mixtures have been investigated for this report: (i) $CF_2Cl_2-O_2$, which has been studied previously using gas chromatographic methods [14], and dispersion IR spectroscopy [15]; (ii) CF_3Br-O_2, which has not been reported before.

2. Experimental details

Three T configuration gas cells, constructed from Pyrex glass, were used in the photolysis experiments. Each was fitted with one Spectrosil B UV window of 1 mm thickness and a pair of KBr, silicon or BaF_2 windows to allow products to be monitored in the IR region. The volumes of the cells were calculated using Boyle's law and found to be 180 ± 1 cm^3, 160 ± 1 cm^3 and 142 ± 1 cm^3 respectively with a UV optical path length of 50 ± 1 mm in each case but differing IR path lengths (102 ± 1, 110 ± 1 and 100 ± 1 mm). A Phillips Spectral LL low pressure mercury arc was employed for photolysis using oxygen-free nitrogen to flush the lamp housing. The gas mixtures were prepared on a mercury-free greaseless vacuum line made of Pyrex glass using an MKS Baratron capacitance manometer (model 310) and a Wallace–Tiernan gauge (model FA141).

IR analysis was carried out on a Digilab FTS 20V FTIR spectrometer using a low spectral resolution of 8 cm^{-1} to determine the partial pressure of COF_2 in the photolysed gas mixtures. A mercury cadmium telluride detector cooled to liquid nitrogen temperature was used and the collected interferograms were zero-filled fourfold before computation in order to improve the definition of the band outline. Each spectrum was ratioed against a stored background of the evacuated cell and plotted out in absorbance mode. The absorbance of the carbonyl band of COF_2 centred at 1943 cm^{-1} was measured at 1930 cm^{-1} and 1943 cm^{-1}. The region from 2250 to 1750 cm^{-1} was plotted out in order to define the baseline as accurately as possible. Baselines which were sloping because of instability of the optics were corrected with specialized software available in the spectrometer minicomputer. Water vapour absorptions were minimized by evacuating the sample and main chambers of the spectrometer for a few minutes before each spectrum was collected. Overtone and combination bands of the parent halocarbon were

eliminated by subtracting out a stored absorption spectrum of pure halo-carbon.

A quadrupole mass spectrometer (VG gas analysis model SX 300) was used to assess the purity of gas samples and to determine the mercury arc incident intensity at 184.9 nm using nitrous oxide as an actinometer. In these experiments photolysis for a known interval of a cell containing nitrous oxide at 200.0 Torr and argon at 1.00 Torr (as an internal standard) was followed by measurement of the ratio of the peak intensities at $m/e = 28$ and $m/e = 40$. The amounts of nitrogen formed for different photolysis times were calculated by comparison of the results with a calibration graph obtained for the relative mass spectrometric sensitivities of nitrogen and argon at known partial pressures. Atmospheric leakage was negligible over the time taken for the experiment.

Each gas except COF_2 was transferred from its cylinder to a glass bulb in which it was stored and then used as required. COF_2 was transferred directly from its cylinder to the photolysis cell. Carbonyl fluoride (stated purity, 98%) was manufactured by PCR Research Chemicals. The IR spectrum of a sample of COF_2 at 50 Torr in a Pyrex gas cell showed the presence of SiF_4 after a few hours of storage. CO_2 was also observed after a total of 5 days storage. The gas was used without further purification. Bromotrifluoromethane and dichlorodifluoromethane (stated purities, better than 99.5%) were obtained from BDH and passed through a column of 1/16 in calcium aluminosilicate pellets (BDH type 5A) to eliminate traces of water vapour. Oxygen (stated purity, better than 99.998%) was manufactured by Messer Griesheim GmbH. Its mass spectrum revealed a small nitrogen impurity (less than 5%). Nitrous oxide (stated purity, 99.997%) was supplied by BDH: it was thoroughly degassed at 77 K and used without further purification. Nitrogen (stated purity, 99.998%) was supplied by Matheson. Argon (stated purity, 99.999%) was manufactured by Messer Griesheim GmbH. A xylene-based shellac (Dow Corning Ltd.) was used for affixing the optical flats to the reaction vessels.

3. Results

3.1. Nitrous oxide actinometer

Nitrous oxide is one of the most commonly used actinometers in the vacuum UV region. The quantum yield $\Phi_{N_2}^{184.9}$ of the nitrogen photoproduct at 184.9 nm is 1.44 ± 0.11 [16]. In the present experiments, nitrous oxide at 200.0 Torr was used in each run since this absorbs over 99% of the incident radiation. For mass spectrometric analysis it was necessary to add argon at 1.00 Torr (0.5%) as an internal standard. Argon was chosen for two main reasons. Firstly, it does not interfere with secondary chemical reactions involving $O(^1D_2)$ and nitrous oxide. Secondly, it does not physically deactivate $O(^1D_2)$ to $O(^3P)$; this would reduce $\Phi_{N_2}^{184.9}$ [17].

The relative mass spectrometer sensitivity of N_2/Ar was measured from calibration mixtures of nitrogen and argon. This factor was calculated to be

1.09 from least-squares analysis with a correlation coefficient of 0.999. The incident light intensity I_0 was measured simultaneously with each CF_2Cl_2–O_2 photolysis run. The ratio of the light fluxes on either side of the lamp was measured by making up a mixture of CF_2Cl_2 at 50.0 Torr and oxygen at 10.00 Torr in both the KBr cell and the BaF_2 cell. The rate $d/dt[COF_2]$ of formation of COF_2 was measured in both cells and the ratio of the light fluxes calculated to be unity.

3.2. Photoproducts of CF_2Cl_2–O_2 mixture

The reactant gas cell contained a mixture of CF_2Cl_2 at 50.0 Torr and oxygen at 10.00 Torr so that light absorption by oxygen was negligible in comparison with light absorbed by CF_2Cl_2 [18]. Hence the carbon-containing radicals produced in the photolysis of the parent halocarbon were scavenged by molecular oxygen.

The major IR-observable product was COF_2 with new absorptions in the spectrum of the gas mixture seen at 1943 cm^{-1}, 1249 cm^{-1} and 774 cm^{-1}, which correspond to the ν_2, ν_4 and ν_6 fundamental vibrations of carbonyl fluoride respectively [19]. In addition, an absorption corresponding to the ν_1 fundamental of COF_2 was seen as a shoulder on the high frequency side of the CF_2Cl_2 absorption centred at 923.1 cm^{-1}. In Fig. 1 the digitized absorbance spectrum of the gas mixture before photolysis has been

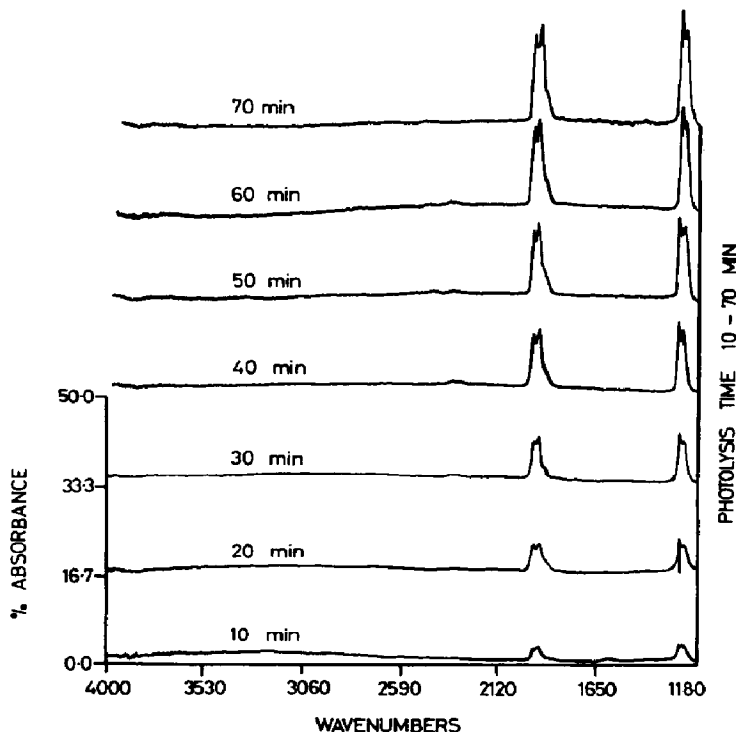Fig. 1. Absorbance subtraction spectra (spectrum after photolysis minus spectrum before photolysis) of a gas mixture of CF_2Cl_2 at 50.0 Torr and oxygen at 10.0 Torr after intervals of 10 min of photolysis. The spectral resolution is 8 cm^{-1}.

subtracted from each of the absorbance spectra taken after set periods of photolysis; the ν_2 and ν_4 fundamentals of COF_2 are shown after every 10 min of photolysis. Very weak absorptions which were characteristic of fundamental vibration–rotation lines of CO and HCl were present in 0.2 cm^{-1} resolution spectra of CF_2Cl_2–O_2 mixtures after 90 min of photolysis. The carbon monoxide was probably produced by photolysis at 184.9 nm of the COF_2 photoproduct. The trace amounts of HCl formed may have resulted from chlorine atom reaction with trace amounts of water in the cell or more likely its attack on the xylene base of the shellac used to affix the optical plates of the cell. Hence molecular chlorine was undoubtedly produced in the experiments although it is not observable in the IR spectra.

Least-squares plots of COF_2 absorbances at 1930 cm^{-1} and 1943 cm^{-1} against the photolysis time were related to partial pressures of COF_2 by calibration mixtures made up of COF_2, CF_2Cl_2 at 50.0 Torr and oxygen at 10.0 Torr.

The quantum yield of formation of COF_2 at 184.9 nm in the photo-oxidation of CF_2Cl_2 was calculated for a total of six runs and the results are presented in Table 1. The mean value of $\Phi_{N_2}^{184.9}$ obtained in these experiments is 1.08 with random error limits of ±0.05 to two standard deviations. However, a systematic error is also introduced by use of the actinometer value given in the literature for $\Phi_{N_2}^{184.9}$ (1.44 ± 0.11). Hence after standard treatment of errors we calculate the measured value of $\Phi_{COF_2}^{184.9}$ in this work to be 1.08 ± 0.08.

TABLE 1

The quantum yield of formation $\Phi_{COF_2}^{184.9}$ of COF_2 at 184.9 nm from CF_2Cl_2–O_2 mixtures

Run	$I_0 \times 10^{-15}$ (quanta s^{-1})	$d/dt[COF_2] \times 100$ (absorbance units min^{-1})		$d/dt[COF_2] \times 10^{-15}$ (molecules s^{-1})			$\Phi_{COF_2}^{184.9}$
		At 1930 cm^{-1}	At 1943 cm^{-1}	At 1930 cm^{-1}	At 1943 cm^{-1}	Mean	
1	1.14	0.201	0.164	1.22	1.16	1.19	1.04
2	0.995	0.182	0.150	1.10	1.06	1.08	1.09
3	1.02	0.181	0.149	1.10	1.05	1.08	1.06
4	1.02	0.189	0.156	1.15	1.10	1.13	1.11
5	0.907	0.164	0.137	0.996	0.969	0.983	1.08
6	0.829	0.151	0.125	0.915	0.882	0.889	1.07

3.3. Photoproducts of CF_2Br–O_2 mixtures

Five reaction mixtures were investigated: CF_3Br at 250.0 Torr with oxygen at 5.0, 10.0, 15.0, 20.0 or 25.0 Torr. In each case, light absorption by oxygen was small in comparison with light absorbed by CF_3Br [18].

The quantum yield of formation of COF_2 at 184.9 nm in a mixture of CF_2Cl_2 at 50.0 Torr and oxygen at 10.0 Torr measured in this work was used

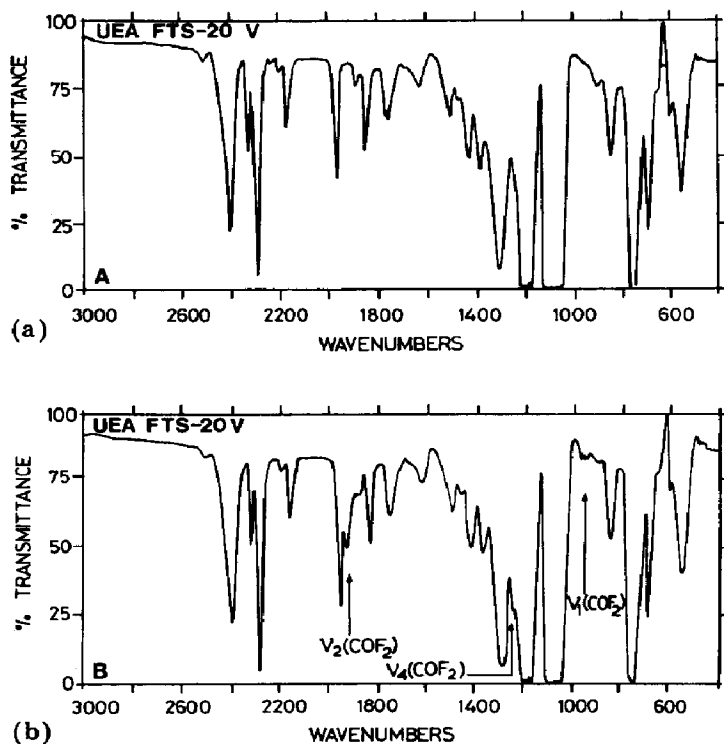Fig. 2. IR spectra at a resolution of 8 cm^{-1} of a gas mixture of CF$_3$Br at 250 Torr and oxygen at 25 Torr: (a) before photolysis; (b) after 1.50 h photolysis at 184.9 nm.

as an actinometer for CF$_3$Br–O$_2$ photolysis experiments. This was a matter of convenience since the same method of analysis could be used for both the sample and the actinometer cells. The COF$_2$ produced in the actinic cell was found to be stable over the time scale of the experiment.

The only product observable in the IR spectra was COF$_2$. Figure 2 shows a comparison between 8 cm^{-1} resolution FTIR spectra of a mixture of CF$_3$Br at 250.0 Torr and oxygen at 25.0 Torr before and after 90 min photolysis at 184.9 nm. Least-squares plots of COF$_2$ absorbances against photolysis time at 1930 cm^{-1} and 1943 cm^{-1} were related to partial pressures of COF$_2$ by calibration mixtures made up of COF$_2$ and CF$_3$Br at 250.0 Torr.

The quantum yield of formation of COF$_2$ at 184.9 nm in the photooxidation of CF$_3$Br was calculated for a total of five runs and the results are summarized in Table 2. The mean value of $\Phi_{COF_2}^{184.9}$ obtained in these experiments is 1.02 ± 0.08, where the error limits include both systematic and random errors dicussed above.

4. Discussion

4.1. The CF$_2$Cl$_2$ photo-oxidation process

The absorption cross section σ of CF$_2$Cl$_2$ at 184.9 nm is calculated to be 1.22 × 10^{-18} cm^2 from a linear interpolation of the preferred σ values of

TABLE 2

The quantum yield of formation $\Phi_{COF_2}^{184.9}$ of COF_2 at 184.9 nm from CF_3Br-O_2 mixtures

Run	$I_0 \times 10^{-15}$ (quanta s^{-1})	$I_a \times 10^{-15}$ (quanta s^{-1})	$d/dt[COF_2] \times 100$ (absorbance units min^{-1})		$d/dt[COF_2] \times 10^{-15}$ (molecules s^{-1})			$\Phi_{COF_2}^{184.9}$
			At 1930 cm^{-1}	At 1943 cm^{-1}	At 1943 cm^{-1}	At 1943 cm^{-1}	Mean	
1	1.51	1.37	0.298	0.246	1.47	1.43	1.45	1.06
2	1.54	1.40	0.291	0.243	1.44	1.42	1.43	1.02
3	1.47	1.34	0.281	0.234	1.39	1.36	1.38	1.03
4	1.44	1.31	0.278	0.231	1.37	1.35	1.36	1.04
5	1.39	1.26	0.246	0.207	1.22	1.21	1.22	0.97

Baulch et al. [20]. The absorption is believed to involve an $n-\sigma^*$ transition resulting in excitation to a repulsive electronic state, which immediately dissociates by breaking the C—Cl bond(s). It is energetically possible for a C—F bond to be broken at this wavelength since one photon of 184.9 nm light is equivalent to 647.5 kJ mol^{-1}. However, the quantum yield of close to unity for $\Phi_{COF_2}^{184.9}$ obtained both in this work and in previous studies [14, 15] coupled with the fact that neither COFCl nor $COCl_2$ was observed in the FTIR spectra are evidence that a C—F bond is not broken in the primary photolytic step.

Pitts, Jr., and coworkers [15] and Milstein and Rowland [14] have previously investigated the photolysis of $CF_2Cl_2-O_2$ mixtures at 184.9 nm and reported values for $\Phi_{COF_2}^{184.9}$ of 1.15 ± 0.15 and 1.11 ± 0.05 respectively. The latter value is the result of an indirect determination of the primary photoproduct quantum yield as the COF_2 was converted to CO_2 on a chromatographic column before measurement. However, the results are in excellent agreement with the value obtained in this study (1.08 ± 0.08) using the in situ non-destructive FTIR technique for sampling. It is concluded that oxygen is a very efficient scavenger of $\dot{C}F_2Cl$ radicals and that reactions such as

$$\dot{C}F_2Cl + Cl \xrightarrow{M} CF_2Cl_2 \qquad (9)$$

and

$$\dot{C}F_2Cl + Cl_2 \longrightarrow CF_2Cl_2 + Cl \qquad (10)$$

which would reduce $\Phi_{COF_2}^{184.9}$ from unity are absent. Combination–disproportionation reactions [21] of $\dot{C}F_2Cl$ are probably also not important at the small concentrations of radicals present (less than 10^{14} cm^{-3} s^{-1}):

$$\dot{C}F_2Cl + \dot{C}F_2Cl \longrightarrow \begin{cases} CF_2ClCF_2Cl & (11a) \\ :CF_2 + CF_2Cl_2 & (11b) \end{cases}$$
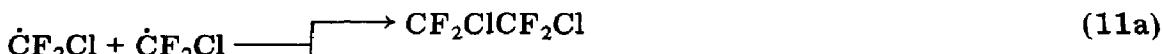
Several schemes have been proposed for the production in the atmosphere of $CF_2Cl\dot{O}$ and COF_2 from the proposed $CF_2Cl\dot{O}\dot{O}$ species, including reaction with NO, $H\dot{O}_2$ radicals or O_3 [22]. These are in addition to the self-reaction of two peroxy species proposed for laboratory studies (reaction (7)). No information about the stability of the oxy species is obtainable in the present static photolysis experiments but this is clearly a factor of some importance in the determination of total release rates of chlorine atoms in the atmosphere. In contrast, some dark and photochemical reactions of the COF_2 end product were observable in this study. For example, the carbonyl fluoride calibration plot did not obey Beer's law unless the CF_2Cl_2 parent halocarbon had been dried over a molecular sieve. This was a result of the reaction

$$COF_2 + H_2O \longrightarrow CO_2 + 2HF \qquad (12)$$

which leads to the formation of CO_2 as observed in the FTIR spectrum. There was also some evidence for the photolysis of COF_2 at 184.9 nm resulting in the production of CO. The absorption cross section of COF_2 has been measured by Chou *et al.* [23] and presented by Baulch *et al.* [20] with a reported value of 4.7×10^{-20} cm^2 at 184.9 nm. On photolysis of COF_2 at 50.0 Torr at this wavelength, a band centred at 2143 cm^{-1} with P and R branch structure was observed in the IR region and assigned to CO. This result is in agreement with the observation by Workman and Duncan [24] of the CO A $^1\Pi \leftarrow$ X $^1\Sigma^+$ UV absorption spectrum for vacuum UV photolysis of COF_2. Energetically possible primary photolytic steps at 184.9 nm and 298 K are

$$COF_2 + h\nu \longrightarrow F\dot{C}O + F \qquad (13a)$$
$$\longrightarrow CO + F_2 \qquad (13b)$$

Reaction (13a) could be followed by the disproportionation of $F\dot{C}O$ radicals to form CO via

$$F\dot{C}O + F\dot{C}O \longrightarrow COF_2 + CO \qquad (14)$$

4.2. The CF_3Br photo-oxidation process

The absorption cross section of CF_3Br at 184.9 nm is calculated to be 5.43×10^{-20} cm^2 after the measurement of Fass and Willard [25]. The absorption is believed to involve an $n-\sigma^*$ transition to a repulsive electronic state which immediately dissociates by breaking the C—Br bond. The standard enthalpy of the analogue of this process

$$CF_3Br \longrightarrow \dot{C}F_3 + Br \qquad (15)$$

is $D^0_{298}(Br—CF_3)$ and its recommended value [26] is given as 295.4 ± 4.2 kJ mol^{-1}. Other photolytic steps to produce BrF

$$CF_3Br + h\nu \longrightarrow :CF_2 + BrF \qquad (16a)$$

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or fluorine atoms

$$CF_3Br + h\nu \longrightarrow {:}CF_2 + Br + F \tag{16b}$$

are considerably more endothermic than this value [18] but are energetically possible at 184.9 nm. Simons and Yarwood [27] reported only a faint absorption spectrum due to :CF$_2$ in the flash photolysis of CF$_3$Br at wavelengths much lower than 200 nm. Therefore it is likely that reactions (16a) and (16b) are at most minor channels at 184.9 nm.

The quantum yield of formation $\Phi_{COF_2}^{184.9}$ of COF$_2$ in the photo-oxidation of CF$_3$Br at 184.9 nm has been measured for the first time in this work and found to be 1.02 ± 0.08. Oxygen is clearly an efficient scavenger of $\cdot$CF$_3$ radicals and reactions such as

$$\dot{C}F_3 + Br + M \longrightarrow CF_3Br + M \tag{17}$$

and

$$\dot{C}F_3 + Br_2 \longrightarrow CF_3Br + Br \tag{18}$$
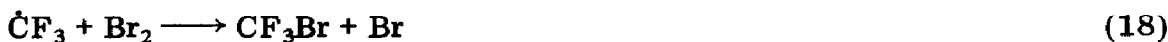
are absent in this study. The data are consistent with the generally accepted mechanism for $\cdot$CF$_3$ oxidation in laboratory studies given by Heicklen [3]:

$$\cdot CF_3 + O_2 \xrightarrow{\text{M}} CF_3O\dot{O} \tag{2}$$

$$2CF_3O\dot{O} \longrightarrow 2CF_3\dot{O} + O_2 \tag{3}$$

$$2CF_3\dot{O} \longrightarrow 2COF_2 + F_2 \tag{5}$$

Although reactions between CF$_3\dot{O}$ and bromine cannot be ruled out, no IR evidence for the formation of Br$_2$F was obtained in this study:

$$CF_3\dot{O} + Br_2 \longrightarrow Br_2F + COF_2 \tag{19}$$

5. Conclusion

FTIR spectroscopy has been applied to the quantitative analysis of two photochemical reactions of atmospheric interest in the gas phase. The results show that the quantum yields of COF$_2$ production at 184.9 nm from CF$_2$Cl$_2$–O$_2$ and CF$_3$Br–O$_2$ mixtures are approximately unity. An advantage of using FTIR spectroscopy for monitoring COF$_2$ is that analysis is *in situ* and non-destructive, whereas COF$_2$ is unstable on standard gas chromatographic columns.

References

1 F. S. Rowland and M. J. Molina, *Rev. Geophys. Space Phys.*, *13* (1975) 1.
2 M. J. Molina and F. S. Rowland, *Nature (London)*, *249* (1974) 810.
3 J. Heicklen, *Adv. Photochem.*, *7* (1969) 57; *J. Phys. Chem.*, *70* (1966) 112.
4 F. Caralp and R. Lesclaux, *Chem. Phys. Lett.*, *102* (1983) 54.
5 R. Cooper, J. B. Cumming, S. Gordon and W. A. Mulac, *Radiat. Phys. Chem.*, *16* (1980) 169.
6 K. C. Clemitshaw and J. R. Sodeau, *Proc. EEC Conf. on Oxidation Reactions in the Troposphere*, Commission of European Communities, Brussels, 1984, p. 22.
7 L. Batt and R. Walsh, *Int. J. Chem. Kinet.*, *15* (1983) 605.
8 V. I. Vedeneer, M. A. Teitel'Voim and A. A. Shoikhet, *Izv. Akad. Nauk. S.S.S.R.*, (1979) 2663.
9 J. S. Francisco and I. H. Williams, *Chem. Phys. Lett.*, *110* (1984) 240.
10 R. K. M. Jayanty, R. Simonaitis and J. Heicklen, *J. Photochem.*, *4* (1975) 381.
11 J. Y. Suong and R. W. Carr, Jr., *J. Photochem.*, *19* (1982) 295.
12 L. T. Molina and M. J. Molina, *J. Phys. Chem.*, *87* (1983) 1306.
13 J. G. Walton, *J. Chem. Soc., Faraday Trans. I*, *68* (1972) 1559.
14 R. Milstein and F. S. Rowland, *J. Phys. Chem.*, *79* (1975) 669.
15 R. Atkinson, G. M. Breuer, J. N. Pitts, Jr., and H. L. Sandoval, *J. Geophys. Res.*, *81* (1976) 5765.
16 M. Zelikoff and L. M. Ashenbrand, *J. Chem. Phys.*, *22* (1954) 1680.
17 H. Yamazaki and R. J. Cvetanović, *J. Chem. Phys.*, *40* (1964) 582.
18 R. Withnall, *Ph.D. Thesis*, University of East Anglia, 1984.
19 A. H. Nielson, T. G. Burke, P. J. H. Woltz and E. A. Jones, *J. Chem. Phys.*, *20* (1952) 596.
20 D. L. Baulch, R. A. Cox, R. F. Hampson, Jr., J. A. Kerr, J. Troe and R. T. Watson, *J. Phys. Chem. Ref. Data*, *9* (1982) 277.
21 P. D. Taylor, R. T. Tuckerman and E. Whittle, *J. Photochem.*, *19* (1982) 277.
22 D. G. Ralph and R. P. Wayne, *J. Chem. Soc., Faraday Trans. II*, *78* (1982) 1815.
23 D. L. Baulch, R. A. Cox, P. J. Crutzen, R. F. Hampson, Jr., J. A. Kerr, J. Troe and R. T. Watson, *J. Phys. Chem. Ref. Data*, *11* (1982) 454.
    C. C. Chou, H. Vera-Ruiz, G. Crescentini, F. S. Rowland and W. S. Smith, *Proc. 173rd American Chemical Society National Meeting, New Orleans, March, 1977*, American Chemical Society, Washington, DC.
24 G. L. Workman and A. B. F. Duncan, *J. Chem. Phys.*, *52* (1970) 3204.
25 R. A. Fass and J. E. Willard, *J. Chem. Phys.*, *52* (1970) 1874.
26 K. C. Ferguson and E. Whittle, *J. Chem. Soc., Faraday Trans. I*, *68* (1972) 295, 641.
27 J. P. Simons and A. J. Yarwood, *Nature (London)*, *192* (1961) 943.

Note added in proof. Two reports have recently appeared regarding the existence of $CF_3\dot{O}$: L. Andrews, M. Hawkins and R. Withnall, *Inorg. Chem.*, *24* (1985) 4234; K. C. Clemitshaw and J. R. Sodeau, *Conf. Proc. of 5th Int. Meet. on Spectroscopy of Matrix-isolated Species, Fontevraud, 1985*.