

Atmospheric Fate Of Various Fluorocarbons

by

Yi Tang

Submitted to the Department of Chemistry  
in Partial Fulfillment of the Requirements for the  
Degree of

Master of Science  
in Atmospheric Chemistry

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## **ABSTRACT**

Twenty two fluorocarbons have been investigated in terms of their chemical reactivities with OH radicals and with O(<sup>1</sup>D) atoms; as well as their photochemical properties under UV irradiation in order to estimate their atmospheric lifetimes. A relative rate technique was developed to measure the rate coefficients of OH and O(<sup>1</sup>D) reactions with the fluorocarbons. This technique was designed to be insensitive to the presence of impurities. With this technique, the disappearance of the compound of interest, not the disappearance of the highly reactive species such as OH radicals and O(<sup>1</sup>D) atoms, was monitored by FTIR using a multiple-path cell. UV absorption cross sections were measured for some of the fluorocarbons.

All eight hydrofluorocarbons and a perfluoroalkene are found to react with OH at rates similar to those of CH<sub>4</sub> or CF<sub>3</sub>H. Only the two sulfur perfluorides among the twenty two fluorocarbons are found to be reactive to O(<sup>1</sup>D); at a rate comparable to that of CF<sub>2</sub>Cl<sub>2</sub>. Measurements of the UV absorption spectra reveal that the perfluoroamine [C<sub>4</sub>F<sub>9</sub>]<sub>3</sub>N, the perfluoroether [C<sub>4</sub>F<sub>9</sub>OC<sub>2</sub>F<sub>4</sub>O]<sub>2</sub>CF<sub>2</sub>, and the perfluorodecalin C<sub>10</sub>F<sub>18</sub> absorb UV light at wavelengths around 190 - 220 nm; the three compounds are also found to photolyze around 220 nm at a rate comparable to that of CF<sub>2</sub>Cl<sub>2</sub>. The two sulfur perfluorides and the two hydrofluoroethers are also found to photolyze at ~220 nm.

Thesis Supervisor: Dr. Mario J. Molina

Title: Professor of Atmospheric Chemistry

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## Table of Contents

Abstract.....	2
Acknowledgements.....	3
Chapter 1 Introduction.....	5
1.1 Purpose of Study.....	5
1.2 Atmospheric Chemistry of the Fluorocarbons.....	6
1.3 Fluorocarbons Investigated.....	8
1.4 Experimental Method.....	15
Chapter 2 Experimental.....	18
2.1 Apparatus.....	18
2.2 Reference Compounds.....	21
2.3 Estimation of Experimental Conditions.....	22
2.4 Experimental Conditions and Procedures.....	25
Chapter 3 Results and Discussion.....	27
3.1 Data Analysis.....	27
3.1.1 Derivation of Rate Coefficients.....	27
3.1.2 Error Analysis.....	29
3.1.3 Estimation of Atmospheric Lifetimes.....	31
3.2 OH Reaction Studies.....	32
3.2.1 OH Reactions with CH <sub>4</sub> as Reference Compound.....	32
3.2.2 OH Reactions With CF <sub>3</sub> H As Reference Compound.....	37
3.3 UV Absorption Studies.....	43
3.4 O( <sup>1</sup> D) Reaction Studies.....	50
Chapter 4 Summary and Conclusions.....	54
Appendix A. Mechanism For the O( <sup>1</sup> D) + CF <sub>2</sub> Cl <sub>2</sub> Reaction System.....	60
Appendix B. Mechanism For the OH + CH <sub>4</sub> Reaction System.....	61
Appendix C. Mechanism For the OH + CF <sub>3</sub> H Reaction System.....	62
Appendix D. A Typical Result of the Simulation by ACUCHEM for the OH + CF <sub>3</sub> H System.....	63
Appendix E. Calculation of the Photolysis Rate of Ozone.....	64
Reference.....	69

# Chapter 1

## Introduction

### 1.1 Purpose of Study

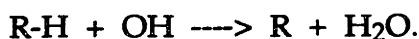
The Molina and Rowland theory states that the release of the man-made Chlorofluorocarbons ( CFCs ) may result in the depletion of ozone in the stratosphere [Molina and Rowland, 1974]. Since CFCs are chemically inert in the atmosphere, when they are transported into the stratosphere, the photolysis of the CFCs releases chlorine atoms, which can catalytically destroy ozone in the stratosphere. This theory is widely accepted not only because of the sound physical and chemical bases on which it is founded, but also because of the recorded loss of ozone at high altitudes since 1970s [Watson et al, 1988] and the appearance of the Antarctic ozone hole [Solomon, 1989]. In addition to destroying ozone, CFCs also accumulate in the atmosphere and contribute to the greenhouse [Mitchell, 1989; and Ramanathan et al, 1985] effect because they are chemically inert in the atmosphere and have strong IR absorption bands where CO<sub>2</sub> is transparent. Because of the ozone depletion concern, the production of CFCs is restricted by an international agreement, the Montreal Protocol on Substances that Destroy Stratospheric Ozone [United Nations Environmental Programme, 1987]. Consequently, substitutes for CFCs are being developed. Some of the potential substitutes for CFCs are the fluorocarbons ( FCs ) that contain no chlorine atoms. The absence of chlorine in the FCs makes their ozone depletion potential negligible. However, they can still contribute to the greenhouse effect if they have a long atmospheric lifetime. Therefore, it is necessary to know their atmospheric lifetime in order to permit calculations of the greenhouse warming potentials

for FCs. This research was carried out to obtain information on chemical properties of twenty two fluorocarbons through laboratory studies in order to estimate the atmospheric lifetimes of these fluorocarbons and to provide a chemical basis for further studies on their greenhouse potentials.

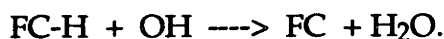
## 1.2 Atmospheric Chemistry of the Fluorocarbons

The atmospheric lifetime of a fluorocarbon is primarily determined by its chemical properties such as solubility in water, reactivity with hydroxyl radicals ( OH ), absorption cross sections in the UV, and reactivity with electronically excited oxygen atoms ( O(<sup>1</sup>D) ). Solubility in water determines whether a compound will be efficiently removed from the atmosphere by rainout or washout. Since all the fluorocarbons in the present study are practically insoluble in water as indicated in the Table 1, rainout or washout will not be a significant removal process for these fluorocarbons. Hence the study was focused on the investigation of other chemical properties.

Homogenous gas-phase reaction with OH radicals is the most efficient destruction process in the troposphere for the water-insoluble organic compounds containing carbon-hydrogen bonds. For alkanes, the reaction proceeds usually via hydrogen abstraction [ Atkinson et al, 1979 ]:



Similarly, the fluoroalkanes that containing C-H bonds also react with OH radicals via hydrogen abstraction:

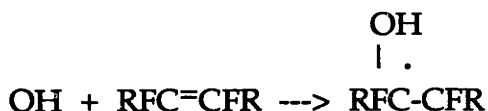


Fluorine-atom substitution tends to increase the carbon-hydrogen bond strength [Atkinson et al, 1979 ] in comparison with the alkanes. Thus, the room temperature rate coefficients of OH reactions with hydrofluorocarbons

are typically smaller than those of the corresponding hydrocarbons. Since halogen abstraction is endothermic, fully fluorinated alkanes are expected to be essentially non-reactive to the OH radicals.

Aside from fluoroalkanes, fluorocarbons under the present study also include a fluoroalkene, fluoroamines, fluoroethers, fluoromorpholines, fluorocycloalkanes, and sulfur fluorides.

For fluoroalkenes, it has been shown [Atkinson et al, 1979 ] that the electron-deficient OH radical adds to the carbon-carbon double bond to form a radical adduct:



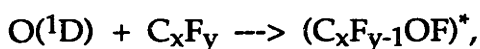
At the low pressure ( $\ll 1$  torr) characteristic of some experimental techniques, this energized adduct may decompose back to reactants. However, at higher pressure such as atmospheric pressure, the adduct is stabilized by collision with another molecule. Possible subsequent reactions of the adduct are decomposition, isomerization and reaction with  $\text{O}_2$ . Elimination of an F-atom from the adduct is endothermic; hence the addition of OH to the double bond is the major route for the reaction of OH with the fluoroalkenes.

For the perfluorocarbons containing oxygen atoms or nitrogen atoms there is virtually no information about their reactivity with OH radicals. For the perfluorocycloalkanes, it is unknown whether the OH radicals react with them by addition or by attacking the carbon-carbon bond to open the fluorinated ring.

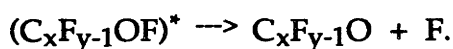
If a fluorocarbon appears non-reactive towards OH radicals, they will not be removed from the troposphere by the reaction with OH. They will then slowly diffuse into the stratosphere, where reaction with  $\text{O}(^1\text{D})$  atoms or

photolysis around 200 nm may become its dominant degradation process. Since many of the perfluorocarbons in this study turned out to be non-reactive towards OH radicals, reactions with O(<sup>1</sup>D) atoms or photolysis may play a more important role in determining their atmospheric fate.

The interaction between O(<sup>1</sup>D) and a fluorocarbon can lead to the chemical removal of the fluorocarbon, or result in quenching the O(<sup>1</sup>D) to O(<sup>3</sup>P) leaving the fluorocarbon reactant intact. The possible mechanism for the chemical removal of a fluorocarbon [Force and Wiesenfeld, 1981, and McElroy et al, 1979] might involve initial insertion of O(<sup>1</sup>D):



followed by dissociation of the excited intermediate, most probably by



In conclusion, in order to estimate the atmospheric lifetime or provide a chemical basis for more quantitative calculation of the lifetime or the greenhouse warming potentials for the fluorocarbons, it is necessary to measure the rate coefficients for the reactions of OH radicals with the fluorocarbons. If the rate coefficient of a fluorocarbon is too small for the reaction with OH radicals to be a significant removal pathway for the fluorocarbon, there is then a need to measure the rate coefficient of the reaction with O(<sup>1</sup>D) atoms and/or the UV absorption cross sections.

### 1.3 Fluorocarbons Investigated

Twenty two fluorocarbons were investigated in the present study; they are listed in Table 1, the list includes eight hydrofluorocarbons, one perfluoroalkene, three perfluoroalkanes, one perfluorocycloalkane, three



**Table 1. Fluorocarbons employed in this study and their physical properties.**

Name	Formula	S <sup>a</sup>	B.P. <sup>b</sup> (C°)	V.P. <sup>c</sup> (torr)	V.D <sup>d</sup>
1,1,1,2,2,3,3- heptafluoroheptane	C <sub>3</sub> F <sub>7</sub> C <sub>4</sub> H <sub>9</sub>	Nil <sup>e</sup>	86	ND <sup>f</sup>	>1
1-hydroperfluoroheptane	C <sub>7</sub> F <sub>15</sub> H	Nil	95	ND	>1
tetrafluorocyclobutane	C <sub>4</sub> F <sub>4</sub> H <sub>4</sub>	Nil	~50	233	4.6
hydrofluoroether 1	C <sub>8</sub> F <sub>17</sub> OC <sub>2</sub> F <sub>4</sub> H	Nil	148	5	ND
hydrofluoroether 2	C <sub>6</sub> F <sub>13</sub> OC <sub>2</sub> F <sub>4</sub> OCF <sub>2</sub> H	Nil	131	ND	ND
hydrofluoroether 3	C <sub>4</sub> F <sub>9</sub> OC <sub>2</sub> F <sub>4</sub> OCF <sub>2</sub> H	Nil	85	ND	ND
hydrofluoroether 4	C <sub>4</sub> F <sub>9</sub> OCFHCF <sub>3</sub>	Nil	65	ND	>1
perfluoromorpholinoethyl hydride	[OC <sub>4</sub> F <sub>8</sub> N]C <sub>2</sub> F <sub>4</sub> H	Nil	ND	ND	ND

**Table 1 Continued.**

Name	Formula	S <sup>a</sup>	B.P. <sup>b</sup> (C°)	V.P. <sup>c</sup> (torr)	V.D. <sup>d</sup>
4-trifluoromethyl-2-perfluoropentene	[CF <sub>3</sub> ] <sub>2</sub> CF=CFCF <sub>3</sub>	Nil	47	ND	>1
perfluorobutane	C <sub>4</sub> F <sub>10</sub>	Nil	2	1980	~8.4
perfluoropentane	C <sub>5</sub> F <sub>12</sub>	Nil	28-38	610	10
perfluorohexane	C <sub>6</sub> F <sub>14</sub>	Nil	56	232	11.7
perfluorodecalin	C <sub>10</sub> F <sub>18</sub>	Nil	142	ND	>1
perfluoroether	[C <sub>4</sub> F <sub>9</sub> OC <sub>2</sub> F <sub>4</sub> O] <sub>2</sub> CF <sub>2</sub>	Nil	180	ND	ND
perfluoro (2-butyltetrahydrofuran)	C <sub>4</sub> F <sub>9</sub> [C <sub>4</sub> F <sub>7</sub> O]	Nil	97	42	~14
mixture of perfluoroethers <sup>g</sup>	CF <sub>3</sub> O[CF(CF <sub>3</sub> )CF <sub>2</sub> O] <sub>n</sub> [CF <sub>2</sub> O] <sub>m</sub> CF <sub>3</sub>	Nil	90	68	>1

**Table 1 Continued.**

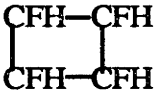
Name	Formula	S <sup>a</sup>	B.P. <sup>b</sup> (C°)	V.P. <sup>c</sup> (torr)	V.D <sup>d</sup>
perfluorodipropyl- sulfurtetrafluoride	C <sub>3</sub> F <sub>7</sub> SF <sub>4</sub> C <sub>3</sub> F <sub>7</sub>	Nil	118	ND	ND
perfluorohexyl- sulfurpentafluoride	C <sub>6</sub> F <sub>13</sub> SF <sub>5</sub>	Nil	118	ND	ND
trifluoromethyl- sulfurpentafluoride	CF <sub>3</sub> SF <sub>5</sub>	Nil	<21	ND	6.8
perfluorotributylamine	[C <sub>4</sub> F <sub>9</sub> ] <sub>3</sub> N	Nil	174	~1.3	23.3
perfluorotriethylamine	[C <sub>2</sub> F <sub>5</sub> ] <sub>3</sub> N	Nil	70	ND	>1
perfluoro-N- methyldmorpholine	[OC <sub>4</sub> F <sub>8</sub> N]CF <sub>3</sub>	Nil	50	274	10.3

**Table 1 Continued.**

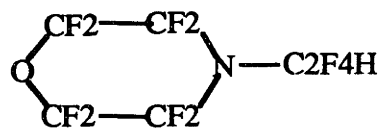
- a. S represents the solubility in water.
- b. B.P. represents boiling point.
- c. V.P. represents vapor pressure at room temperature.
- d. V.D. represents vapor density ( air =1 ).
- e. Nil represents insoluble in water.
- f. ND represents not detected.
- g. A mixture of at least four separate compounds all of which are perfluoroethers; the individual structures are not known but are of the general form  $\text{CF}_3\text{O}[\text{CF}(\text{CF}_3)\text{CF}_2\text{O}]_n[\text{CF}_2\text{O}]_m\text{CF}_3$ .

perfluoroethers, three sulfur perfluorides, two perfluoroamines, and one perfluoromorpholine.

Among the eight hydrofluorocarbons are two hydrofluoroalkanes: 1,1,1,2,2,3,3 - heptafluoroheptane (  $C_3F_7C_4H_9$  ), and 1-hydroperfluoroheptane (  $C_7F_{15}H$  ).  $C_3F_7C_4H_9$  has six secondary and three primary C-H bonds, hence one would expect that its reaction with OH radicals to be the fastest among the hydrofluorocarbons.

The other hydrofluoroalkane is tetrafluorocyclobutane:  (  $C_4F_4H_4$  ), which has four C-H bonds. Hence its reaction with OH radicals is also expected to be fast.

The other five hydrofluorocarbons contain only one C-H bond. They are four hydrofluoroethers:  $C_8F_{17}OC_2F_4H$ ,  $C_6F_{13}OC_2F_4OCF_2H$ ,  $C_4F_9OC_2F_4OCF_2H$ ,  $C_4F_9OCFHCF_3$  and one hydrofluoromorpholine:

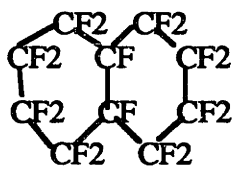


(  $[OC_4F_8N]C_2F_4H$  ). Since they all contain one abstractable hydrogen atom, they should be reactive towards OH radicals.

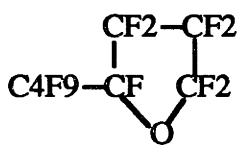
Only one perfluoroalkene has been investigated in this research. It is the dimer of hexafluoropropene, and can be named as 4-trifluoromethyl-2-perfluoropentene (  $[CF_3]_2CFCF=CFCF_3$  ). As previously mentioned, it may react with OH radicals via the addition of OH to the C=C double bond.

There are three perfluoroalkanes among the fourteen perfluorocarbons. They are perfluorobutane (  $C_4F_{10}$  ), perfluoropentane (  $C_5F_{12}$  ), and perfluorohexane (  $C_6F_{14}$  ). Since all the hydrogen atoms are substituted by the fluorine atoms, they are, as discussed previously, expected to be essentially non-reactive towards OH radicals.

There is one perfluorocycloalkane, perfluorodecalin with a molecular

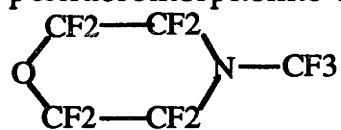
structure:  . It was unknown a priori whether OH radicals react with the compound by attacking the C-C bond to open the ring.

Among the nine perfluorocarbons that contain oxygen atoms or nitrogen atoms or both are three perfluoroethers:  $[C_4F_9OC_2F_4O]_2CF_2$ ,

perfluoro(2-butyltetrahydrofuran) with the structure of  , and a mixture of at least four perfluoroethers, of which the individual structures are unknown, but are of the general form  $CF_3O[CF(CF_3)CF_2O]_n[CF_2O]_mCF_3$ .

The three sulfur perfluorides are perfluorodipropyl-sulfur tetrafluoride ( $C_3F_7SF_4C_3F_7$ ), perfluorohexyl-sulfur pentafluoride ( $C_6F_{13}SF_5$ ), and trifluoromethyl-sulfur pentafluoride ( $CF_3SF_5$ ).

The two perfluoroamines are perfluorotriethylamine ( $[C_4F_9]_3N$ ), and perfluorotriethylamine ( $[C_2F_5]_3N$ ).

The only perfluoromorpholine is perfluoro-N-methylmorpholine with the structure of  .

There have been no previous published studies to measure the reactivity with OH radicals, reactivity with  $O(^1D)$  atoms, or the UV absorption spectrum for the perfluorocarbons that contain nitrogen, oxygen, or sulfur atoms, such as perfluoroethers, perfluoroamines, and perfluoromorpholines. The results of this study should then provide some information on the chemical properties for these compounds.

## 1.4 Experimental Method

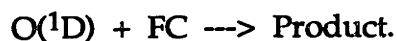
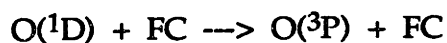
Most of the reported rate coefficients of the reactions with OH radicals or O(<sup>1</sup>D) atoms with halogenated compounds have been measured by absolute rate techniques: the decay rate of OH radicals or the decay rate of O(<sup>1</sup>D) atoms ( and O(<sup>3</sup>P) yield ) are directly monitored, and the absolute rate coefficients are deduced from these decays.

For the measurement of the rate coefficients of the reactions with OH radicals, the most widely used absolute rate techniques are fast flow, and flash photolysis resonance fluorescence [ for example: Talukdar et al, 1991; Gierczak et al, 1991; Liu et al, 1990; Jeong and Kaufman, 1982; Nip et al, 1979]. The kinetics for these two methods is typically pseudo-first order with the halogenated compound of interest in great excess over the OH radicals generated by flash photolysis or the reactions of precursor molecules, such as the H + NO<sub>2</sub> reaction. The decay of the OH radicals can be monitored by fluorescence, mass spectrometry, or laser magnetic resonance spectroscopy in the fast flow method; or by measuring the laser-induced fluorescence in the flash photolysis method. The rate coefficient k can then be deduced from the equation:

$$\ln\left(\frac{[\text{OH}]}{[\text{OH}]_0}\right) = -k \cdot [\text{FC}]_0 \cdot t,$$

where [FC]<sub>0</sub> is the initial concentration of the halogenated compound of interest, [OH] is the concentration of the OH radicals at time t, and [OH]<sub>0</sub> is the concentration at time t = 0.

For the measurement of the rate coefficients of the reactions with O(<sup>1</sup>D) atoms, the typical absolute technique is time-resolved atomic resonance fluorescence method [ for example, Warren et al, 1991; Shi and Barker, 1990, Force and Wiesenfeld, 1981; Fletcher and Husain, 1976 ]. In this technique, O(<sup>1</sup>D) atoms are produced by the photolysis of ozone via repetitive laser pulses at ~248 nm. The rate coefficient is determined by observing the temporal profiles of O(<sup>1</sup>D) or O(<sup>3</sup>P) using the time-resolved attenuation of atomic resonance radiation. However, there is a complication because of the physical quenching of the O(<sup>1</sup>D) atoms. The interaction between O(<sup>1</sup>D) atoms and the halogenated compound FC can either lead to chemical removal of the FC reactant, or result in quenching the O(<sup>1</sup>D) to O(<sup>3</sup>P) leaving the reactant FC intact:



Observing the temporal profile of the O(<sup>1</sup>D) or O(<sup>3</sup>P) can only yield an overall rate coefficient for the above two reactions. To determine the rate coefficient of the FC-removal reaction, the branching ratio for the different pathways has to be determined.

These absolute techniques, for measuring OH reaction rate coefficient or for measuring O(<sup>1</sup>D) reaction rate coefficient, share a common aspect: the rate coefficient is determined by following the decay rate of the highly reactive species such as OH radicals, O(<sup>1</sup>D) atoms, or the production rate of the O(<sup>3</sup>P) atoms, rather than the decay of the halogenated compound of interest. This characteristic makes all the absolute rate techniques vulnerable to interference from impurities, especially when the reaction rate coefficient to be measured is very small. The impurities compete for the OH radicals with the FC reactant and might react very much faster than the FC compound of interest. Hence a



measurement of the decays of OH, O(<sup>1</sup>D), or O(<sup>3</sup>P) concentration alone provides ambiguous results because it can be due partially or entirely to the impurities. As discussed previously, many compounds in the present study are perfluorinated and are expected to be essentially non-reactive towards , or react very slowly with OH radicals. Therefore, an absolute rate technique with high sensitivity to impurities is not suitable; and a different experimental approach has to be taken to better serve the purpose of this study.

Therefore, an experimental technique was designed to measure the rate coefficients of OH reaction and O(<sup>1</sup>D) reaction with the fluorocarbons. It enables the measurement of very slow reaction rates with OH radicals or with O(<sup>1</sup>D) atoms. It consists of measuring the disappearance of small amounts of a fluorocarbon of interest relative to the disappearance of a reference compound in these reactions. The advantage of this technique, especially when the reaction rate to be measured is very slow, is that it is insensitive to the presence of the impurities.

In addition to the insensitivity to impurities, the technique designed for this study is also easier to perform than the absolute techniques because what it measures is the concentration of very stable fluorocarbons, which can be easily monitored, rather than the highly reactive free radicals or atoms. Furthermore, since it requires only relative concentrations, rather than absolute concentrations, to be measured, better precision can be provided with this technique than with the absolute technique.

# Chapter 2

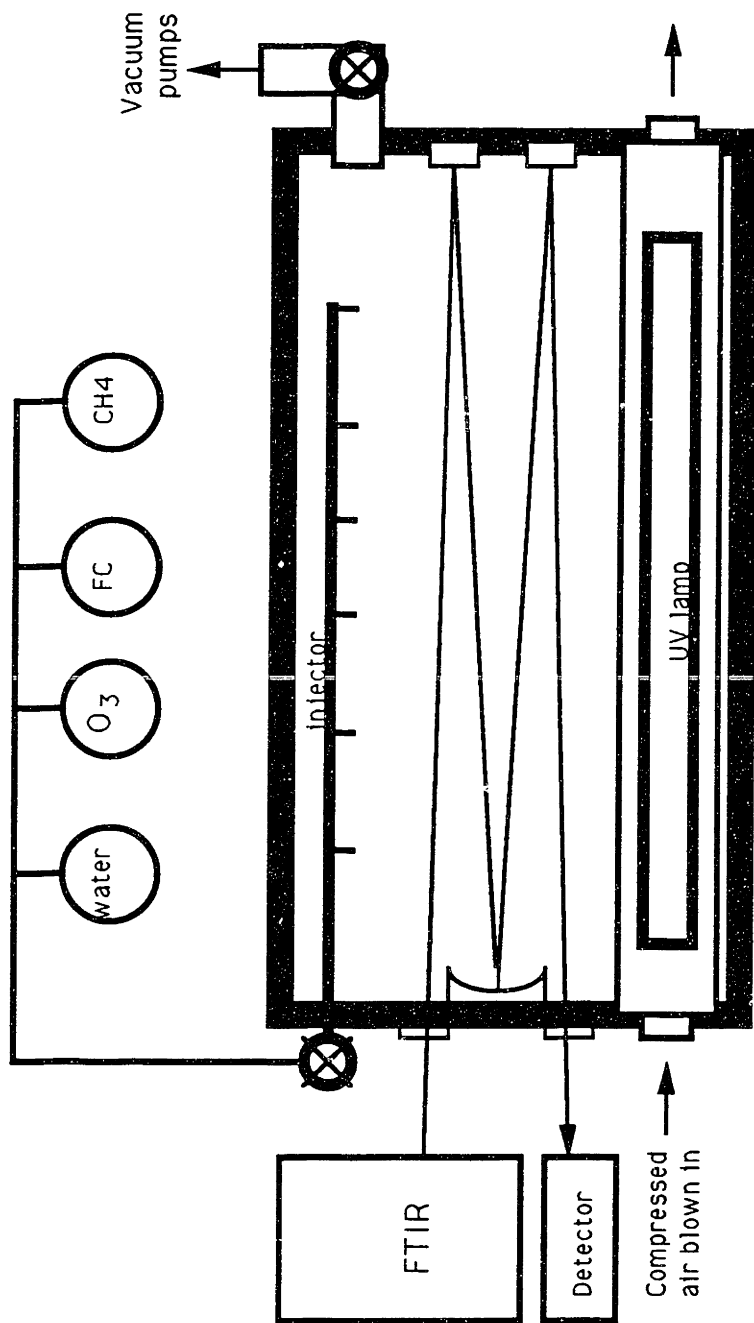
## Experimental

### 2.1 Apparatus

The apparatus used in the present study consists of a multiple-pass cell with a mercury lamp ( ACE-HANOVIA medium pressure mercury vapor lamp ) embedded inside, as shown schematically in Figure 1. The multiple-path cell has a base length of 0.6 m. The three mirrors inside the cell were adjusted for a total of 24 passes, which yielded an optical path of 14.40 m. This long effective pathlength for absorption enables the measurement of very low concentrations. The mercury lamp emits ~5.8 watts of its radiated energy at 254 nm wavelength, where ozone has highest absorption cross sections, and ~3.8 watts at 222 nm wavelength. The cell was made of Pyrex glass and has a volume of 7600 cm<sup>3</sup>. The mercury lamp was enveloped in a Vycor tubing which transmits the UV radiation from the mercury lamp at the 254 nm mercury line but absorbs the 185 nm line. Compressed air was blown through the Vycor tubing\* to cool the mercury lamp when the lamp was turned on. The concentrations were monitored by Fourier-Transform Infrared Spectroscopy ( Nicolet 20SX ). The gases were added into the cell through a multi-orificed injector which was made of Pyrex glass and laid along the length of the cell so that the injected gases can be better

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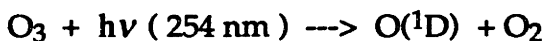
\* In the earlier stage of this study, the mercury lamp was enveloped in a quartz tubing which does transmit UV radiation at the 185 nm line; and nitrogen gas was blown through the Quartz tubing to cool the lamp. O<sup>1</sup>D reaction rate coefficients were measured with such apparatus for six fluorocarbons: perfluorobutane, perfluoropentane, perfluorohexane, perfluoro(2-butyltetrahydrofuran), perfluorotributylamine, and perfluoro-N-methylmorpholine. Later in the research when measuring the rate coefficients of the OH reactions with these fluorocarbons, the reference compound CF<sub>3</sub>H was found to photolyze in the control experiment, which resulted from the absorption of the UV radiation at ~185 nm by the CF<sub>3</sub>H. Therefore the quartz tubing was replaced with Vycor tubing.



**Figure 1. Schematic representation of the optics and gas flow system in the long path absorption cell.**

mixed in the cell. The amount of gases added was monitored with a MKS Baratron 220CA-type pressure gauge.

Photolysis of ozone at around 254 nm generated the O(<sup>1</sup>D) atoms, which in the presence of water vapor is converted to OH radicals. This is the same process that generates these very reactive species in the atmosphere:



Ozone was prepared by first trapping ozonized oxygen from an ozonizer in a silica gel trap which was cooled in an isopropanol - dry ice bath. The trapped ozone was then desorbed by vacuum pumping the silica gel trap through a liquid nitrogen cold trap. The liquidized ozone in the liquid nitrogen trap was then gradually exposed to room temperature, and was allowed to slowly evaporate into a glass reservoir with a volume of 12 liters. With this approach, a large amount of ozone can be obtained. The mole fraction of the ozone freshly produced was typically 0.9. Helium was added into the glass reservoir to bring the molar mixing ratio down to 0.3 ~ 0.4. Such mixture of ozone and helium can stay for several days with little decay of the ozone.

When measuring the rate coefficients of the reactions with OH radicals, ozone had to be injected into the cell continuously to maintain the supply of the O(<sup>1</sup>D) while the reactions were taking place. The flow rate of the ozone was controlled by a Teflon needle valve while monitoring the pressure change with time.

The fluorocarbon gases were prepared by first degassing the fluorocarbon liquid samples and then mixing the vapor of the liquid with helium to yield a molar fraction of ~1%.

For the measurement of UV absorption cross sections of the fluorocarbons, a Cary 219 UV spectrometer equipped with a quartz cell with a pathlength of 10 cm ( fitted with SUPRASIL quartz windows ) was used. The Cary 219 UV spectrometer was also used to monitor the amount of ozone being added into the cell by measuring the absorbance of ozone at 254 nm.

## 2.2 Reference Compounds

The reference compound for the OH reaction study was first chosen to be methane. The rate coefficient of the OH + CH<sub>4</sub> reaction is  $6.5 \times 10^{-15}$  cm<sup>3</sup> molec<sup>-1</sup> s<sup>-1</sup> [Vaghjani and Ravishankara, 1991]. The methane was chosen as the reference compound because its OH reaction rate is well established and is relatively slow in comparison with other hydrocarbons; yet its main sink in the atmosphere is the reaction with OH radicals. For similar reasons, CF<sub>2</sub>Cl<sub>2</sub> ( CFC-12 ) was chosen to be the reference compound for the reactions with O(<sup>1</sup>D) atoms.

The results of the OH reaction study with methane as the reference compound indicated that for most of the fluorocarbons under study, their OH reaction rates were much slower than that of methane. In contrast with an average of 15% decay of methane in the reactions with OH radicals, most fluorocarbons under study showed virtually no decay. To obtain a measurable decay of these fluorocarbons in order to give an estimate of the rate coefficients or to establish an upper limit to the rate coefficients with a better accuracy, extended reaction time and a reference compound with a slower OH reaction rate than that of methane are needed.

Since reaction with O(<sup>1</sup>D) and photolysis around 200 nm occur almost exclusively in the stratosphere, and diffusion into the stratosphere proceeds

rather slowly, the reactions with OH radicals are potentially more important in determining the atmospheric fate of a fluorocarbon. Therefore, it is necessary to use a reference compound with a slower OH reaction rate to give a better estimate of the rate coefficients or the upper limit to the rate coefficients. This reference compound was then chosen to be CF<sub>3</sub>H, whose rate coefficient of the reaction with the OH has been recently measured in A. R. Ravishankara's group. The value of the rate they reported is  $3.1 \times 10^{-16} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ , which is about 20 times slower than the corresponding reaction of methane with OH.

### 2.3 Estimation of Experimental Conditions

Estimation of the experimental conditions, such as the initial concentration of each reactant and an appropriate length of the reaction time, was carried out to provide guidance to the experiments.

Ozone is the precursor molecule of the O(<sup>1</sup>D) atom, which in turn is the precursor of the OH radical. Hence the concentration of ozone should be high enough to produce O(<sup>1</sup>D) atoms or OH radicals to react with the fluorocarbon and the reference compound. However, if ozone concentration  $C$  is too high, according to the Beer - Lambert's Law:

$$\frac{I}{I_0} = \exp(-\sigma \cdot C \cdot l)$$

the intensity  $I$  of the light transmitted could be virtually zero at a certain distance  $l$  from the lamp with the intensity of incident light  $I_0$ ; and the photolysis of ozone could not proceed to produce O(<sup>1</sup>D) in the blackout of the UV light. Suppose at least 10% of the incident light intensity at 254 nm

wavelength from the lamp be transmitted at an average distance of 6 cm from the lamp, the concentration of ozone should be less than

$$\begin{aligned} C &= \frac{1}{\sigma \cdot l} \cdot \ln\left(\frac{I}{I_0}\right) \\ &= \frac{1}{1150 \times 10^{-20} (\text{cm}^2 \cdot \text{molec}^{-1}) \cdot 6 (\text{cm})} \cdot \ln(10) \\ &= 3.3 \times 10^{-16} \text{ molecules/cm}^3 \end{aligned}$$

$$= 1 \text{ torr,}$$

where the  $\sigma = 1150 \times 10^{-20} \text{ cm}^2 \text{ molec}^{-1}$  is the absorption cross section of ozone at 254 nm wavelength.

Since the concentration of ozone has an upper limit, the initial concentration of the fluorocarbon or the reference compound is also limited; otherwise, the amount of decay of the fluorocarbon or the reference compound would be too small, which would yield a poor accuracy in the estimate of the relative rate coefficient. On the other hand, the concentration of the fluorocarbon or the reference compound is also limited by the detection limit of the FTIR - multipath cell. With a total of 14.40 m of effective pathlength for absorption, the detection limit can be as low as 0.5 millitorr for the reference compounds  $\text{CF}_3\text{H}$  and  $\text{CF}_2\text{Cl}_2$ , and 2.0 millitorr for  $\text{CH}_4$ . The detection limits are different for different compounds because they have different IR band strength.

To determine a reasonable range of the initial concentrations of the fluorocarbons and the reference compounds, a computer program of chemical kinetics simulation, ACUCHEM, was used to simulate the complex chemical

reaction system. The goal of the simulation is to find an appropriate concentration range for the reference compound, ozone and water vapor, so that a 20 - 30% decay of the reference compound can be achieved within a reasonable length of time. The kinetics mechanisms used in the ACUCHEM for  $\text{CH}_4$ ,  $\text{CF}_3\text{H}$ , and  $\text{CF}_2\text{Cl}_2$  are summarized in Appendix A, B, and C respectively. A typical result of the simulation for OH reaction system is shown in Appendix D. The photolysis rate of ozone used in the mechanisms was calculated based on the power of the mercury lamp and the geometry of the lamp in the multipath cell. The calculation and the estimated photolysis rate of ozone are shown in Appendix E.

The results of the simulation suggest that with an initial concentration of 1 torr  $\text{O}_3$  and less than  $\sim 20$  millitorr of  $\text{CF}_2\text{Cl}_2$ , a  $\sim 20\%$  decay of the  $\text{CF}_2\text{Cl}_2$  occurs after  $\text{CF}_2\text{Cl}_2$  reacts with  $\text{O}(^1\text{D})$  atoms for  $\sim 3$  minutes, with  $\text{O}_3$  injected into the reaction system continuously in a rate  $\sim 0.5$  torr per minute.

In the OH reactions, high concentration of water vapor should be used to ensure that most of  $\text{O}(^1\text{D})$  atoms react with  $\text{H}_2\text{O}$  molecules to produce OH radicals rather than react with ozone or be deactivated. The results of the simulation show that with 1 torr or higher concentration of  $\text{H}_2\text{O}$ , more than 95% of the  $\text{O}(^1\text{D})$  atoms should react with  $\text{H}_2\text{O}$ . Since the saturation vapor pressure of  $\text{H}_2\text{O}$  at room temperature is  $\sim 25$  torr, to avoid condensation of  $\text{H}_2\text{O}$  on the wall of the cell, the concentration of  $\text{H}_2\text{O}$  should be much lower than 25 torr. Therefore, 1 to 10 torr should be the appropriate concentration range for  $\text{H}_2\text{O}$ .

The simulation shows that with an initial concentration of 1 torr  $\text{O}_3$ , 1 torr  $\text{H}_2\text{O}$ , and less than  $\sim 30$  millitorr of  $\text{CH}_4$ , a  $\sim 20\%$  decay of the  $\text{CH}_4$  can be obtained after  $\text{CH}_4$  reacts with OH radicals for  $\sim 3$  minutes, with  $\text{O}_3$  injected into the reaction system continuously in a rate  $\sim 0.5$  torr per minute. With



CF<sub>3</sub>H as the reference compound, the reaction time needs to be prolonged to ~ 60 minutes to achieve ~ 20% decay of 20 millitorr of CF<sub>3</sub>H, as shown in Appendix E.

## 2.4 Experimental Conditions and Procedures

The ACUCHEM simulation provided the appropriate guidance to the design of the experiment. The actual experimental measurements were very close to the model predictions.

For the measurements of the coefficients of the reactions with O(<sup>1</sup>D) atoms, 5 to 30 millitorr of a fluorocarbon of interest, ~10 millitorr of CF<sub>2</sub>Cl<sub>2</sub>, and 1 torr of O<sub>3</sub> were mixed with helium as the buffer gas at a total pressure of 200 to 700 torr in the cell. The mercury lamp was turned on to start the reaction. O<sub>3</sub> was injected at a rate of ~0.4 torr per minute while the reaction was taking place. The mercury lamp was turned off to stop the reaction after 3 to 8 minutes of reaction time.\* The IR spectra of the mixture of O<sub>3</sub> + FC + CF<sub>2</sub>Cl<sub>2</sub> + helium was recorded before and after the reaction in the 4000 - 400 cm<sup>-1</sup> range with a resolution of 0.1 cm<sup>-1</sup>. Several experiments showed that the decays of methane were independent of the total pressure within 100 - 760 torr range.

The experimental conditions for the OH reaction with CH<sub>4</sub> as the reference compound were the same as the experimental conditions for O(<sup>1</sup>D) reaction discussed above, except that the initial concentration of CH<sub>4</sub> was ~30

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\* For the six perfluorocarbons that were studied with the apparatus using quartz tubing surrounding the mercury lamp, as described in the footnote on page 18, ozone was not injected while reactions were taking place, and the reaction time was 60 seconds. After the quartz tubing was replaced with the Vycor tubing, and the nitrogen gas was replaced with the compressed air to cool the lamp, the UV light intensity was decreased because Vycor is less transparent than quartz; and air absorbs UV light. Therefore, prolonged reaction time was needed, ozone was injected to yield more decay of the compounds.

millitorr; and ~5 torr of water vapor was added into the cell before the reaction was started.

The experimental conditions for the OH reactions with CF<sub>3</sub>H as the reference compound were the same as above except that the initial concentration of CF<sub>3</sub>H was ~10 millitorr and the initial concentration of H<sub>2</sub>O was 10 torr and the reaction time was 60 minutes.

For each run, a control experiment was also carried out to determine if the decay of the fluorocarbon resulted from the reaction with O(<sup>1</sup>D) or OH radicals. The conditions for the control experiments were the same as the conditions of the corresponding experiments except that ozone was not present to produce O(<sup>1</sup>D) or OH.

All experiments were performed at room temperature (  $298 \pm 2$  K ).

# Chapter 3

## Results and Discussion

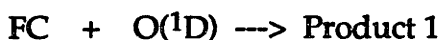
### 3.1 Data Analysis

#### 3.1.1 Derivation of Rate Coefficients

The decay of a fluorocarbon or a reference compound was determined by subtracting the reference spectrum of the fluorocarbon or the reference compound from the IR spectrum of the mixture of all the reactants before and after the reaction. The reference spectrum of a compound is the IR spectrum of the compound alone mixed with helium at the same total pressure and recorded in the same wavelength range as the IR spectrum of the mixture of all reactants. The subtraction was performed on the computer by visually removing all features of the fluorocarbon of interest from the spectrum of the mixture over the entire recording wavelength range 4000 - 400  $\text{cm}^{-1}$ . The degree of subtraction, which is called the Factor of Reference (FCR), is also the ratio of the concentration of the compound in the mixture [FC] to the concentration of the compound in the reference spectrum  $[\text{FC}]_r$ :

$$\text{FCR} = \frac{[\text{FC}]}{[\text{FC}]_r}$$

The rate coefficient of a fluorocarbon is estimated relative to the known rate coefficient of the reference compound. For example, in the following reaction:





the fluorocarbon FC and the reference compound  $\text{CF}_2\text{Cl}_2$  compete for the  $\text{O}(^1\text{D})$  atoms. The rate laws are as follows:

$$-\frac{d[\text{FC}]}{dt} = k_{\text{FC}} \cdot [\text{FC}] \cdot [\text{O}(^1\text{D})]$$

$$-\frac{d[\text{CF}_2\text{Cl}_2]}{dt} = k_{\text{ref}} \cdot [\text{CF}_2\text{Cl}_2] \cdot [\text{O}(^1\text{D})]$$

Rearranging one obtains

$$-\frac{d(\ln[\text{FC}])}{dt} = k_{\text{FC}} \cdot [\text{O}(^1\text{D})] \quad (1)$$

$$-\frac{d(\ln[\text{CF}_2\text{Cl}_2])}{dt} = k_{\text{ref}} \cdot [\text{O}(^1\text{D})] \quad (2)$$

Combining (1) and (2) to remove  $[\text{O}(^1\text{D})]$  yields

$$[\text{O}(^1\text{D})] = -\frac{1}{k_{\text{FC}}} \cdot \frac{d(\ln[\text{FC}])}{dt} = -\frac{1}{k_{\text{ref}}} \cdot \frac{d(\ln[\text{CF}_2\text{Cl}_2])}{dt} \quad (3)$$

Integrating from time  $t = 0$  when the initially concentrations are  $[\text{FC}]_0$  and  $[\text{CF}_2\text{Cl}_2]_0$  to time  $t$  when reactions are completed and the concentrations are  $[\text{FC}]$  and  $[\text{CF}_2\text{Cl}_2]$ , one obtains

$$\frac{k_{\text{FC}}}{k_{\text{ref}}} = \ln\left(\frac{[\text{FC}]}{[\text{FC}]_0}\right) / \ln\left(\frac{[\text{CF}_2\text{Cl}_2]}{[\text{CF}_2\text{Cl}_2]_0}\right) \quad (4)$$

where  $k_{FC}$  is the rate coefficient of the fluorocarbon of interest,  $k_{ref}$  is the rate coefficient of the reference compound  $CF_2Cl_2$ .

$$\text{Substituting } [FC] = FCR_{FC} \cdot [FC]_r,$$

$$[FC]_0 = FCR_{FC,0} \cdot [FC]_r,$$

$$[CF_2Cl_2] = FCR_{ref} \cdot [CF_2Cl_2]_r,$$

and  $[CF_2Cl_2]_0 = FCR_{ref,0} \cdot [CF_2Cl_2]_r$  into (4) yields

$$\frac{k_{FC}}{k_{ref}} = \ln\left(\frac{FCR_{FC}}{FCR_{FC,0}}\right) / \ln\left(\frac{FCR_{ref}}{FCR_{ref,0}}\right)$$

### 3.1.2 Error Analysis

The error of the ratio  $\frac{k_{FC}}{k_{ref}}$  can be estimated as follows.

$$\text{Let } x = \frac{k_{FC}}{k_{ref}} = \frac{\ln(y)}{\ln(z)},$$

$$\text{where } y = \frac{FCR_{FC}}{FCR_{FC,0}}, \quad z = \frac{FCR_{ref}}{FCR_{ref,0}}.$$

The error of the  $x$ ,  $\sigma_x$ , can be estimated as follows.

$$\sigma_x^2 = \sigma_y^2 \cdot \left(\frac{\partial x}{\partial y}\right)^2 + \sigma_z^2 \cdot \left(\frac{\partial x}{\partial z}\right)^2 + 2 \cdot \sigma_{yz} \cdot \left(\frac{\partial x}{\partial y}\right) \cdot \left(\frac{\partial x}{\partial z}\right)$$

Neglecting the 2nd order term,  $2 \cdot \sigma_{yz} \cdot \left(\frac{\partial x}{\partial y}\right) \cdot \left(\frac{\partial x}{\partial z}\right)$ , one obtains

$$\begin{aligned}
\sigma_x^2 &= \sigma_y^2 \cdot \left( \frac{\partial x}{\partial y} \right)^2 + \sigma_z^2 \cdot \left( \frac{\partial x}{\partial z} \right)^2 \\
&= \sigma_y^2 \cdot \left( \frac{1}{y \cdot \ln(z)} \right)^2 + \sigma_z^2 \cdot \left( -\frac{\ln(y)}{(\ln(z))^2} \cdot \frac{1}{z} \right)^2 \\
&= \frac{1}{(\ln(z))^2} \cdot \left[ \frac{\sigma_y^2}{y^2} + \frac{\sigma_z^2}{z^2} \cdot \left( \frac{\ln(y)}{\ln(z)} \right)^2 \right]
\end{aligned}$$

Therefore,

$$\sigma_x = \frac{1}{\ln(z)} \cdot \sqrt{\frac{\sigma_y^2}{y^2} + \frac{\sigma_z^2}{z^2} \cdot \left( \frac{\ln(y)}{\ln(z)} \right)^2}$$

Similarly, for  $y = \frac{\text{FCR}_{\text{FC}}}{\text{FCR}_{\text{FC},0}}$ ,  $\sigma_y^2$  can be estimated as

$$\sigma_y^2 = \sigma_{\text{FCR}}^2 \cdot \frac{1}{\text{FCR}_{\text{FC},0}^2} + \sigma_{\text{FCR},0}^2 \cdot \left( \frac{\text{FCR}_{\text{FC}}}{\text{FCR}_{\text{FC},0}} \right)^2$$

where  $\sigma_{\text{FCR}}$  and  $\sigma_{\text{FCR},0}$  are experimental errors at time  $t = 0$  and time  $t$  respectively. Normally, they equal each other,  $\sigma_{\text{FCR}} = \sigma_{\text{FCR},0}$ , and have a value of 0.02, higher when complication arises such as overlapping of the spectra of the fluorocarbon of interest and the reference compound. Therefore,

$$\sigma_y = \frac{\sigma_{\text{FCR}}}{\text{FCR}_{\text{FC},0}} \sqrt{1 + \left( \frac{\text{FCR}_{\text{FC}}}{\text{FCR}_{\text{FC},0}} \right)^2}$$

Similarly, for  $z = \frac{\text{FCR}_{\text{ref}}}{\text{FCR}_{\text{ref},0}}$ ,

$$\sigma_z = \frac{\sigma_{\text{FCR}}}{\text{FCR}_{\text{ref},0}} \sqrt{1 + \left( \frac{\text{FCR}_{\text{ref}}}{\text{FCR}_{\text{ref},0}} \right)^2}.$$

### 3.1.3 Estimation of Atmospheric Lifetimes

The atmospheric lifetime calculation requires complex atmospheric modeling. However, the lifetime of a compound with respect to a certain destruction process can be approximately estimated based on the known lifetime of another compound if its lifetime is predominantly determined by the same destruction process. The lifetime  $\tau_i$  of a compound with respect to a certain destruction process is inversely proportional to the reaction rate  $k_i$  of a certain destruction process:

$$\tau_i \propto \frac{1}{k_i},$$

$$\text{Thus, } \tau_2 = \tau_1 \cdot \frac{k_1}{k_2}.$$

For example, the well established lifetime of methane, which is about 12 years [Prinn et al, 1990], is predominantly determined by the reaction with OH radicals in the troposphere. If methane was used as the reference compound in the OH reaction with a fluorocarbon, the lifetime of this fluorocarbon with respect to the OH reaction, can be estimated by dividing the 12 years by the

measured ratio  $\frac{k_{FC}}{k_{ref}}$ . If CF<sub>3</sub>H was used as the reference compound, the lifetime with respect to OH reaction can be estimated as

$$\tau_{FC} = \frac{\tau_{CH_4} \cdot \frac{k_{FC}}{k_{ref}}}{\frac{k_{ref}}{k_{CH_4}}}$$

For hydrofluorocarbons, the lifetime with respect to OH reaction is also referred to as the tropospheric lifetime, since reaction with OH occurs predominantly in the lower atmosphere.

### 3.2 OH Reaction Studies.

For all the twenty two fluorocarbons, the rate coefficients for the reaction with OH radicals were measured. CF<sub>3</sub>H was used as the reference compound for nineteen fluorocarbons; the results are summarized in Table 3. The other three fluorocarbons: C<sub>3</sub>F<sub>7</sub>C<sub>4</sub>H<sub>9</sub>, [CF<sub>3</sub>]<sub>2</sub>CF<sub>2</sub>=CF<sub>2</sub>CF<sub>3</sub>, and tetrafluorocyclobutane ( C<sub>4</sub>F<sub>4</sub>H<sub>4</sub> ) appeared to react with OH radicals much faster than CF<sub>3</sub>H. Hence CH<sub>4</sub>, whose rate coefficient is ~20 times larger than that of CF<sub>3</sub>H, was used as the reference compound for these three fluorocarbons. The results are summarized in Table 2.

#### 3.2.1 OH Reactions with CH<sub>4</sub> as Reference Compound.

The results of the OH reaction studies, as summarized in Table 2, show that C<sub>3</sub>F<sub>7</sub>C<sub>4</sub>H<sub>9</sub>, C<sub>4</sub>F<sub>4</sub>H<sub>4</sub> , and [CF<sub>3</sub>]<sub>2</sub>CF<sub>2</sub>=CF<sub>2</sub>CF<sub>3</sub>, react with OH radicals very



**Table 2. Results of studies of OH reaction with various fluorocarbons, using CH<sub>4</sub> as the reference compound**

Fluorocarbons (FCs)	FC decay in control experiment (%)	CH <sub>4</sub> decay (%)	FC decay (%)	k <sub>FC</sub> /k <sub>CH<sub>4</sub></sub>	k <sub>FC</sub> (cm <sup>3</sup> molec <sup>-1</sup> s <sup>-1</sup> )	tropospheric lifetime (yrs)
C <sub>3</sub> F <sub>7</sub> C <sub>4</sub> H <sub>9</sub>	no decay	8.1±1.0	82.0±2.0	20.3±2.9	(1.3±0.2)×10 <sup>-13</sup>	0.6
[CF <sub>3</sub> ] <sub>2</sub> CFCF=CFCF <sub>3</sub>	no decay	12.0±1.0	77.8±2.0	11.8±1.3	(7.7±0.8)×10 <sup>-14</sup>	1.0
C <sub>4</sub> F <sub>4</sub> H <sub>4</sub>	no decay	11.3±1.0	33.9±2.0	3.45±0.41	(2.2±0.3)×10 <sup>-14</sup>	3.5

**Table 3. Results of studies of OH reaction with various fluorocarbons, using CF<sub>3</sub>H as the reference compound.**

Fluorocarbons (FCs)	FC decay in control experiment (%)	CF <sub>3</sub> H decay (%)	FC decay (%)	k <sub>FC</sub> /k <sub>CF<sub>3</sub>H</sub>	k <sub>FC</sub> (cm <sup>3</sup> molec <sup>-1</sup> s <sup>-1</sup> )	tropospheric lifetime (yrs)
C <sub>8</sub> F <sub>17</sub> OC <sub>2</sub> F <sub>4</sub> H	no decay	25.1±4.0	61.6±13.7	3.31±1.34	(1.0±0.4)×10 <sup>-15</sup>	80
C <sub>7</sub> F <sub>15</sub> H	no decay	12.8±4.0	31.9±4.0	2.8±1.0	(8.7±3.2)×10 <sup>-16</sup>	90
[OC <sub>4</sub> F <sub>8</sub> N]C <sub>2</sub> F <sub>4</sub> H	no decay	30.0±4.0	45.6±12.0	1.71±0.44	(5.3±1.4)×10 <sup>-16</sup>	150
C <sub>6</sub> F <sub>13</sub> OC <sub>2</sub> F <sub>4</sub> OCF <sub>2</sub> H	13.0±2.0	22.7±6.0	22.7±6.0	0.77±0.66	(2.4±2.0)×10 <sup>-16</sup>	>170
C <sub>4</sub> F <sub>9</sub> OC <sub>2</sub> F <sub>4</sub> OCF <sub>2</sub> H	6.3±4.0	16.9±5.0	16.9±5.0	0.85±0.60	(2.6±1.9)×10 <sup>-16</sup>	>170
C <sub>4</sub> F <sub>9</sub> OCFHCFC <sub>3</sub>	3.0±2.0	11.3±2.0	19.8±2.0	1.8±0.4	(5.7±1.2)×10 <sup>-16</sup>	140

**Table 3 continued.**

Fluorocarbons (FCs)	FC decay in control experiment (%)	CF <sub>3</sub> H decay (%)	FC decay (%)	$k_{FC}/k_{CF_3H}$	$k_{FC}$ (cm <sup>3</sup> molec <sup>-1</sup> s <sup>-1</sup> )	tropospheric lifetime (yrs)
C <sub>4</sub> F <sub>10</sub>	no decay	9.9±1.0	no decay	<0.10	<3.1x10 <sup>-17</sup>	>2000
C <sub>5</sub> F <sub>12</sub>	no decay	14.4±1.0	no decay	<0.064	<1.9x10 <sup>-17</sup>	>2000
C <sub>6</sub> F <sub>14</sub>	no decay	17.3±1.0	no decay	<0.053	<1.6x10 <sup>-17</sup>	>2000
C <sub>10</sub> F <sub>18</sub>	5.8±1.0	11.7±1.0	5.4±1.0	<0.54	<1.6x10 <sup>-16</sup>	
[C <sub>4</sub> F <sub>9</sub> OC <sub>2</sub> F <sub>4</sub> O] <sub>2</sub> CF <sub>2</sub>	20.1±2.0	16.4±2.0	9.2±2.0	<0.68	<2.1x10 <sup>-16</sup>	
C <sub>4</sub> F <sub>9</sub> [C <sub>4</sub> F <sub>7</sub> O]	no decay	11.3±1.0	no decay	<0.083	<2.5x10 <sup>-17</sup>	>2000
mixture of perfluoroethers	no decay	13.4±1.0	no decay	<0.10	<4.3x10 <sup>-17</sup>	>2000

**Table 3 continued.**

Fluorocarbons (FCs)	FC decay in control experiment (%)	CF <sub>3</sub> H decay (%)	FC decay (%)	k <sub>FC</sub> /k <sub>CF<sub>3</sub>H</sub>	k <sub>FC</sub> (cm <sup>3</sup> molec <sup>-1</sup> s <sup>-1</sup> )	tropospheric lifetime (yrs)
C <sub>3</sub> F <sub>7</sub> SF <sub>4</sub> C <sub>3</sub> F <sub>7</sub>	5.4±2.0	27.4±2.0	no decay	<0.15	<4.7x10 <sup>-17</sup>	>1500
C <sub>6</sub> F <sub>13</sub> SF <sub>5</sub>	4.9±2.0	12.0±2.0	no decay	<0.16	<5.0x10 <sup>-17</sup>	>1500
CF <sub>3</sub> SF <sub>5</sub>	no decay	10.0±2.0	no decay	<0.09	<2.8x10 <sup>-17</sup>	>2000
[C <sub>4</sub> F <sub>9</sub> ] <sub>3</sub> N	13.0±1.0	16.9±1.0	10.9±1.0	<0.79	<2.5x10 <sup>-16</sup>	>2000
[C <sub>2</sub> F <sub>5</sub> ] <sub>3</sub> N	no decay	12.8±1.0	no decay	<0.073	<2.2x10 <sup>-17</sup>	>2000
[OC <sub>4</sub> F <sub>8</sub> N]CF <sub>3</sub>	no decay	19.0±1.0	no decay	<0.047	<1.4x10 <sup>-17</sup>	>2000

rapidly. As discussed previously,  $C_3F_7C_4H_9$ , which has six secondary and three primary C-H bonds, is expected to be the fastest among the fluorocarbons under study in the reaction with OH. The rate coefficient estimated for  $C_3F_7C_4H_9$  is about 20 times larger than that of  $CH_4$ . For  $C_4F_4H_4$ , which has 4 secondary C-H bonds, its rate coefficient is estimated to be about 3 times larger than that of methane; and for the unsaturated perfluoroalkene  $[CF_3]_2CFCF=CFCF_3$  its rate coefficient is about 12 times larger than that of  $CH_4$ . Based on the lifetime of  $CH_4$ , the tropospheric lifetime estimated for these compounds are 0.6 year for  $C_3F_7C_4H_9$ , 1.0 year for  $[CF_3]_2CFCF=CFCF_3$ , and 3.5 years for  $C_4F_4H_4$ . The fact that these three fluorocarbons did not decay in their control experiments indicates that they do not absorb near UV and photolyze. Since the three compounds react with OH so rapidly and do not photolyze in the UV, the OH reaction in the troposphere will most likely be their dominant atmospheric sink, as it is for  $CH_4$ .

### 3.2.2 OH Reactions with $CF_3H$ as Reference Compound

#### Fluorocarbons Containing One C-H Bond

For the six fluorocarbons that contain one C-H bond,  $C_7F_{15}H$ ,  $C_8F_{17}OC_2F_4H$ ,  $C_6F_{13}OC_2F_4OCF_2H$ ,  $C_4F_9OC_2F_4OCF_2H$ ,  $C_4F_9OCFHCF_3$ , and  $[OC_4F_8N]C_2F_4H$ , experiments show that their reaction rates with OH are much slower than that of  $CH_4$ . No measurable decay or hardly measurable decay was observed for these compounds after three to five minutes of reaction time, in contrast to the ~15% decay of  $CH_4$ . Therefore,  $CF_3H$  was used as the reference compound and the reaction time was prolonged to 60 minutes for these

compounds. The results, as summarized in Table 3, show that all the six compounds decayed significantly after 60 minutes of reaction with OH.

The rate coefficients estimated for  $C_8F_{17}OC_2F_4H$ ,  $[OC_4F_8N]C_2F_4H$ , and  $C_7F_{15}H$  are one to three times larger than that of  $CF_3H$ . The tropospheric lifetimes of these compounds with respect to the reaction with OH are estimated as 90 years for  $C_7F_{15}H$ , 80 years for  $C_8F_{17}OC_2F_4H$ , and 150 years for  $[OC_4F_8NC]_2F_4H$ .

The two homologous hydrofluoroethers,  $C_4F_9OC_2F_4OCF_2H$  and  $C_6F_{13}OC_2F_4OCF_2H$ , reacted with OH radicals with about the same rate as that of  $CF_3H$  with OH, yielding ~20% decays. However, they also decayed ~10% in the control experiments. Therefore, part of the decay observed in the OH reaction experiments is attributed to the photolysis of these compounds in the UV. A conservative estimate of the reaction rate was made by subtracting the amount of decay in the control experiment from the lower limit of the observed decay in the OH reaction. Thus, the uncertainties of the estimates are large. Their estimated tropospheric lifetimes are at least 170 years.

A measurement for  $CF_2Cl_2$  with the same experimental conditions as those for the control experiments of the above two hydrofluoroethers was carried out. After 60 minutes of UV irradiation,  $CF_2Cl_2$  yielded ~8% decay, which is comparable in magnitude with the ~10% decay of the two hydrofluoroethers in their control experiments. Since  $CF_2Cl_2$  has a lifetime of 150 years, which is predominantly determined by the photolysis in the stratosphere, the lifetimes of these two hydrofluoroethers against photolysis in the stratosphere are also very likely at the order of 150 -300 years. Both destruction paths, reaction with OH in the troposphere and photolysis in the stratosphere, are of comparable importance in determining the atmospheric fate of the two compounds.

The hydrofluoroether  $C_4F_9OCF_2CF_3$  yielded ~20% decay in the OH reaction experiment. It also slightly decayed in the corresponding control experiment, but the magnitude of the decay was much smaller than that of the above two homologous hydrofluoroethers. The conservatively estimated rate coefficient for the OH reaction is about 2 times as large as the rate coefficient of  $CF_3H$ . Its tropospheric lifetime is estimated to be about 140 years. Since it decayed much slower in the UV than  $CF_2Cl_2$ , photolysis in the stratosphere for this compound is not likely to be a significant sink compared to the reaction with OH in the troposphere.

### **Perfluorocarbons**

The rest of the fluorocarbons for which the OH reaction rate coefficients were measured, with  $CF_3H$  as the reference compound, are perfluorocarbons. Among them only three compounds,  $[C_4F_9]_3N$ ,  $C_{10}F_{18}$ , and  $[C_4F_9OC_2F_4O]_2CF_2$ , yielded measurable decays in the OH reaction experiments. However, these three compounds decayed even more in their control experiments. Since the only reactant in the control experiments is the fluorocarbon of interest, mixed with the buffer gas helium, the decay of the fluorocarbon in the control experiment can only be attributed to photolysis in the UV. Therefore, the decays of the three perfluorocarbons in the OH reaction experiments could also result from the photolysis. The fact that the three compounds decayed less in the reactions with OH radicals than they decayed in the control experiments can be explained by the absorption of some of the UV radiation by the ozone molecules.

A very approximate calculation can be made to illustrate that the decrease of the decay can result from the reduction of the available UV light. As discussed previously in Chapter 2, the mercury lamp used in this study emits ~3.8 watts of its radiated energy at 222 nm wavelength, where the Vycor tubing is virtually transparent. The experimental conditions are the same for the OH reaction experiment and the corresponding control experiment except that the ozone is not present. Since the absorption cross sections of ozone are still fairly large around this wavelength, when ozone is present the light intensity should be significantly attenuated. The concentration of ozone C was typically maintained at 1 torr within the 60 minutes of the OH reaction experiments. The absorption cross section  $\sigma$  of ozone at 222 nm is  $228 \times 10^{-20} \text{ cm}^2 \text{ molec}^{-1}$ . At an average distance l of 6 cm from the lamp, according to Beer - Lambert's Law, the UV light intensity available for the photolysis of the fluorocarbons is reduced by

$$\begin{aligned} \frac{I_{\text{OH reaction}}}{I_{\text{control experimet}}} &= \exp(-\sigma \cdot C \cdot l) \\ &= \exp(-228 \times 10^{-20} \text{ cm}^2 \cdot \text{molec}^{-1} \cdot 0.6 \cdot 3.2 \times 10^{16} \text{ molec} \cdot \text{cm}^3 \cdot 6 \text{ cm}) \\ &= 64\% \end{aligned}$$

From the measurements of the UV absorption spectra of the three perfluorocarbons, which will be discussed later in section 3.2.3, all three compounds are found to absorb UV light at around 222 nm. Hence it is very likely that the decays of the compounds in the OH reaction experiments resulted from the photolysis at around 222 nm. Since the photolysis rate J is



proportional to the light intensity, the photolysis rates of the perfluorocarbons will also be reduced by about 64%. From the rate law

$$\frac{dC}{dt} = -J \cdot C,$$

one can obtain

$$\ln\left(\frac{C}{C_0}\right) = J \cdot t \quad \text{or} \quad \ln(1 - \text{decay}(\%)) = J \cdot t.$$

For the same length of reaction time,

$$\frac{\ln(1 - \text{decay in OH reaction})}{\ln(1 - \text{decay in control})} = \frac{J_{\text{OH reaction}}}{J_{\text{control}}} = 64\%.$$

For  $(\text{C}_4\text{F}_9)_3\text{N}$ , its decay in the control experiment was 13%. Then according to the equation of the simple estimation above, its decay in the OH reaction experiment should be 8.5% if the decay was due entirely to the photolysis at 222 nm. The observed decay in the OH reaction experiment was 10.9%, which agrees well with the estimate.

For  $[\text{C}_4\text{F}_9\text{OC}_2\text{F}_4\text{O}]_2\text{CF}_2$ , its decay in the control experiment was 20.1%. The calculated decay in the OH reaction is 13%, which also agrees well with the observed 9.2%.

Therefore, the decays of  $(\text{C}_4\text{F}_9)_3\text{N}$  and  $[\text{C}_4\text{F}_9\text{OC}_2\text{F}_4\text{O}]_2\text{CF}_2$  are most likely due entirely to the photolysis. If this is taken into account, these two compounds are, as the perfluoroalkanes, essentially non-reactive to OH radicals, and the upper limits to the reaction rate coefficients of the two

compounds are comparable to those of the perfluoroalkanes. The tropospheric lifetimes for them are also likely to be above 2000 years.

For  $C_{10}F_{18}$ , the decay in the control experiment was 5.8%. The estimated decay in the OH reaction should be 3.8%. The observed ~5.4% decay in the OH reaction experiment is very close to ( although smaller than ) the decay in the control experiment. Thus the decay of in the OH reaction experiment could be due to a combination of photolysis and reaction with OH. To determine the branching ratio, more studies are needed. But we can at least conclude that its rate coefficient of the reaction with OH is at most one half as large as that of  $CF_3H$ , and that its tropospheric lifetime is at least 500 years.

The three perfluoroalkanes,  $C_4F_{10}$ ,  $C_5F_{12}$ , and  $C_6F_{14}$ , as expected, were essentially non-reactive to OH. None of them yielded a measurable decay after 60 minutes of reaction with OH radicals, in contrast to the average of 15% of decay of the reference compound  $CF_3H$ . A upper limit to the rate coefficient of the OH reaction with each perfluoroalkane was then estimated based on the experimental errors. The estimate shows that their rate coefficients of OH reaction are at most one tenth as large as that of  $CF_3H$ , and their lifetimes with respect to the OH reaction are likely above 2000 years.

The three sulfur perfluorides,  $C_3F_7SF_4C_3F_7$ ,  $C_6F_{13}SF_5$ , and  $CF_3SF_5$ , did not decay in the reaction with OH, as was the case for the perfluoroalkanes. The estimated upper limit to their rate coefficients for the OH reaction revealed that the reaction rate coefficients of the sulfur perfluorides are at most one sixth as large as that of  $CF_3H$ . Their tropospheric lifetimes are then estimated to be above 1500 years. The difference of the upper limits to the rate coefficients and lifetimes between the sulfur perfluorides and the perfluoroalkanes is due to the observation errors in the experiments; there is

no indication that the sulfur perfluorides are more reactive towards OH than the perfluoroalkanes.

Besides  $[\text{C}_4\text{F}_9\text{OC}_2\text{F}_4\text{O}]_2\text{CF}_2$ , the other two perfluoroethers,  $\text{C}_4\text{F}_9[\text{C}_4\text{F}_7\text{O}]$  and the mixture of the perfluoroethers, did not show measurable decays in the OH reaction experiments. Considering that the decay of  $[\text{C}_4\text{F}_9\text{OC}_2\text{F}_4\text{O}]_2\text{CF}_2$  was, as discussed above, due to photolysis, one can conclude that all perfluoroethers under study are non-reactive to OH. The upper limit to their rate coefficients of OH reaction is about one tenth of the  $\text{CF}_3\text{H}$ . This means that their lifetime against OH reaction loss process are likely above 2000 years.

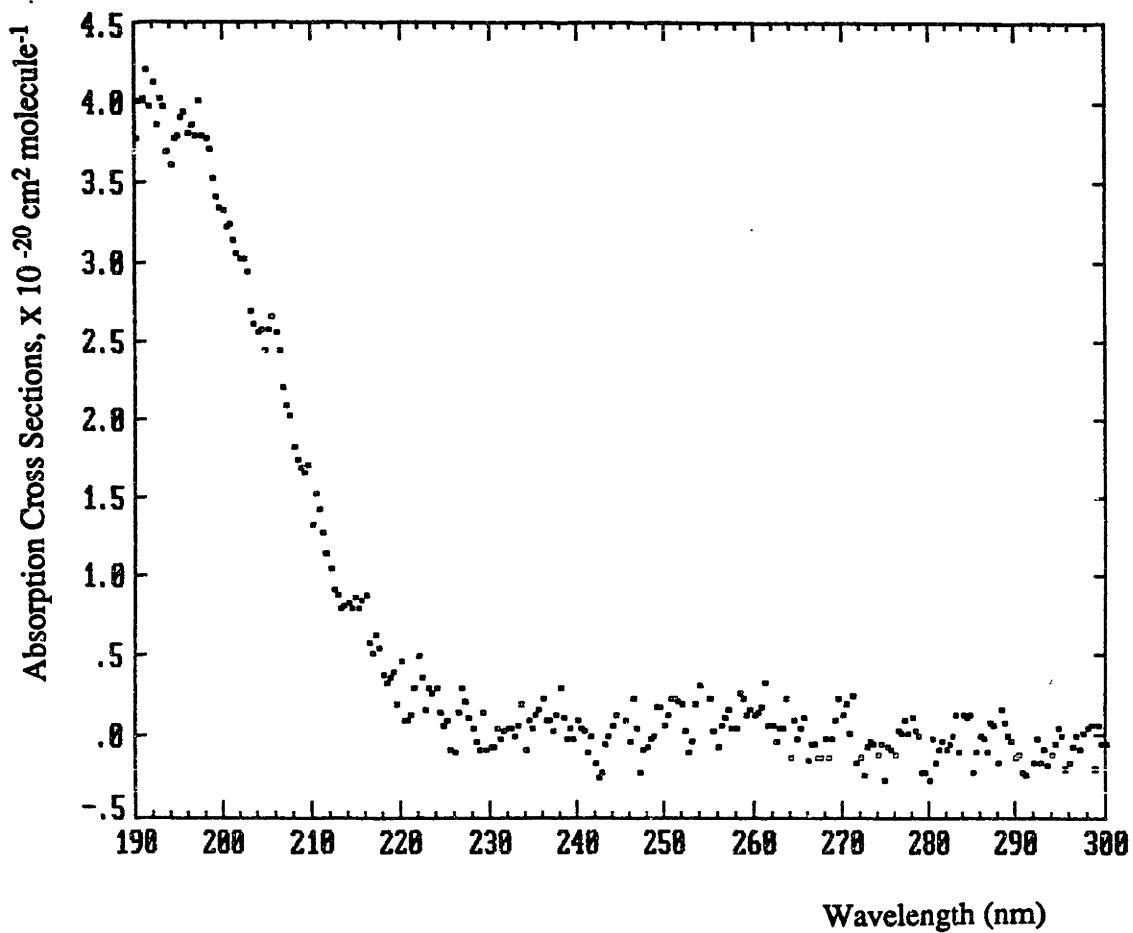
Unlike  $[\text{C}_4\text{F}_9]_3\text{N}$ ,  $[\text{C}_2\text{F}_5]_3\text{N}$  did not decay in the control experiment nor in the OH reaction experiment. Since the decay of  $[\text{C}_4\text{F}_9]_3\text{N}$  is most likely due to photolysis, the conclusion can be made that all perfluoroamines under the present study are essentially non-reactive to OH, and that their lifetimes with respect to reaction with OH are likely above 2000 years.

The perfluoromorpholine,  $[\text{OC}_4\text{F}_8\text{N}]\text{CF}_3$ , the heterocyclic perfluorocarbon containing both N and O atoms, did not decay in the OH reaction. Like perfluoroalkanes, the perfluoromorpholine  $[\text{OC}_4\text{F}_8\text{N}]\text{CF}_3$  is virtually non-reactive to OH, and its lifetime against OH reaction is likely above 2000 years.

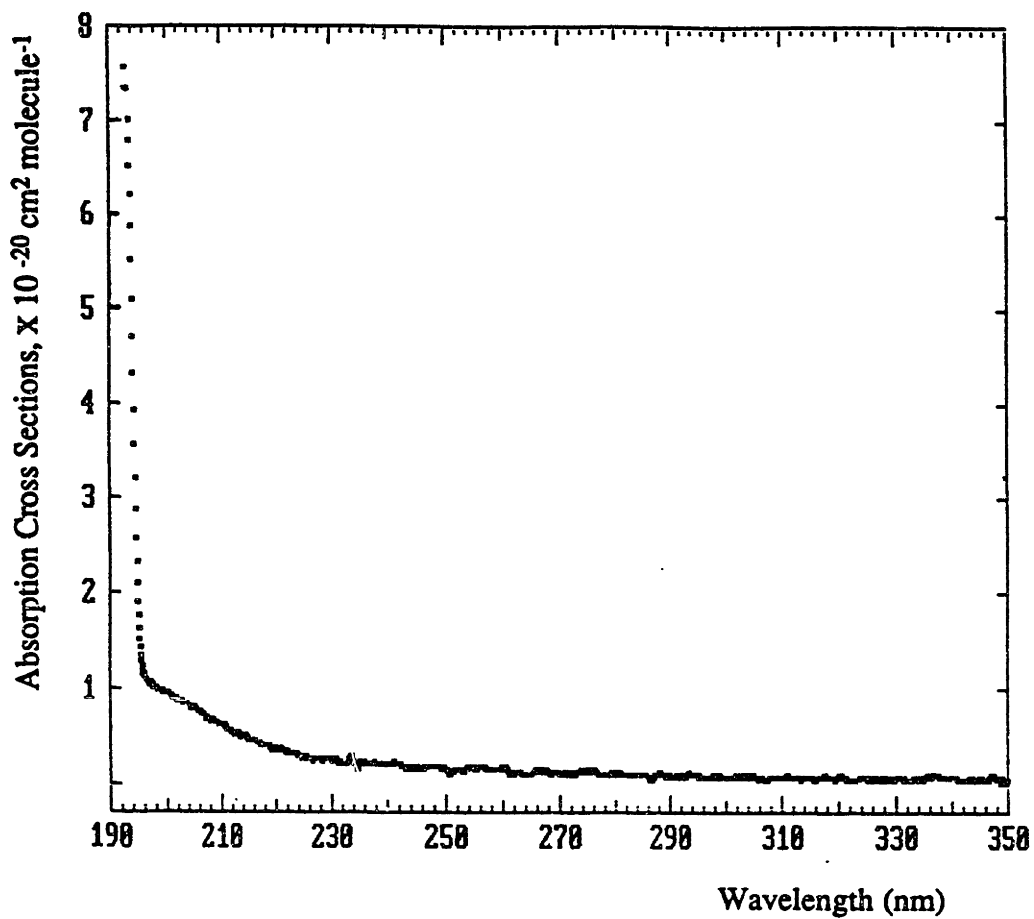
### 3.3 UV Absorption Studies

In order to further investigate the photolytic decomposition process of  $[\text{C}_4\text{F}_9]_3\text{N}$ ,  $\text{C}_{10}\text{F}_{18}$ , and  $[\text{C}_4\text{F}_9\text{OC}_2\text{F}_4\text{O}]_2\text{CF}_2$ , their UV absorption cross sections were measured at wavelengths 190 -300 nm.

The absorption spectra of  $[\text{C}_4\text{F}_9]_3\text{N}$  and  $\text{C}_{10}\text{F}_{18}$ , as shown in Figure 2 , Figure 3 and Table 5, reveals that the two compounds absorb in the 190 - 220



**Figure 2.** Absorption spectrum of the perfluorotributylamine at 298 K, measured with Cary UV spectrometer, using a pathlength of 10 cm and a pressure of 0.6 torr.



**Figure 3.** Absorption spectrum of the perfluorodecalin at 298 K, measured with Cary UV spectrometer, using a pathlength of 10 cm and a pressure of 6.0 torr.

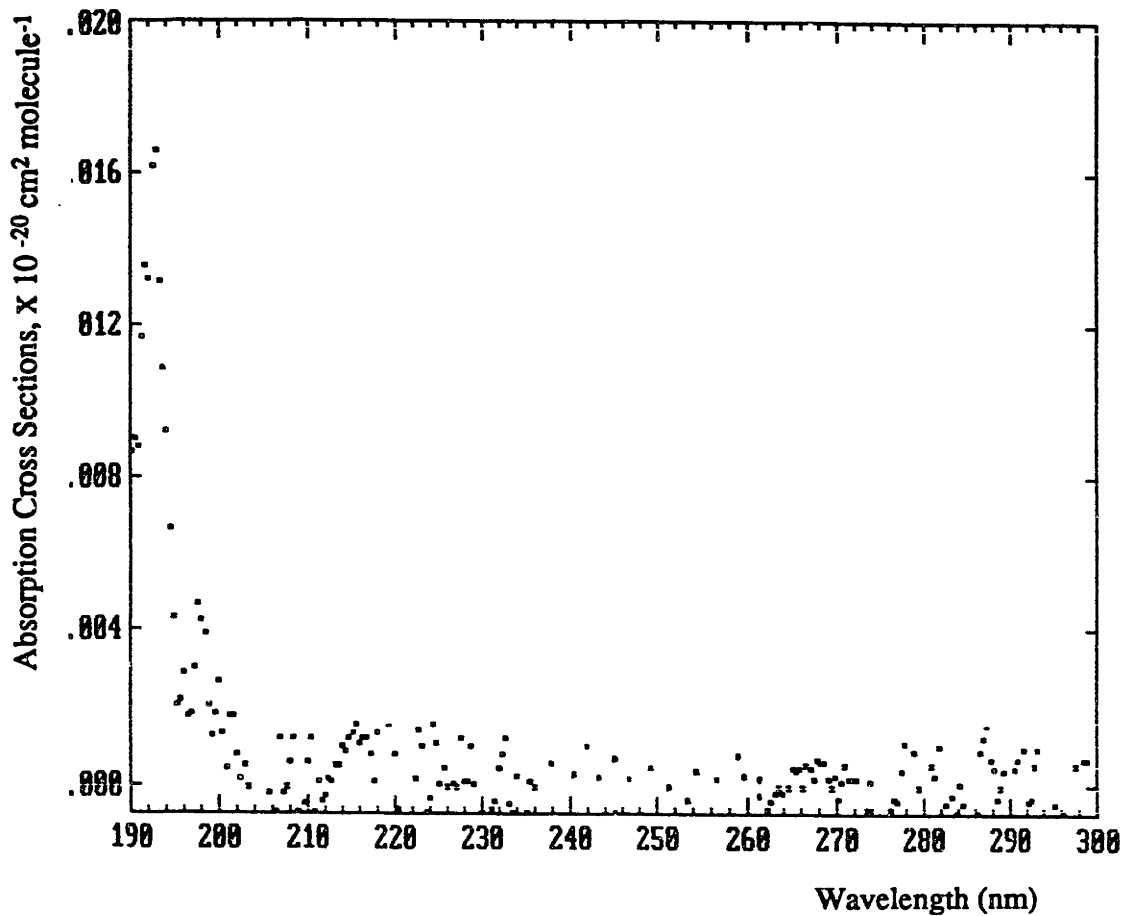
**Table 5. Absorption Cross Sections of Perfluorobutylamine and Perfluorodecalin**

Wavelength (nm)	Perfluorobutylamine ( $10^{-20}$ cm <sup>2</sup> molecule <sup>-1</sup> )	Perfluorodecalin ( $10^{-20}$ cm <sup>2</sup> molecule <sup>-1</sup> )
195	3.9	1.4
197	3.8	0.96
199	3.6	0.89
201	3.2	0.82
203	2.9	0.78
205	2.6	0.71
207	2.2	0.62
209	1.8	0.56
211	1.3	0.50
213	0.97	0.43
215	0.79	0.38
217	0.60	0.32
219	0.37	0.28
221	0.27	0.26
223	0.24	0.24
225	0.15	0.20
227	0.08	0.18
229	0.04	0.18
231	--	0.14
233	--	0.13
235	--	0.13
237	--	0.13
239	--	0.12
241	--	0.12
243	--	0.08
245	--	0.08
247	--	0.08
249	--	0.08
251	--	0.06

“--” denotes that the measured values are lower than the detection limit.

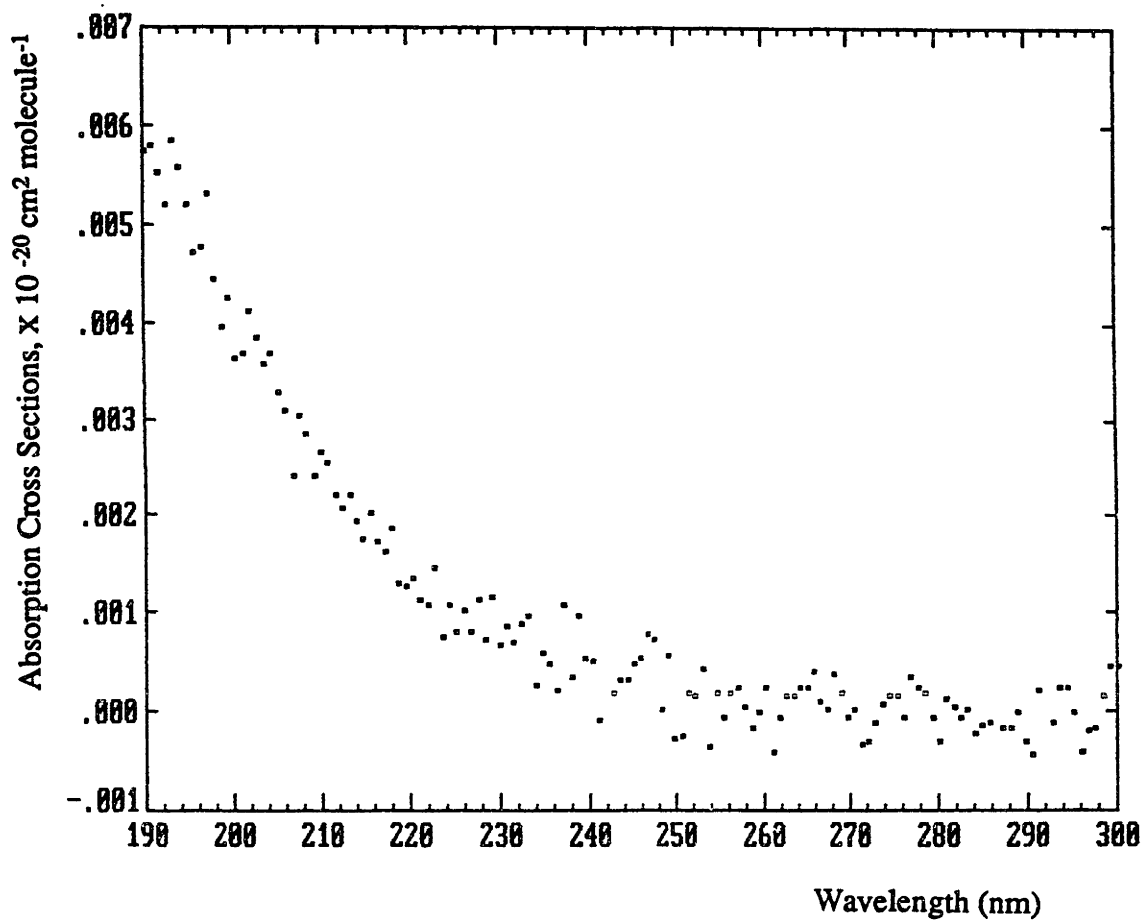
nm wavelength region and have absorption cross sections of  $\sim 1 \times 10^{-20} \text{ cm}^2 \text{ molec}^{-1}$  around 210 nm, which are comparable in magnitude to those of  $\text{CF}_2\text{Cl}_2$ . The vapor pressure of  $[\text{C}_4\text{F}_9\text{OC}_2\text{F}_4\text{O}]_2\text{CF}_2$  is so low ( about 0.5 torr at room temperature) that the available amount of the compound in the short pathlength (10 cm) absorption cell is very small; hence the measured absorption spectrum is very noisy. It appears that its absorption cross sections around 210 nm are at the order of  $10^{-20} \text{ cm}^2 \text{ molecule}^{-1}$ . UV absorption spectra were also measured for perfluoroethylamine  $[\text{C}_2\text{F}_5]_3\text{N}$  and perfluoroamine  $[\text{OC}_4\text{F}_8\text{N}]\text{CF}_3$ , which did not decay in their control experiments or the OH reaction experiments. The spectra of the two compounds, as shown in Figure 4 and Figure 5 respectively, show that their absorption cross sections are at least 100 times smaller than those of  $[\text{C}_4\text{F}_9]_3\text{N}$ ,  $\text{C}_{10}\text{F}_{18}$ , or  $[\text{C}_4\text{F}_9\text{OC}_2\text{F}_4\text{O}]_2\text{CF}_2$ .

As discussed previously, the mercury lamp in the cell emits about 3.8 watts of its radiated energy at the 222.4 nm mercury line and at this wavelength the Vycor tubing surrounding the lamp is transparent. The decays of these compounds in their control experiments strongly indicate that these compound absorbed the 222 nm light and photolyzed. This is corroborated by the observed 8% decay of 20 millitorr of  $\text{CF}_2\text{Cl}_2$  with 300 torr helium after being irradiated in the cell for 60 minutes. The main sink for  $\text{CF}_2\text{Cl}_2$  in the environment is photolysis in the stratosphere in the 190 -220 nm region, which leads to a lifetime of 150 years. Hence, the main sink for  $[\text{C}_4\text{F}_9]_3\text{N}$ ,  $\text{C}_{10}\text{F}_{18}$ , and  $[\text{C}_4\text{F}_9\text{OC}_2\text{F}_4\text{O}]_2\text{CF}_2$  is most likely also photolysis in the stratosphere, yielding an atmospheric lifetime of the order of 150 - 300 years for these compounds. Additional studies would be required to take into account potential artifacts in the UV absorption measurements due to impurities, and



**Figure 4.** Absorption spectrum of the perfluorotriethylamine at 298 K, measured with Cary UV spectrometer, using a pathlength of 10 cm and a pressure of 71.5 torr.





**Figure 5.** Absorption spectrum of the perfluoro-N-methylmorpholine at 298 K, measured with Cary UV spectrometer, using a pathlength of 10 cm and a pressure of 230.4 torr.

to carefully quantify the solar photodissociation rates in order to refine the atmospheric estimates.

### 3.4 O(<sup>1</sup>D) Reaction Studies

Experiments on the reactions with O(<sup>1</sup>D) atoms were carried out for nine fluorocarbons: the three perfluoroalkanes, the three sulfur perfluorides, the perfluoroether C<sub>4</sub>F<sub>9</sub>[C<sub>4</sub>F<sub>7</sub>O], the perfluoroamine [C<sub>4</sub>F<sub>9</sub>]<sub>3</sub>N, and the perfluoromorpholine [OC<sub>4</sub>F<sub>8</sub>N]CF<sub>3</sub>. The results are summarized in Table 4.

The three perfluoroalkanes, C<sub>4</sub>F<sub>10</sub>, C<sub>5</sub>F<sub>12</sub>, and C<sub>6</sub>F<sub>14</sub>, did not decay in the reaction with O(<sup>1</sup>D), in contrast to the average of 23% decay of the reference compound CF<sub>2</sub>Cl<sub>2</sub>. Hence the perfluoroalkanes under study are, in comparison with the CF<sub>2</sub>Cl<sub>2</sub>, essentially non-reactive towards O(<sup>1</sup>D) atoms. The estimated upper limits to the O(<sup>1</sup>D) reaction rate coefficients of these perfluoroalkanes are at most one tenth of the rate coefficient of CF<sub>2</sub>Cl<sub>2</sub>. If compared with CFC-115 ( C<sub>2</sub>F<sub>5</sub>Cl ) whose reaction with O(<sup>1</sup>D) has a rate constant of 5 X10<sup>-11</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>, the reaction rate constants of the compounds under study are at most one third as large as the rate constant of CFC-115; the 500 year atmospheric lifetime for this compound is dominated by the O(<sup>1</sup>D) reaction. This means that the atmospheric lifetimes of the fluoroalkanes under study are at least 500 years with respect to reaction with O(<sup>1</sup>D).

The perfluoroamine [C<sub>4</sub>F<sub>9</sub>]<sub>3</sub>N showed ~1.9% decay after one minute of reaction time in the O(<sup>1</sup>D) reaction experiment. As was the case in the OH reaction experiment, its control experiment yielded 3.9% decay, which is even higher. As discussed previously, the decay of [C<sub>4</sub>F<sub>9</sub>]<sub>3</sub>N is most likely due to photolysis. If this is taken into account, the upper limit to its rate coefficient

**Table 4. Results of studies of O(1D) reaction with various fluorocarbons**

Fluorocarbons (FCs)	FC decay in control experiment (%)	CF <sub>2</sub> Cl <sub>2</sub> decay (%)	FC decay (%)	k <sub>FC</sub> /k <sub>C<sub>2</sub>F<sub>2</sub>Cl<sub>2</sub></sub> (cm <sup>3</sup> molec <sup>-1</sup> s <sup>-1</sup> )	k <sub>FC</sub>
C4F10	no decay	23.6±1.5	<1.5	<0.068	<9.5x10 <sup>-12</sup>
C5F12	no decay	24.0±1.5	<1.5	<0.070	<9.8x10 <sup>-12</sup>
C6F14	no decay	22.8±1.5	<1.5	<0.054	<7.6x10 <sup>-12</sup>
C4F9[C4F7O]	no decay	24.7±1.5	<1.5	<0.048	<6.7x10 <sup>-12</sup>
[OC4F8N]CF3	no decay	23.1±1.5	1.5±1.5	<0.11	<1.5x10 <sup>-11</sup>
[C4F9]3N	3.9±1.5	24.7±1.5	1.9±1.5	<0.13	<1.7x10 <sup>-11</sup>
C3F7SF4C3F7	no decay	37.1±8.0	6.3±2.0	0.14±0.08	(2.0±1.1)x10 <sup>-11</sup>
C6F13SF5	no decay	42.2±8.0	11.9±3.0	0.23±0.09	(3.2±1.2)x10 <sup>-11</sup>
CF3SF5	no decay	29.1±2.0	no decay	<0.13	<1.8x10 <sup>-11</sup>

for the O(<sup>1</sup>D) reaction is comparable to that of the perfluoroalkanes, and its lifetime against the O(<sup>1</sup>D) reaction process is also likely to be above 500 years.

The perfluoroether C<sub>4</sub>F<sub>9</sub>[C<sub>4</sub>F<sub>7</sub>O] and the perfluoromorpholine [OC<sub>4</sub>F<sub>8</sub>N]CF<sub>3</sub> were found to be essentially non-reactive towards O(<sup>1</sup>D). The upper limits to their rate coefficients for reaction with O(<sup>1</sup>D) are at most one tenth of the rate coefficient of CF<sub>2</sub>Cl<sub>2</sub>. Their atmospheric lifetimes are estimated to be at least 500 years with respect to reaction with O(<sup>1</sup>D).

The two sulfur perfluoride isomers with long side chains, C<sub>3</sub>F<sub>7</sub>SF<sub>4</sub>C<sub>3</sub>F<sub>7</sub> and C<sub>6</sub>F<sub>13</sub>SF<sub>5</sub>, reacted with O(<sup>1</sup>D), as indicated by the measurable decays. The rate coefficient estimated for C<sub>3</sub>F<sub>7</sub>SF<sub>4</sub>C<sub>3</sub>F<sub>7</sub> is about one seventh as large as that of CF<sub>2</sub>Cl<sub>2</sub>; and for C<sub>6</sub>F<sub>13</sub>SF<sub>5</sub> it is about one fourth of that of CF<sub>2</sub>Cl<sub>2</sub>. By comparing with the lifetime of CFC-115, the lifetimes with respect to O(<sup>1</sup>D) reaction are likely to be longer than 500 years for the two compounds.

In the control experiments for the O(<sup>1</sup>D) reaction rate measurements in which 8 minutes of reaction time were used, the above two sulfur perfluorides did not show measurable decays, as shown in Table 2. However, the two compounds did yield about 5% decay in the control experiments for the OH reaction experiments after 60 minutes of being irradiated with UV light, as shown in Table 3. The 5% decay is comparable in magnitude with the 8% decay of CF<sub>2</sub>Cl<sub>2</sub> in the photolysis experiment with the same experimental conditions. Comparing the estimated 500 year lower limit to the lifetime of the two sulfur perfluorides against the O(<sup>1</sup>D) reaction with the 150 years lifetime of CF<sub>2</sub>Cl<sub>2</sub> (which is predominantly determined by the photolysis in the stratosphere), we conclude that the main atmospheric sink for these two sulfur perfluorides is most likely also the photolysis in the stratosphere, while the reaction with O(<sup>1</sup>D) will only be a minor destruction path. The overall

atmospheric lifetimes of the two compounds should be also comparable in magnitude to the lifetime of  $\text{CF}_2\text{Cl}_2$ , most likely in the range of 150 -300 years.

The other sulfur perfluoride  $\text{CF}_3\text{SF}_5$  did not decay in the  $\text{O}(^1\text{D})$  reaction experiment nor in the control experiment. Its rate coefficient of the reaction with  $\text{O}(^1\text{D})$  is at most one tenth of that of  $\text{CF}_2\text{Cl}_2$ ; and its lifetime with respect to  $\text{O}(^1\text{D})$  reaction is at least 500 years.

## Chapter 4

# Summary and Conclusions

Twenty two fluorocarbons have been investigated in this study for their chemical reactivities towards OH radicals and O(<sup>1</sup>D) atoms and their photochemical properties under UV irradiation, in order to estimate their atmospheric lifetimes and provide a chemical basis for further calculations of their greenhouse potentials.

A relative rate technique was developed for the present study to measure the rate coefficients of OH reactions and O(<sup>1</sup>D) reactions with the fluorocarbons. This technique was designed to be insensitive to the presence of impurities, in comparison with other absolute rate techniques. With this technique, the disappearance of the compound of interest, not the disappearance of the highly reactive species such as OH radicals and O(<sup>1</sup>D) atoms, was easily monitored by FTIR using a multiple-path cell. Since only relative concentrations need to be measured, better precision can be obtained with this technique compared with other absolute techniques.

UV absorption cross sections were measured for some of the fluorocarbons under study to determine if photolysis in the stratosphere will be the main destruction process for these compounds.

All eight hydrofluorocarbons are found to be reactive to the OH radicals.

1,1,1,2,2,3,3-heptafluoroheptane ( C<sub>3</sub>F<sub>7</sub>C<sub>4</sub>H<sub>9</sub> ) is most reactive to OH among the eight hydrofluorocarbons. The estimated rate coefficient for the OH + C<sub>3</sub>F<sub>7</sub>C<sub>4</sub>H<sub>9</sub> reaction is about 20 times larger than that of CH<sub>4</sub>. Hence, the dominant atmospheric sink for this compound will be the reaction with OH

in the troposphere. The atmospheric lifetime of this compound is estimated to be 0.6 years.

Tetrafluorocyclobutane ( $C_4F_4H_4$ ) is also found to be very reactive towards OH. The rate coefficient for the  $OH + C_4F_4H_4$  reaction is about three times larger than that for the corresponding  $OH + CH_4$  reaction. The dominant sink for this compound will also be the reaction with OH in the troposphere. The atmospheric lifetime estimated for this compound is 1.0 year.

The rate coefficient for the  $OH + C_7F_{15}H$  is estimated to be about three times larger than that of  $OH + CF_3H$ . The atmospheric lifetime with respect to the OH reaction is about 90 years. Therefore, reaction with OH will be a significant destruction process for this compound.

The hydrofluoroether  $C_8F_{17}OC_2F_4H$  reacts with OH radicals with a rate about three times faster than  $CF_3H$ . Its estimated atmospheric lifetime against the OH reaction is about 80 years. Thus reaction with OH will be a significant destruction pathway in the environment for this compound.

Perfluoromorpholinoethylhydride ( $[OC_4F_8N]C_2F_4H$ ) reacts with OH radicals with a rate about two times faster than  $CF_3H$ . Its atmospheric lifetime against OH reaction is estimated to be about 150 years. Hence reaction with OH will be a significant destruction process for this compound.

The hydrofluoroether  $C_6F_{13}OC_2F_4OCF_2H$  reacts with OH radicals with a roughly the same rate as that of  $OH + CF_3H$ . Its atmospheric lifetime with respect to the OH reaction is at least 170 years. Since this compound also photolyzes in the UV with a rate comparable to that of  $CF_2Cl_2$ , photolysis of this compound in the stratosphere will probably be as significant a sink as the reaction with OH in the troposphere; and the lifetime with respect to

photolysis is likely to be in the range from 150 to 300 years. Better estimates of the overall atmospheric lifetime will require further atmospheric modeling.

Like its homologous compound  $C_6F_{13}OC_2F_4OCF_2H$ , the hydrofluoroether  $C_4F_9OC_2F_4OCF_2H$  also reacts with OH with a rate which is roughly the same as that of OH +  $CF_3H$ . It also photolyzes in the UV with a rate comparable to that of  $CF_2Cl_2$ . Therefore, its estimated atmospheric lifetime is at least 170 years with respect to reaction with OH in the troposphere, and 150 - 300 years with respect to photolysis in the stratosphere.

The hydrofluoroether  $C_4F_9OCFHCF_3$  reacts with OH with a rate which is about twice the rate of  $CF_3H$  with OH. The estimated atmospheric lifetime against OH reaction is about 140 years for this compound. It decays slowly in the near UV; but photolysis in the stratosphere is not likely to be a significant sink compared to reaction with OH in the troposphere for this compound.

4-trifluoromethyl-2-perfluoropentene ( $[CF_3]_2CFCF=CFCF_3$ ) reacts with OH radicals very rapidly. The estimated rate coefficient for the OH +  $[CF_3]_2CFCF=CFCF_3$  reaction is about 12 times larger than that of  $CH_4$ . Hence, the dominant atmospheric sink for this compound will be the reaction with OH in the troposphere. The atmospheric lifetime of this compound is estimated to be 0.6 years. Reaction with  $NO_3$  radicals is also likely to occur for this compound and will further shorten its atmospheric lifetime.

The three perfluoroalkanes: perfluorobutane ( $C_4F_{10}$ ), perfluoropentane ( $C_5F_{12}$ ), and perfluorohexane ( $C_6F_{14}$ ), are all found to be essentially non-reactive both to OH radicals and to  $O(^1D)$  atoms. Neither do they photolyze in the near UV. Therefore, these compounds will be extremely inert in the environment and will stay in the atmosphere for a long time. The lifetimes estimated for the three perfluoroalkanes are at least 2000 years with



respect to reaction with OH in the troposphere and at least 500 years with respect to reaction with O(<sup>1</sup>D) in the stratosphere.

The rate coefficient for the OH reaction with perfluorodecalin ( C<sub>10</sub>F<sub>18</sub> ) is estimated to be at most one half as large as the rate coefficient of CF<sub>3</sub>H. The estimated lifetime against the OH reaction is at least 500 years. The measured UV absorption spectrum reveals that this compound absorbs UV light at wavelengths 190 - 220 nm, with absorption cross sections comparable in magnitude to those of CF<sub>2</sub>Cl<sub>2</sub> around 210 nm. It also photolyzes in the UV with a rate comparable to that of CF<sub>2</sub>Cl<sub>2</sub>. Therefore, the major sink in the atmosphere for this compound will most likely be photolysis in the stratosphere; and its lifetime should be at the order of 150 - 300 years.

The perfluoroether [C<sub>4</sub>F<sub>9</sub>OC<sub>2</sub>F<sub>4</sub>O]<sub>2</sub>CF<sub>2</sub> is most likely non-reactive towards OH, in comparison with CF<sub>3</sub>H. The atmospheric lifetime against OH reaction is likely above 2000 years. The measurement of the UV absorption cross sections reveals that this compound absorbs light around 210 nm and has cross sections of the order of 10<sup>-20</sup> cm<sup>2</sup> molec<sup>-1</sup>. The control experiment for the OH reaction rate measurement shows that it photolyzes with a rate comparable to that of CF<sub>2</sub>Cl<sub>2</sub> around 210 nm. Therefore, the main sink for this compound in the atmosphere is most likely the photolysis in the stratosphere, yielding a lifetime of the order of 150 - 300 years.

Perfluoro(2-butyltetrahydrofuran) ( C<sub>4</sub>F<sub>9</sub>[C<sub>4</sub>F<sub>7</sub>O] ) is found to be essentially non-reactive towards both OH radicals and O(<sup>1</sup>D) atoms. Neither does it photolyze in the near UV. Like perfluoroalkanes, it will also have a long atmospheric lifetime. The lifetimes estimated are at least 2000 years with respect to the OH reaction in the troposphere, and at least 500 years with respect to the O(<sup>1</sup>D) reaction in the stratosphere.

The mixture of perfluoroethers with the general formula  $\text{CF}_3\text{O}[\text{CF}(\text{CF}_3)\text{CF}_2\text{O}]_n[\text{CF}_2\text{O}]_m\text{CF}_3$ , like the other two perfluoroethers discussed above, is essentially non-reactive towards OH in comparison with  $\text{CF}_3\text{H}$ . The atmospheric lifetime with respect to OH reaction is at least 2000 years for this compound. It does not photolyze in the near UV. The  $\text{O}(^1\text{D})$  reaction rate was not measured for this compound; but it is unlikely to be reactive to  $\text{O}(^1\text{D})$  atoms. Hence its overall atmospheric lifetime should be comparable to that of the perfluoroalkanes.

Unlike the hydrogen-containing fluoromorpholine  $[\text{OC}_4\text{F}_8\text{N}]\text{C}_2\text{F}_4\text{H}$ , perfluoro-N-methylmorpholine  $[\text{OC}_4\text{F}_8\text{N}]\text{CF}_3$  is found to be non-reactive to OH. Also, it does not photolyze in the UV, and is virtually non-reactive towards  $\text{O}(^1\text{D})$ . Hence, like the perfluoroalkanes, it will be extremely stable in the atmosphere. Its atmospheric lifetimes are estimated to be above 2000 years against OH reaction and at least 500 years against  $\text{O}(^1\text{D})$  reaction.

The measured UV absorption spectrum for perfluorobutylamine  $[\text{C}_4\text{F}_9]_3\text{N}$  reveals that this compound absorbs UV light at wavelengths 190 - 220 nm, with an absorption cross section around 210 nm comparable in magnitude to that of  $\text{CF}_2\text{Cl}_2$ . It also photolyzes in the UV with a rate comparable to that of  $\text{CF}_2\text{Cl}_2$ . Since this compound is most likely non-reactive towards both OH radicals and  $\text{O}(^1\text{D})$  atoms, its major sink in the atmosphere will most likely be photolysis in the stratosphere; and its lifetime should be at the order of 150 - 300 years. The atmospheric lifetimes with respect to OH reactions are at least 2000 years, and at least 500 years with respect to  $\text{O}(^1\text{D})$  reaction.

Unlike perfluorobutylamine  $[\text{C}_4\text{F}_9]_3\text{N}$ , perfluoroethylamine  $[\text{C}_2\text{F}_5]_3\text{N}$  does not photolyze in UV. Its UV absorption spectrum also reveals that it has virtually no absorption in the 190 -300 nm region. It is also found to be non-

reactive towards OH, in comparison with  $\text{CF}_3\text{H}$ . The atmospheric lifetime against the OH reaction is estimated to be above 2000 years. The  $\text{O}(^1\text{D})$  reaction rate was not measured for this compound; but it is unlikely to be reactive towards  $\text{O}(^1\text{D})$  atoms. Hence its overall atmospheric lifetime should be comparable to that of the perfluoroalkanes.

The two sulfur perfluoride isomers with long side chains,  $\text{C}_3\text{F}_7\text{SF}_4\text{C}_3\text{F}_7$  and  $\text{C}_6\text{F}_{13}\text{SF}_5$ , are found to be essentially non-reactive towards OH radicals but reactive towards  $\text{O}(^1\text{D})$  atoms. The  $\text{O}(^1\text{D})$  reaction rate coefficient estimated for  $\text{C}_3\text{F}_7\text{SF}_4\text{C}_3\text{F}_7$  is about one seventh as large as that of  $\text{CF}_2\text{Cl}_2$ ; and for  $\text{C}_6\text{F}_{13}\text{SF}_5$  it is about one fourth of that of  $\text{CF}_2\text{Cl}_2$ . The lifetimes with respect to  $\text{O}(^1\text{D})$  reaction are estimated to be at least 500 years for the two compounds. Since the two compounds also photolyze in the UV with a rate comparable to that of  $\text{CF}_2\text{Cl}_2$ , the main atmospheric sink for these two sulfur perfluorides is most likely also photolysis in the stratosphere, while reaction with  $\text{O}(^1\text{D})$  will only be a minor destruction path. The overall atmospheric lifetimes for the two compounds should be also comparable in magnitude to the lifetime of  $\text{CF}_2\text{Cl}_2$ , most likely in the range of 150 -300 years.

The other sulfur perfluoride,  $\text{CF}_3\text{SF}_5$ , is found to be essentially non-reactive towards both OH radicals and  $\text{O}(^1\text{D})$  atoms. Neither does it photolyze in the near UV. Therefore, like the perfluoroalkanes, this compound will be extremely inert in the environment. Its lifetime is estimated to be at least 2000 years with respect to the OH reaction in the troposphere, and at least 500 years with respect to the  $\text{O}(^1\text{D})$  reaction in the stratosphere.

## Appendix A. Mechanism For the O(<sup>1</sup>D) + CF<sub>2</sub>Cl<sub>2</sub> Reaction System

Reaction Mechanism					Rate Constant*
					(cm <sup>3</sup> molec <sup>-1</sup> s <sup>-1</sup> )
1.	O <sub>3</sub>		-->	O( <sup>1</sup> D) + O <sub>2</sub>	3.00 x10 <sup>-02</sup>
2.	O <sub>3</sub>	+	O( <sup>1</sup> D)	--> O <sub>2</sub> + O <sub>2</sub>	1.20 x10 <sup>-10</sup>
3.	O <sub>3</sub>	+	O( <sup>1</sup> D)	--> O <sub>2</sub> + 2O	1.20 x10 <sup>-10</sup>
4.	2O	+		--> O + O	1.00 x10 <sup>+10</sup>
5.	O( <sup>1</sup> D)	+	CF <sub>2</sub> Cl <sub>2</sub>	--> Product	1.40 x10 <sup>-10</sup>
6.	O( <sup>1</sup> D)	+	O <sub>2</sub>	--> O + O <sub>2</sub>	3.20 x10 <sup>-11</sup>
7.	O( <sup>1</sup> D)	+	N <sub>2</sub>	--> O + N <sub>2</sub>	1.80 x10 <sup>-11</sup>
8.	O( <sup>1</sup> D)	+	H <sub>2</sub> O	--> OH + OH	2.20 x10 <sup>-10</sup>
9.	O( <sup>1</sup> D)	+	Product	--> Product'	2.00 x10 <sup>-11</sup>
10.	OH	+	O <sub>3</sub>	--> HO <sub>2</sub> + O <sub>2</sub>	6.80 x10 <sup>-14</sup>
11.	OH	+	OH	--> H <sub>2</sub> O + O	1.90 x10 <sup>-12</sup>
12.	OH	+	H <sub>2</sub> O <sub>2</sub>	--> H <sub>2</sub> O + HO <sub>2</sub>	1.70 x10 <sup>-12</sup>
13.	HO <sub>2</sub>	+	HO <sub>2</sub>	--> H <sub>2</sub> O <sub>2</sub> + O <sub>2</sub>	1.70 x10 <sup>-12</sup>
14.	HO <sub>2</sub>	+	O <sub>3</sub>	--> OH + 2O <sub>2</sub>	2.00 x10 <sup>-15</sup>
15.	O <sub>2</sub>	+	O	--> O <sub>3</sub>	1.50 x10 <sup>-14</sup>

\* The rate constants are from JPL Publication #92-20.

## Appendix B. Mechanism For the OH + CH<sub>4</sub> Reaction System

Reaction Mechanism						Rate Constant*
						(cm <sup>3</sup> molec <sup>-1</sup> s <sup>-1</sup> )
1.	O <sub>3</sub>			→	O( <sup>1</sup> D) + O <sub>2</sub>	3.00 × 10 <sup>-02</sup>
2.	O <sub>3</sub>	+	O( <sup>1</sup> D)	→	O <sub>2</sub> + O <sub>2</sub>	1.20 × 10 <sup>-10</sup>
3.	O <sub>3</sub>	+	O( <sup>1</sup> D)	→	O <sub>2</sub> + 2O	1.20 × 10 <sup>-10</sup>
4.	2O	+		→	O + O	1.00 × 10 <sup>+10</sup>
5.	O( <sup>1</sup> D)	+	CH <sub>4</sub>	→	CH <sub>2</sub> O + O <sub>2</sub>	1.40 × 10 <sup>-11</sup>
6.	O( <sup>1</sup> D)	+	CH <sub>4</sub>	→	CH <sub>3</sub> + OH	1.40 × 10 <sup>-11</sup>
7.	O( <sup>1</sup> D)	+	O <sub>2</sub>	→	O + O <sub>2</sub>	3.20 × 10 <sup>-11</sup>
8.	O( <sup>1</sup> D)	+	N <sub>2</sub>	→	O + N <sub>2</sub>	1.80 × 10 <sup>-11</sup>
9.	O( <sup>1</sup> D)	+	H <sub>2</sub> O	→	OH + OH	2.20 × 10 <sup>-10</sup>
10.	OH	+	CH <sub>4</sub>	→	Product"	6.50 × 10 <sup>-15</sup>
11.	OH	+	O <sub>3</sub>	→	HO <sub>2</sub> + O <sub>2</sub>	6.80 × 10 <sup>-14</sup>
12.	OH	+	OH	→	H <sub>2</sub> O + O	1.90 × 10 <sup>-12</sup>
13.	OH	+	H <sub>2</sub> O <sub>2</sub>	→	H <sub>2</sub> O + HO <sub>2</sub>	1.70 × 10 <sup>-12</sup>
14.	CH <sub>3</sub>	+	O	→	Product	1.10 × 10 <sup>-10</sup>
15.	O( <sup>1</sup> D)	+	Product	→	Product'	1.20 × 10 <sup>-10</sup>
16.	HO <sub>2</sub>	+	HO <sub>2</sub>	→	H <sub>2</sub> O <sub>2</sub> + O <sub>2</sub>	1.70 × 10 <sup>-12</sup>
17.	HO <sub>2</sub>	+	O <sub>3</sub>	→	OH + 2O <sub>2</sub>	2.00 × 10 <sup>-15</sup>
18.	O <sub>2</sub>	+	O	→	O <sub>3</sub>	1.50 × 10 <sup>-14</sup>

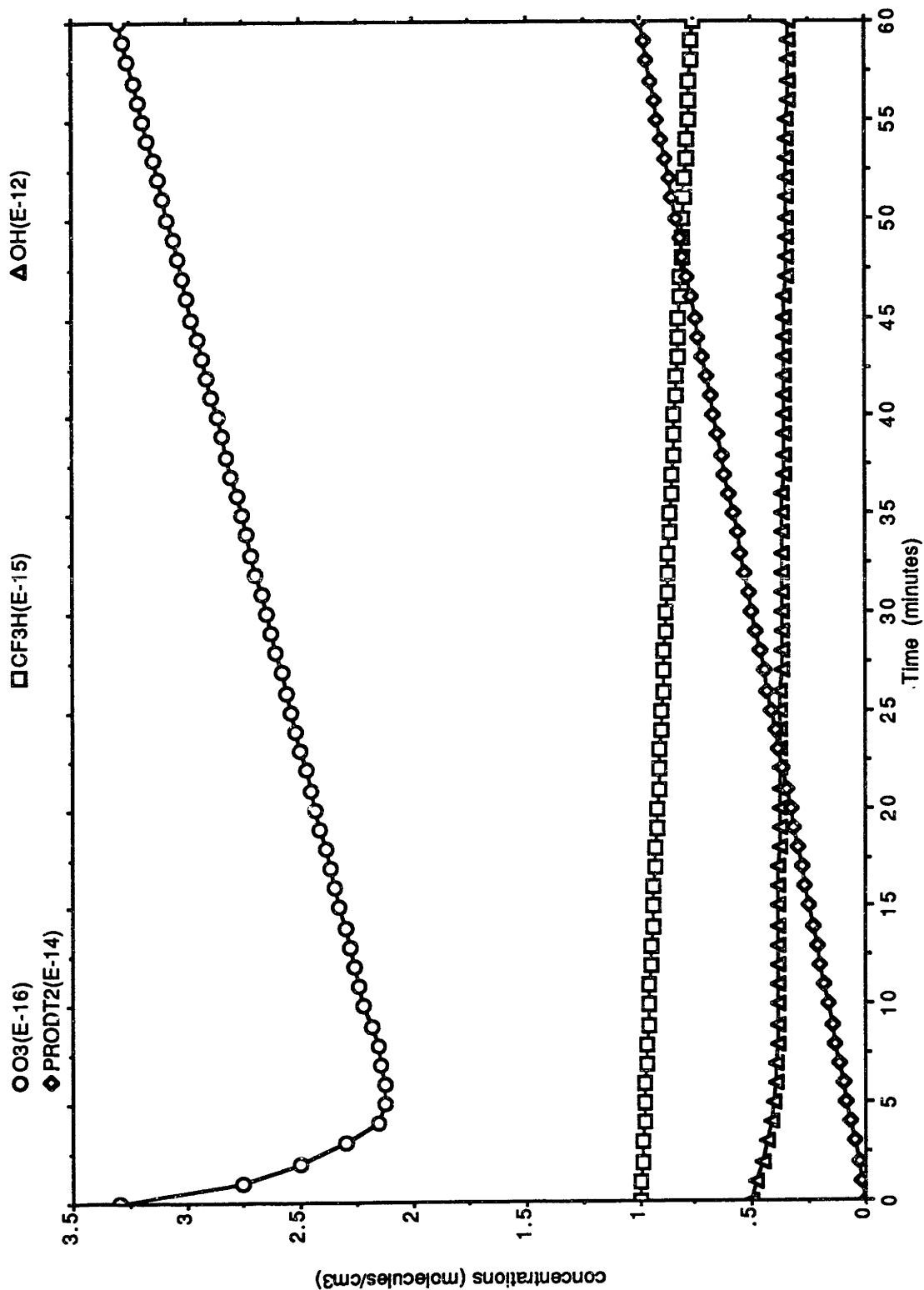
\* The rate constants are from JPL Publication #92-20.

## Appendix C. Mechanism For the OH + CF<sub>3</sub>H Reaction System

Reaction Mechanism				Rate Constant*
				(cm <sup>3</sup> molec <sup>-1</sup> s <sup>-1</sup> )
1.	Injection of	O <sub>3</sub>	---> O <sub>3</sub>	1.50 x10 <sup>-05</sup>
2.	O <sub>3</sub>		--> O( <sup>1</sup> D) + O <sub>2</sub>	3.00 x10 <sup>-02</sup>
3.	O <sub>3</sub>	+ O( <sup>1</sup> D)	--> O <sub>2</sub> + O <sub>2</sub>	1.20 x10 <sup>-10</sup>
4.	O <sub>3</sub>	+ O( <sup>1</sup> D)	--> O <sub>2</sub> + 2O	1.20 x10 <sup>-10</sup>
5.	2O	+	--> O + O	1.00 x10 <sup>+10</sup>
6.	O( <sup>1</sup> D)	+ CF <sub>3</sub> H	--> PRODT2	1.20 x10 <sup>-10</sup>
7.	O( <sup>1</sup> D)	+ O <sub>2</sub>	--> O + O <sub>2</sub>	3.20 x10 <sup>-11</sup>
8.	O( <sup>1</sup> D)	+ N <sub>2</sub>	--> O + N <sub>2</sub>	1.80 x10 <sup>-11</sup>
9.	O( <sup>1</sup> D)	+ H <sub>2</sub> O	--> OH + OH	2.20 x10 <sup>-10</sup>
10.	OH	+ CF <sub>3</sub> H	--> CF <sub>3</sub> + H <sub>2</sub> O	3.10 x10 <sup>-16</sup>
11.	OH	+ O <sub>3</sub>	--> HO <sub>2</sub> + O <sub>2</sub>	6.80 x10 <sup>-14</sup>
12.	OH	+ OH	--> H <sub>2</sub> O + O	1.90 x10 <sup>-12</sup>
13.	OH	+ H <sub>2</sub> O <sub>2</sub>	--> H <sub>2</sub> O + HO <sub>2</sub>	1.70 x10 <sup>-12</sup>
14.	HO <sub>2</sub>	+ HO <sub>2</sub>	--> H <sub>2</sub> O <sub>2</sub> + O <sub>2</sub>	1.70 x10 <sup>-12</sup>
15.	HO <sub>2</sub>	+ O <sub>3</sub>	--> OH + 2O <sub>2</sub>	2.00 x10 <sup>-15</sup>
16.	O <sub>2</sub>	+ O	--> O <sub>3</sub>	1.50 x10 <sup>-14</sup>

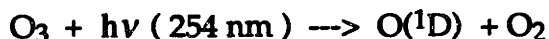
\* The rate constants are from JPL Publication #92-20.

Appendix D. A Typical Result of the Simulation by ACUCHEM for the OH + CF<sub>3</sub>H System.



## Appendix E. Calculation of the Photolysis Rate of Ozone

The photolysis rate coefficient for the reaction



can be estimated based on the power of the lamp and the geometry of the mercury lamp in the cell.

The mercury lamp used in this study has ~5.8 watts of radiated energy at the 254 nm mercury line. However, it is attenuated by the Vycor tubing that surrounds the lamp and by the air passing through the tubing. Assuming the attenuation factor is 20%, the effective power at 254 nm is then ~4.6 watts. The energy of a 254 nm photon is

$$\frac{hc}{\lambda} = \frac{1.986 \times 10^{-23} \text{ J} \cdot \text{cm}}{254 \times 10^{-7} \text{ cm}} = 7.8 \times 10^{-19} \text{ J}.$$

A 4.6 watt source thus generates photons at a rate

$$\frac{4.6 \text{ J} \cdot \text{S}^{-1}}{7.8 \times 10^{-19} \text{ J}} = 5.9 \times 10^{18} \text{ s}^{-1}.$$

divided by the surface area of the lamp, the light intensity at the surface of the lamp is obtained:

$$I_{\text{lamp}} = \frac{5.9 \times 10^{18} \text{ s}^{-1}}{2\pi r_{\text{lamp}} \cdot l_{\text{cell}}} = \frac{5.9 \times 10^{18} \text{ s}^{-1}}{2\pi \cdot 1\text{cm} \cdot 60\text{cm}} = 1.6 \times 10^{16} \text{ s}^{-1} \cdot \text{cm}^{-2}.$$

The attenuation of light intensity is assumed to satisfy Beer - Lambert's

Law:



$$\frac{I}{I_0} = \exp(-\sigma \cdot C \cdot l) \quad \text{or} \quad \frac{I_0 - I}{I_0} = 1 - \exp(-\sigma \cdot C \cdot l),$$

where  $I_0$  is the intensity of the incident light from the lamp;  $I$  is the intensity of the transmitted light at a distance  $l$  from the lamp;  $\sigma$  is the absorption cross section of ozone at 254 nm, which is  $1150 \times 10^{-20} \text{ cm}^2 \text{ molec}^{-1}$ ;  $C$  is the concentration of ozone.

Assume weak absorption of UV light by ozone molecules, hence  $\sigma \cdot C \cdot l$  is small; and the above formula can be simplified as

$$\frac{I_0 - I}{I_0} \approx \sigma \cdot C \cdot l,$$

$$\text{or } \Delta I = I_{\text{abs}} = I_0 - I = I_0 \cdot \sigma \cdot C \cdot l,$$

Where  $I_{\text{abs}}$  is the light absorbed by the ozone molecules.

Because of the weak absorption assumption,  $I_0$  at a certain distance  $r$  from the lamp can be defined as

$$I_0(r) = \frac{r_{\text{lamp}}}{r} \cdot I_{\text{lamp}}.$$

$$\text{Thus, } I_{\text{abs}} = \frac{r_{\text{lamp}}}{r} \cdot I_{\text{lamp}} \cdot \sigma \cdot C \cdot l$$

And the photolysis rate at a distance  $r$  is

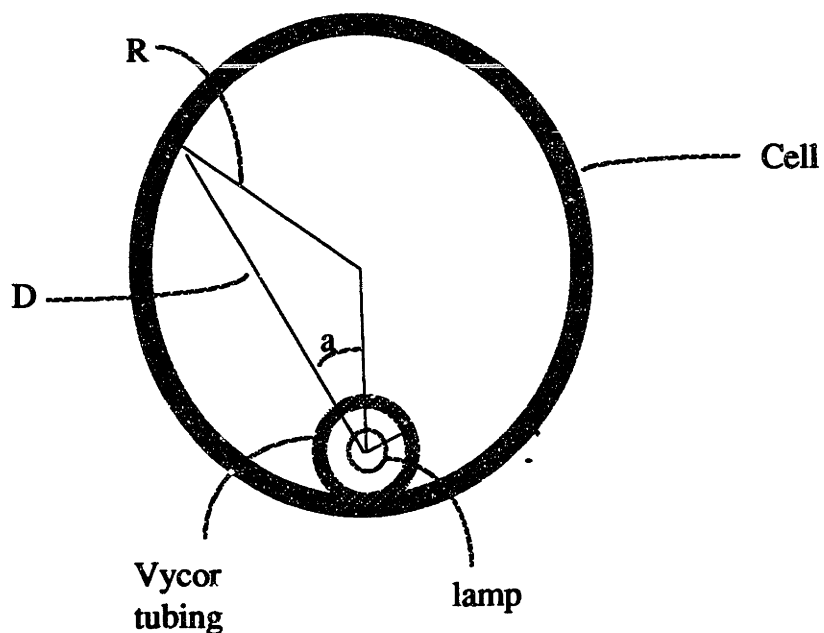
$$J(r) = \frac{I_{\text{abs}}}{l \cdot C} \cdot \Phi = \frac{r_{\text{lamp}}}{r} \cdot I_{\text{lamp}} \cdot \sigma \cdot \Phi,$$

where  $\Phi$  is the quantum yield for  $O(^1D)$  production, which is  $\sim 0.9$  at 254 nm ( JPL Publication 92-20).

The average photolysis rate of ozone can be defined as

$$\bar{j} = \frac{N}{C \cdot V_{\text{cell}}},$$

where  $N$  is the number of ozone molecules photolyzed per second in the cell;  $V_{\text{cell}}$  is the volume of the cell;  $C \cdot V_{\text{cell}}$  is the number of ozone molecules in the cell. The geometry of the lamp in the cell is shown schematically in the following plot:



Hence N can be mathematically derived as

$$N = I_{\text{cell}} \cdot \int_{r_{\text{lamp}}}^{D+r_{\text{lamp}}} [J(r) \cdot C \cdot r] da,$$

$$\text{where, } D = (R - r_{\text{lamp}}) \cdot \cos(a) + R \cdot \sqrt{1 - \left(\frac{R - r_{\text{lamp}}}{R}\right)^2 \sin^2(a)}$$

The above integration gives

$$N = r_{\text{lamp}} \cdot I_{\text{lamp}} \cdot \sigma \cdot C \cdot \Phi \cdot I_{\text{cell}} (5 \cdot R - 2 \cdot \pi \cdot r_{\text{lamp}})$$

$$\text{Thus, } \bar{J} = \frac{N}{C \cdot V_{\text{cell}}} = \frac{N}{C \cdot I_{\text{cell}} \cdot \pi \cdot (R^2 - r_{\text{lamp}}^2)}$$

$$= \frac{(5 \cdot R - 2 \cdot \pi \cdot r_{\text{lamp}}) \cdot r_{\text{lamp}}}{\pi \cdot (R^2 - r_{\text{lamp}}^2)} \cdot I_{\text{lamp}} \cdot \sigma \cdot \Phi$$

Substituting the values of  $R = 6 \text{ cm}$ ,  $r_{\text{lamp}} = 1 \text{ cm}$ ,  $I_{\text{lamp}} = 1.56 \times 10^{16} \text{ cm}^{-2} \text{ s}^{-1}$ ,  $\sigma = 1150 \times 10^{-20} \text{ cm}^2 \text{ molec}^{-1}$ , and  $\Phi = 0.9$ , yields the average photolysis rate of ozone in the cell:

$$\bar{J} = 0.03 \text{ s}^{-1}.$$

The half life of ozone  $t_{1/2}$  according to this estimate of the photolysis rate is given by

$$t_{1/2} = \frac{0.693}{\lambda} = 22 \text{ s},$$

which agrees well with the observations.

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