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The quantum-yield of formation of CF_2O in the gas-phase photo-oxidation of CF_3I at 253.7 nm

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Abstract

The quantum-yield of formation of CF_2O in the gas-phase photo-oxidation of CF_3I at 253.7 nm, $\Phi^{253.7}_{CF_2O}$, has been measured for the first time. The value obtained, 1.05 ± 0.11 ($\pm\sigma$), was determined using Fourier transform infrared (FTIR) spectroscopy. CF_2O concentrations were measured by performing a Beer's Law analysis on the P and R branches of the ν_2 absorption of CF_2O at 1956.1 and 1943.1 cm^{-1}, respectively. Actinometry at 253.7 nm was carried out using the trifluoroaceticanhydride, $(CF_3CO)_2O$, (TFAA) system recommended previously (G.A. Chamberlain and E. Whittle, *J. Chem. Soc. Faraday Trans. I, 71* (1975) 1978), and was based on comparison of the intensities of eight P and R vibration–rotation lines of the CO photoproduct with those of CO recorded for calibration mixtures composed of CO and TFAA. A quantum-yield of I_2 formation of 0.47 ± 0.04 was also measured by optical absorption techniques. It is suggested that CF_2O and I_2 are formed via the decomposition of CF_3OOI, trifluoromethylperoxyhypoiodite. This species is produced in the reaction of $CF_3O_2^{\bullet}$ radicals with atomic I, which acts as a chaperone for the observed chemistry.

Keywords: Photo-oxidation; FTIR spectroscopy

1. Introduction

Understanding the mechanism of the oxidation of $CF_3^{\bullet}$ radicals to carbonyl fluoride, CF_2O, has assumed greater importance since recent recognition [1] that $CF_3^{\bullet}$ radicals are probable intermediates in the tropospheric degradation of the substitute CFC compounds CF_3CCl_2H (HCFC-123), CF_3CClFH (HCFC-124), CF_3CF_2H (HFC-125), and CF_3CFH_2 (HFC-134a). It is now well established from several kinetic and spectroscopic studies [1] that under such conditions, $CF_3^{\bullet}$ radical oxidation will be initiated by rapid association with molecular O_2 to form $CF_3O_2^{\bullet}$ radicals:

$$CF_3^{\bullet} + O_2 + M \longrightarrow CF_3O_2^{\bullet} + M$$

where M is a third body. $CF_3O_2^{\bullet}$ may then react in the troposphere with NO to produce $CF_3O^{\bullet}$ radicals directly [2]:

$$CF_3O_2^{\bullet} + NO \longrightarrow CF_3O^{\bullet} + NO_2$$

or with $H_2O^{\bullet}$ radicals to form $CF_3O^{\bullet}$ via the photolytic decomposition of CF_3OOH [1]:

$$CF_3O_2^{\bullet} + HO_2^{\bullet} + M \longrightarrow CF_3OOH + O_2 + M$$

$$CF_3OOH + h\nu \longrightarrow CF_3O^{\bullet} + {}^{\bullet}OH$$

The reaction of $CF_3O_2^{\bullet}$ with the dominant tropospheric oxide of nitrogen, NO_2, is reversible and therefore does not lead to $CF_3O^{\bullet}$:

$$CF_3O_2^{\bullet} + NO_2 + M \longrightarrow CF_3OONO_2 + M$$

$$CF_3OONO_2 + M \longrightarrow CF_3O_2^{\bullet} + NO_2 + M$$

Experimental evidence from laboratory studies of the oxidation of $CF_3^{\bullet}$ radicals in the absence of NO, NO_2 and $HO_2^{\bullet}$ [3], suggests that, although probably of minor importance in the troposphere, $CF_3O_2^{\bullet}$ may also yield $CF_3O^{\bullet}$ by reaction with atomic iodine and/or photolysis:

$$CF_3O_2^{\bullet} + I + M \longrightarrow [CF_3OOI + M] \longrightarrow CF_3O^{\bullet} + IO^{\bullet} + M$$

$$CF_3O_2^{\bullet} + h\nu \longrightarrow CF_3O^{\bullet} + O$$

However, in both the laboratory studies and in the troposphere, the mechanistic pathway from $CF_3O^{\bullet}$ to CF_2O is not well understood and might involve het-

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erogeneous chemistry. F-atom elimination from $CF_3O^\cdot$ is an endothermic process [4] with a calculated [5] activation energy of 35 kcal mol^{-1}, and therefore likely to occur very slowly:

$$CF_3O^\cdot \longrightarrow CF_2O + F \quad (\Delta H_r^\circ = 23.9 \text{ kcal mol}^{-1})$$

In addition, the reactions of $CF_3O^\cdot$ with itself and with O_2 are also endothermic:

$$CF_3O^\cdot + CF_3O^\cdot \longrightarrow 2CF_2O + F_2 \quad (\Delta H_r^\circ = 9.8 \text{ kcal mol}^{-1})$$

$$CF_3O^\cdot + O_2 \longrightarrow CF_2O + FO_2^\cdot \quad (\Delta H_r^\circ = 11.1 \text{ kcal mol}^{-1})$$

By contrast, the reactions of $CF_3O^\cdot$ with atomic I and with NO_2 which either form CF_2O directly by F-atom abstraction or which proceed via CF_3OI and CF_3ONO_2, respectively, are both exothermic:

$$CF_3O^\cdot + I + M \longrightarrow [CF_3OI] \longrightarrow CF_2O + IF + M \quad (\Delta H_r^\circ = -43.5 \text{ kcal mol}^{-1})$$

$$CF_3O^\cdot + NO_2 + M \longrightarrow [CF_3ONO_2] \longrightarrow CF_2O + FNO_2 + M (\Delta H_r^\circ = -29.0 \text{ kcal mol}^{-1})$$

Note that the overall reaction of $CF_3O^\cdot$ with $HO_2^\cdot$ which probably proceeds via trifluoromethanol, CF_3OH, is potentially a highly exothermic source of CF_2O:

$$CF_3O^\cdot + HO_2^\cdot \longrightarrow [CF_3OH + O_2] \longrightarrow CF_2O + HF + O_2 (\Delta H_r^\circ = -63.9 \text{ kcal mol}^{-1})$$

as are the analogous reactions of $CF_3O^\cdot$ with CH_4 and C_2H_6 which are both suprisingly rapid [6]:

$$CF_3O^\cdot + CH_4 \longrightarrow [CF_3OH + CH_3^\cdot] \longrightarrow CF_2O + HF + CH_3^\cdot (\Delta H_r^\circ = -7.8 \text{ kcal mol}^{-1})$$

$$CF_3O^\cdot + C_2H_6 \longrightarrow [CF_3OH + C_2H_5^\cdot] \longrightarrow CF_2O + HF + C_2H_5^\cdot (\Delta H_r^\circ = -12.4 \text{ kcal mol}^{-1})$$

The overall reaction of $CF_3O_2^\cdot$ with NO which forms CF_2O and FNO_2 via CF_3ONO_2 in low-temperature matrices [7] is an exothermic pathway to CF_2O ($\Delta H_r^\circ = -52.3$ kcal mol^{-1}) that does not involve $CF_3O^\cdot$. By contrast, the gas-phase reaction between $CF_3O^\cdot_2$ and NO is believed to produce $CF_3O^\cdot$ directly [2].

Reported here is a quantitative measurement by FTIR spectroscopy of the quantum-yield of CF_2O formed upon 253.7 nm photolysis of gas-phase CF_3I/O_2 mixtures. This study complements our previous low-temperature matrix-isolation investigations in which the intermediate species involved in the reactions of $CF_3O_2^\cdot$ with NO [7] and with atomic I [3] were directly identified by FTIR spectroscopy. The quantum-yield of CF_2O formation of unity measured in this work further supports the mechanism put forward for the $CF_3I/O_2/Ar$ system [3], and is also consistent with a similarly measured value of unity for the quantum-yield of CF_2O formed upon 184.9 nm photolysis of CF_3Br/O_2 mixtures [8].

2. Experimental details

Gas mixtures were prepared on a mercury-free, pyrex-glass vacuum line fitted with greaseless taps, in blackened, 'X'-configuration pyrex cells that were equipped with pairs of KBr and Spectrosil B quartz windows. The volume and infrared and ultraviolet–visible optical path lengths of the TFAA actinometer cell were 208 cm^3 and 11.3 and 8.7 cm, respectively; those of the CF_3I/O_2 sample cell, which was internally coated with Tel-X teflon spray to prevent wall decomposition of the CF_2O photoproduct, were 189 cm^3 and 11.3 and 7.6 cm, respectively. Gas pressures were measured with an MKS Instruments model 310 Baratron capacitance manometer ($10^{-5}-1.000$ torr) and with a Wallace–Tiernan model FA141 precision dial manometer (0.0–800.0 torr). Simultaneous irradiation of the CF_3I/O_2 mixtures and the TFAA actinometer was carried out with a Philips Spectral LL low-pressure mercury lamp (Catalogue No. 92190E) fitted into a 2-port lamp housing with equal light outputs. FTIR spectra were recorded with a Digilab FTS-20V FTIR spectrometer. Each spectrum was zero-filled two fold, box-car apodised, phase corrected and computed from the co-addition of 500 scans at 0.2 cm^{-1} resolution for TFAA and TFAA/CO calibration mixtures, and from 100 scans at a resolution of 1.0 cm^{-1} for CF_3I/O_2 samples and $CF_3I/O_2/CF_2O$ calibration mixtures. Ultra-violet visible absorption spectra were recorded between 190 and 700 nm at a bandwidth of 1.0 nm using a Pye–Unicam SP8-500 spectrometer.

O_2 (Matheson, 99.999% stated purity) and CO (Chromatography Services, 99.999% stated purity) were used as received. CF_3I (Fluorochem, 97.99% stated purity) was thoroughly degassed at 77 K by a repeated freeze–pump–thaw cycle to eliminate traces of fluorine, followed by condensation onto a column of BDH type 4A molecular sieve at 77 K to remove traces of iodine. TFAA (Fluka, >99% stated purity) was degassed as above at 77 K and then at 195 K. CF_2O (Lancaster Synthesis, 98% stated purity) was transferred from its cylinder into the actinometer cell via a cold trap held at 77 K in order to minimise the introduction of CO_2 and SiF_4 which are formed by heterogeneous wall reactions. Sample assays employing FTIR or ultraviolet–visible absorption spectroscopy and mass spectrometry (Spectrum Scientific Dataquad 200 M) revealed no impurities.

3. Results and discussion

3.1. Actinometry

The output of the low-pressure mercury lamp at 253.7 nm, $I_O^{253.7}$, was measured using FTIR spectroscopy to monitor the CO product of the gas-phase photolysis of TFAA, for which the quantum-yield of formation of CO at 253.7 nm, $\Phi_{CO}^{253.7}$, has been determined at 298 K as 0.29±0.02 [9]. The use of FTIR spectroscopy allowed the same method of analysis for actinometry and for quantification of the photoproducts of the CF_3I/O_2 reactant mixtures. Mass spectrometric detection at m/e = 119 of the $[C_2F_5^{\cdot}]^+$ fragment of the C_2F_6 photoproduct of TFAA was also demonstrated but not pursued. CO and C_2F_6 are formed according to the following mechanism [9]:

$$(CF_3CO)_2O + h\nu \longrightarrow CF_3CO^{\cdot} + CF_3C(O)O^{\cdot} (\lambda = 253.7 \text{ nm})$$

$$CF_3CO^{\cdot} + M \longrightarrow CF_3^{\cdot} + CO + M$$

$$CF_3C(O)O^{\cdot} + M \longrightarrow CF_3^{\cdot} + CO_2 + M$$

$$CF_3^{\cdot} + CF_3^{\cdot} + M \longrightarrow C_2F_6 + M$$

The concentration of the CO photo-product was determined by comparison of the measured intensities of the P_7, P_8, P_9, P_{10} and R_5, R_7, R_8 and R_9 vibration–rotation lines of the 1–0 band of CO with those of CO recorded in calibration mixtures composed of CO (0.600 – 0.900 torr in 0.025 torr increments) in 65.0 torr TFAA. For example, in experiment 1 of Table 1, 65.0 torr of TFAA was photolysed at 253.7 nm for 60.0 mins. The mean value of the ratios of the intensities of the above 8 vibration–rotation lines of the CO photoproduct was closest to unity (0.99±0.005, error $=\sigma$) for the mixture containing 0.750 torr CO/65.0 torr TFAA. Therefore an estimate for the concentration or partial pressure of CO produced in experiment 1 is 0.750 torr.

The output of the low-pressure mercury lamp at 253.7 nm, $I_O^{253.7}$, was calculated from the expression:

$$I_O^{253.7} = \frac{d[CO]/dt}{\Phi_{CO}^{253.7}[1 - \exp(-\sigma.c.l.)]} \qquad \text{(i)}$$

where σ is the absorption cross-section of TFAA at 253.7 nm and 298 K (2.26×10^{-19} cm^2 mol^{-1} [9]); c is the concentration of TFAA (65.0 torr; 2.09×10^{18} mol cm^{-3} at 300 K); and l is the optical path length (8.7 cm). The fraction of 253.7 nm light absorbed by TFAA, $[1 - \exp(-\sigma.c.l.)]$, is therefore 0.989. d[CO]/dt, the rate of formation of CO, is given by:

$$\frac{d[CO]}{dt} = \frac{P_{CO}}{P} \frac{V_A}{V} \frac{T}{T_A} \frac{L}{t} \frac{1}{60} \text{mol s}^{-1} \qquad \text{(ii)}$$

where P_{CO} is the partial pressure of the CO photoproduct (0.750 torr) formed after a photolysis time, t, of 60.0 mins; T_A is ambient temperature (300 K); V_A is the volume of the actinometer cell (208 cm^3); V is the ideal gas molar volume at 273 K and 1 atmosphere (P, 760 torr), and L is Avogadro's number. d[CO]/dt is therefore equal to 1.394×10^{15} mol s^{-1}. Substituting values for $\Phi_{CO}^{253.7}$), $[1 - \exp(-\sigma.c.l.)$ and d[CO]/dt in Eq. (1) leads to a measure of the output of the low-pressure mercury lamp at 253.7 nm in experiment 1 of $(4.86 \pm 0.34) \times 10^{15}$ quanta s^{-1}. The error of 7% arises from the uncertainty in $\Phi_{CO}^{253.7}$.

3.2. Photoproducts of CF_3I/O_2

The sole infrared observable photoproduct was carbonyl fluoride, CF_2O. New absorptions in FTIR spectra of CF_3I/O_2 gas mixtures were recorded at 1956.1 and 1943.1, 1249.3, 965.8 and 774.5 cm^{-1}, which correspond to the ν_2, ν_4, ν_1 and ν_6 fundamental vibrations of CF_2O, respectively [10]. Fig. 1 shows FTIR absorption spectra between 2040–1840 cm^{-1} of a mixture of 36.0 torr

Table 1
Summary of CF_3I/O_2 reactant mixture compositions and calculated quantum-yields of formation of CF_2O, $\Phi_{CF_2O}^{253.7}$, at $T = 300$ K and at 1943.1 and 1956.1 cm^{-1}

Experiment no.	$[CF_3I]$ (torr)	$[O_2]$ (torr)	$I_o^{235.7}$ (10^{15} qs^{-1})	$I_a^{253.7}$ (10^{15} qs^{-1})	d[CF_2O]/dt (10^{-2} a.u. min^{-1})		d[CF_2O]/dt (10^{15} molec s^{-1})			$\Phi_{CF_2O}^{253.7}$
					1943.1 cm^{-1}	1956.1 cm^{-1}	1943.1 cm^{-1}	1956.1 cm^{-1}	Mean value	
1	36.0	12.0	4.86	4.80	0.797	0.860	5.21	5.25	5.23	1.09
2	36.0	12.0	4.77	4.71	0.733	0.788	4.79	4.81	4.80	1.02
3	36.0	12.0	4.37	4.32	0.728	0.790	4.76	4.82	4.79	1.11
4	36.0	12.0	4.58	4.53	0.676	0.731	4.42	4.46	4.44	0.98
5	27.0	12.0	4.69	4.53	0.718	0.763	4.69	4.63	4.66	1.03
6	18.0	12.0	4.63	4.15	0.658	0.708	4.30	4.32	4.31	1.04
7	9.0	12.0	4.72	3.21	0.552	0.562	3.37	3.43	3.40	1.06
Mean ± σ										1.05 ± 0.04

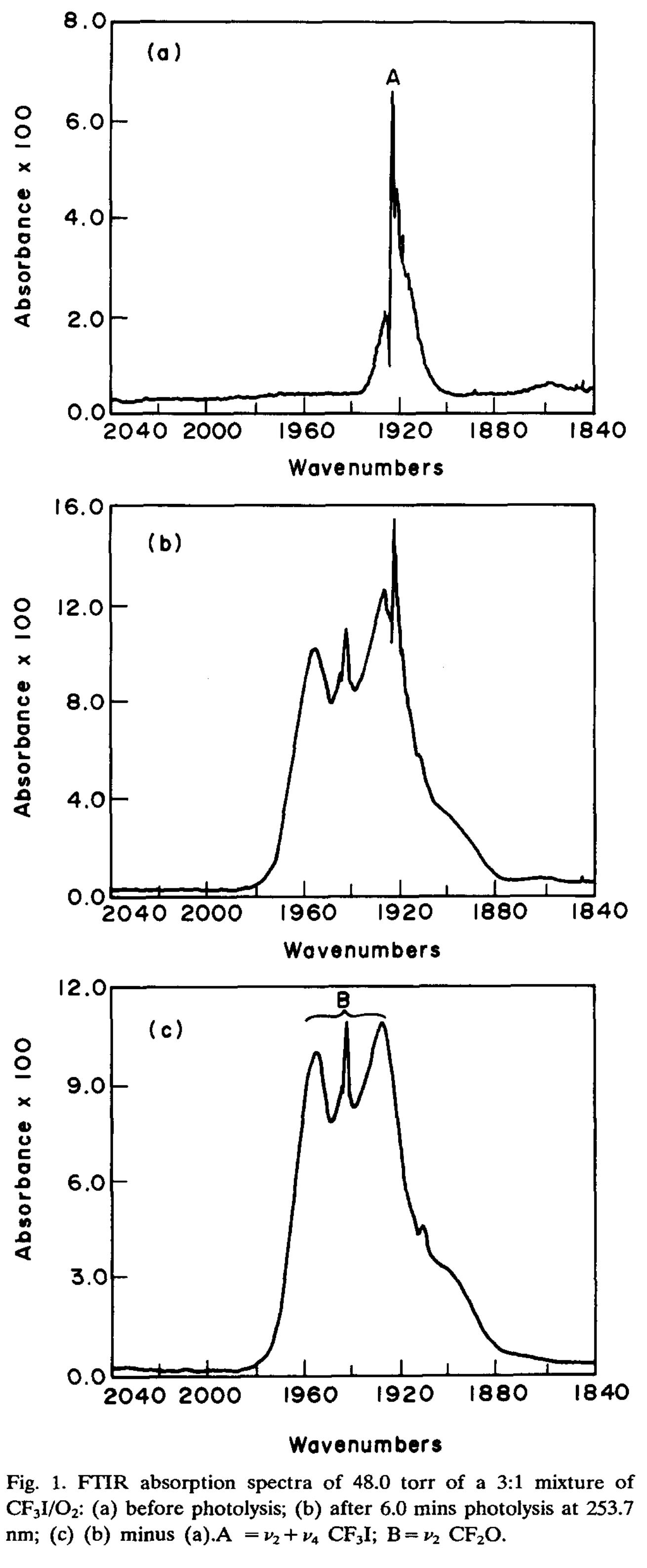


Fig. 1. FTIR absorption spectra of 48.0 torr of a 3:1 mixture of CF_3I/O_2: (a) before photolysis; (b) after 6.0 mins photolysis at 253.7 nm; (c) (b) minus (a).A $= \nu_2 + \nu_4$ CF_3I; B $= \nu_2$ CF_2O.

CF_3I/12.0 torr O_2 before and after 6.0 mins photolysis at 253.7 nm. The difference between these spectra is also shown. The rate of production of CF_2O, $d[CF_2O]/dt$, was measured in the following manner.

FTIR spectra were recorded after each of several successive low-pressure mercury lamp photolysis periods of 2.0 or 3.0 mins. The spectra resulting from the difference between the absorbance spectrum of the CF_3I/O_2 sample obtained after photolysis for a time, t, and that of the CF_3I/O_2 sample recorded prior to photolysis were plotted. The optical density of the P and R branches of the ν_2 C=O stretching mode of CF_2O at 1956.1 and 1943.1 cm^{-1} respectively were then measured as a function of photolysis time. Least-squares plots of the CF_2O absorbances at 1956.1 and 1943.1 cm^{-1} versus photolysis time were related to partial pressures of CF_2O by calibration mixtures made up of CF_2O (0.00–1.00 torr in 0.05 torr increments) in 48.0 torr of a 3:1 CF_3I/O_2 mixture. The gradient of the absorption at 1956.1 cm^{-1} was 15.5×10^{-2} absorbance units $torr^{-1}$; that at 1943.1 cm^{-1} was 16.6×10^{-2} absorbance units $torr^{-1}$.

In addition to the observation of CF_2O by FTIR spectroscopy, molecular I_2 was identified in three separate experiments as a photoproduct of CF_3I/O_2 mixtures by optical absorption techniques. Comparison of the rate of loss of CF_3I, which was monitored at 270 nm ($\sigma = 6.05 \times 10^{-19}$ cm^2 mol^{-1} [11]) with the rate of formation of I_2, monitored at 500 nm, ($\sigma = 2.18 \times 10^{-18}$ cm^2 mol^{-1} [12]) gave an estimate for the quantum-yield of formation of I_2, $\Phi_{I_2}^{253.7}$, of 0.47 ± 0.04 (error = σ). A quantum-yield of 0.5 would be consistent with the production of I_2 via recombination of atomic I:

$$2(CF_3I + h\nu \longrightarrow CF_3^{\cdot} + I) \qquad (\lambda = 253.7\ \text{nm})$$

$$I + I + M \longrightarrow I_2 + M$$

The slightly lower value of 0.47 may be partly explained by the observed absorption of I_2 on the xylene-based shellac that was used to equip the CF_3I/O_2 sample cell with optical windows.

3.3. Quantum-yield of CF_2O

Table 1 summarises the compositions of the CF_3I/O_2 sample mixtures in the seven experiments carried out, together with values of $I_0^{253.7}$ in units of quanta s^{-1} and of $d[CF_2O]/dt$ measured at 1943.1 and 1956.1 cm^{-1}, in absorbance units min^{-1}. Conversion of these units for $d[CF_2O]/dt$ to mol s^{-1} requires the appropriate gradient of the $CF_2O/CF_3I/O_2$ calibration plot, and was calculated in a manner analogous to that illustrated above for $d[CO]/dt$. The means of the two values of $d[CF_2O]/dt$ measured in each experiment were used to determine $\Phi_{CF_2O}^{253.7}$ from the expression:

$$\Phi_{CF_2O}^{253.7} = \frac{d[CF_2O]\ dt}{I_a} \qquad \text{(iii)}$$

where I_a is the light intensity absorbed by CF_3I in units of quanta s^{-1}. I_a is given by

$$I_a = I_0[1 - \exp(-\sigma.c'.l')] \qquad \text{(iv)}$$

where σ' is the absorption cross-section of CF_3I at 253.7 nm and 298 K (4.75×10^{-13} cm^2 mol^{-1} [11]), c' is the concentration of CF_3I (36.0 torr; 1.15×10^{18} mol cm^{-3} at 300 K) and l' is the optical path length (7.6 cm).

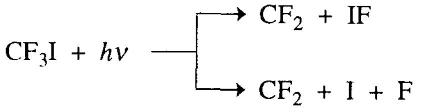
The mean value of $\Phi_{CF_2O}^{253.7}$ listed in Table 1 is 1.05 ± 0.04 (error $= \sigma$). The major sources of this error arise from: (i) changes in the alignment of the CF_3I/O_2 sample and TFAA actinometer gas cells relative to the low-pressure mercury lamp upon their replacement for photolysis after recording FTIR spectra; (ii) uncertainties in the measurement of the intensities of the vibration–rotation lines of the CO photo-product of the TFAA actinometer; (iii) uncertainties in the measurements of the absorbances of the ν_2 P and R branches of the CF_2O photo-product. These errors are random errors. The error in the published value of $\Phi_{CO}^{253.7}$, which is required for actinometry, introduces a systematic error of 7%. $\Phi_{CF_2O}^{253.7}$ is therefore revised to 1.05 ± 0.11 where the error limit encompasses both random and systematic errors.

3.4. *Mechanism of CF_2O formation*

The primary photolytic step for CF_3I is absorption involving an n–σ^* transition to a repulsive electronic state which immediately dissociates by breaking the weaker C–I bond:

$$CF_3I + h\nu \longrightarrow CF_3^{\bullet} + I \qquad (\lambda = 253.7 \text{ nm})$$

Two other primary photolytic steps that produce difluorocarbene, CF_2, and either molecular IF or atomic I and F, are also energetically possible since one photon of wavelength 253.7 nm is equivalent to 113 kcal mol^{-1}:



$$CF_3I + h\nu \longrightarrow \begin{cases} CF_2 + IF \\ CF_2 + I + F \end{cases}$$

Although CF_2 is formed by secondary photolysis of $CF_3^{\bullet}$ radicals isolated in argon matrices at 4.2 K [13], the present study confirms that in the gas-phase, $CF_3^{\bullet}$ radicals are produced exclusively upon 253.7 nm photolysis of CF_3I since there was no FTIR spectroscopic evidence for IF or for C_2F_4. This latter species would be produced from the self-reaction of ground-state $^1CF_2$, which unlike $^3CF_2$ does not readily combine with O_2 to form CF_2O at room temperature [14]. The absence of IF is not unexpected since it is unstable and disproportionates heterogeneously into I_2 and IF_3 or IF_5.

The reaction between $CF_3^{\bullet}$ radicals and O_2 is rapid and leads to the formation of CF_2O with a quantum-yield of unity. In the presence of sufficient O_2, $CF_3^{\bullet}$ radicals neither react with atomic I or molecular I_2 to reform CF_3I, nor with themselves to yield C_2F_6, since these products would both reduce $\Phi_{CF_2O}^{253.7}$. CH_3OOI has recently been detected by ultraviolet absorption spectroscopy [15]. It is formed via the reaction of $CH_3O_2^{\bullet}$ with atomic I in the gas-phase 253.7 nm photolysis of $CH_3I/O_2/N_2$ mixtures and supports our previous proposal [3] that CF_3OOI is a key intermediate in the matrix-isolated $CF_3I/O_2/Ar$ system which leads to CF_2O/IF molecular complexes via CF_3OI. However, IF was not observable in the present gas-phase CF_3I/O_2 system. It is therefore suggested that a mechanism consistent with the quantum yields of 1.05 for CF_2O and 0.47 for I_2 measured here involves CF_3OOI. This species is produced in the reaction of $CF_3O_2^{\bullet}$ radicals with atomic I, which acts as a chaperone for the observed chemistry. CF_3OOI quantitatively and rapidly decomposes to CF_2O and FOI, with the latter dissociating to yield I_2 and F_2 and O_2:

$$CF_3I + h\nu \longrightarrow CF_3^{\bullet} + I$$

$$CF_3^{\bullet} + O_2 + M \longrightarrow CF_3O_2^{\bullet} + M$$

$$CF_3O_2^{\bullet} + I + M \longrightarrow CF_3OOI + M$$

$$CF_3OOI \longrightarrow CF_2O + FOI$$

$$FOI + M \longrightarrow I + OF + M$$

$$I + I + M \longrightarrow I_2 + M$$

$$OF + OF + M \longrightarrow F_2 + O_2 + M$$

Recent ultraviolet absorption spectroscopic detection of RO_2Br species in the gas-phase [16] suggests that the mechanism of the photo-oxidation of CF_3Br, in which CF_2O is also produced with a quantum-yield of unity, may proceed via CF_3OOBr in a manner analogous to that above, rather than by successive self-reactions of $CF_3O_2^{\bullet}$ and $CF_3O^{\bullet}$ radicals [8]. In the absence of a halogen atom chaperone, it appears that $CF_3O_2^{\bullet}$ and $CF_3O^{\bullet}$ radicals may react together to form CF_3OOOCF_3 [17] which reduces the quantum-yield of CF_2O. Finally, the possibility remains that the gas-phase reaction of $CF_3O^{\bullet}_2$ with NO may proceed via CF_3OONO and its isomer, CF_3ONO_2, with NO acting in a similar manner to atomic I and Br.

4. Conclusion

The quantum-yield of formation of CF_2O in the 253.7 nm photolysis of CF_3I/O_2 gas mixtures has been determined as approximately unity by using FTIR spectroscopy to measure CF_2O concentrations and to monitor the CO photoproduct of the TFAA actinometer system employed. The value of unity is consistent with that of the quantum-yield of CF_2O formed upon 184.9 nm photolysis of CF_3Br/O_2 gas mixtures [8]. A quantum-yield of iodine formation of 0.47 was also measured by ultraviolet–visible absorption spectroscopy. It is suggested that CF_2O and I_2 are formed via the dissociation of CF_3OOI which is produced in the reaction of $CF_3O_2^{\bullet}$ with I.

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