

ATMOSPHERIC REACTIONS OF HALOTHANE AND HALOGENATED ALKANES

Mary B Hande B.Sc.(Hons.)

**A thesis submitted at Dublin City University for the
Degree of Master of Science**

**Based on research carried out in the School of
Chemical Sciences, Dublin City University, under the
direction and supervision of Doctor Imelda Shanahan**

**Dublin City University
Glasnevin**

January 1995

Declaration

This thesis is submitted in fulfilment of the requirements for a Masters Degree by research and thesis. It has not been submitted as an exercise for a degree at this or any other University. Except when otherwise indicated, this work has been carried out by the author alone, at Dublin City University.

Signed. Mary B. Hande
Mary B. Hande

ID No 57700441

Date 22/9/95

To the kindness, patience and understanding of my parents
and sisters.

Acknowledgements

I would like to express by sincere appreciation to the following people

To my supervisor Dr Imelda Shanahan for her advice, understanding and constant good humour throughout this work

I wish to express my gratitude to the technical staff of the School of Chemical Sciences at Dublin City University especially Mick Burke, Veronica Dobbyn, Theresa McDonnell and Ita Bolger - Theresa and Ita have left to pursue their careers in other areas

I wish to thank my colleagues in the Chemistry Department, especially Carol, Susan, Celia, Joe, Pat, Aodhmar and Michelle, Graham, Philip, the list is endless'

In particular I would like to thank the mob in the 'twilight zone' A115 that is no more!! especially Maureen McLoughlin, (Redzer) Curly, Rosaleen Kane, Fintan O'Donnell, Conor Tonra, Francis, Stephen Fitzpatrick, my old buddy Michael Dreelan and Teri Donaghy

All the mob in the Chemistry Department, UCD for their constant scoops and soccer get togethers'

I would like to thank the school of chemical sciences at Dublin City University and Carlow Co Council for financial support throughout this work

A big thank you to Ruth for all the chats and encouragement, to 'Dr' Jim Lynam for his guidance

A very special thanks to all the team in Laboratory Instruments and Supplies Ltd, Ashbourne, especially Mr Tom O'Keeffe, for all their constant patience and understanding in completing this thesis

Last, but not least, I would like to express sincere gratitude to my family for their support over the many years I have spent in college and I now hope to be able to repay them for their patience and kindness

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ATMOSPHERIC REACTIONS OF HALOTHANE AND HALOGENATED ALKANES

ABSTRACT

It has been established that OH radical and Cl atom reactions are important removal mechanisms for water insoluble volatile organic chemicals (VOCs) in the troposphere. To determine the tropospheric fate of a haloalkane and hence the possible significance in stratospheric ozone depletion, we must first determine the rate of reaction of this species with both OH radicals and Cl atoms and thus the efficiency with which it is removed from the troposphere.

To establish the ultimate atmospheric fate of one such haloalkane, halothane (CF_3CHClBr), a widely used anaesthetic, tropospheric and stratospheric photooxidation reaction mechanisms were investigated for this species using two well established initiation steps. Results indicated that halothane will yield CF_3CClBr radicals in the troposphere via hydroxyl radical attack:

$$\text{CF}_3\text{CHClBr} + \text{OH}^\bullet \rightarrow \text{CF}_3\text{CClBr}^\bullet + \text{H}_2\text{O}$$

and CF_3CHCl radicals in the stratosphere via photolysis:



under simulated atmospheric conditions. The stratospheric reaction mechanisms ultimately led to the formation of CF_3COCl found to be a primary product, and CF_2O and CO_2 both secondary products, from the oxidation of CF_3CHCl radicals. A study of the quantum yields of formation of these species would confirm this result.

Studies of the chlorine-sensitised photooxidation of halothane showed that the two major products were $\text{CF}_3\text{CCl}_2\text{Br}$ and $(\text{CF}_3\text{CClBr})_2$, confirming that chlorine atom attack on halothane yielded CF_3CClBr radicals. The effect of varying the $[\text{Cl}_2]/[\text{CF}_3\text{CHClBr}]$ ratio on the ratio of product concentrations showed that at all times, both products were formed, although the relative amounts of the two products varied. Further work initiated by this study would allow us to assess quantitatively the oxidation of CF_3CHCl and CF_3CClBr radicals.

The kinetic data reported in this work is among the first dealing with the reaction of Cl atoms with a series of brominated and chlorinated alkanes. Their atmospheric lifetimes were established, with respect to reaction with Cl atoms using a relative rate smog chamber technique. The

chlorine atoms were produced by the photolysis of chlorine gas. We report the first measurements of rate constants for the reactions of the chlorine atom with 2-chloropropane, 1,3-dichloropropane, 2-chloro-2-methylpropane, bromoethane, 1-bromopropane, 2-bromopropane, 1-bromobutane, 1-bromopentane and 1-bromohexane excepting $K(\text{Cl} + 1\text{-chloropropane})$ previously reported. Cl atom reactions were measured at 298K and using a value of $2.0 \times 10^3 \text{ cm}^{-3}$ for $[\text{Cl}]$, the lifetimes of the haloalkanes were calculated. The atmospheric lifetimes with respect to Cl atoms are long, 1,3-dichloropropane has the longest tropospheric lifetime of the compounds studied (1.5 years) and sufficiently long tropospheric lifetimes will allow transportation of these species to the stratosphere where they may release their chlorine atoms, ultimately resulting in ozone depletion.

By Mary Hande

CHAPTER 1.0

GENERAL INTRODUCTION

1.1 THE ATMOSPHERE, CFCS AND THIS THESIS

Our understanding of the Physics and Photochemistry/Chemistry of atmospheres has advanced significantly since the early 1960s, primarily as a result of two unrelated activities

- a new awareness of and concern for the role of anthropogenic activities in determining atmospheric composition and climate.
- a vigorous programme of planetary exploration

The present and future effects of anthropogenic activities on atmospheric composition and climate have become environmental problems of great national and international concern. These problems include the general deterioration of the quality of the air we breathe, the increase in air pollution and acid precipitation throughout the world, the possible depletion of ozone (O_3) in the stratosphere and the effects of increasing atmospheric levels of carbon dioxide (CO_2) and other trace-level atmospheric gases produced or perturbed by anthropogenic activities. Most anthropogenic emissions are transformed by various atmospheric photochemical and chemical processes

The Atmosphere

The earth's atmosphere extends to several thousand kilometres above the surface, where it eventually merges with interplanetary space. The composition of the atmosphere at the earth's surface is such that electrically neutral molecules account for almost the entire mass of the atmosphere. Superimposed on the neutral atmosphere are distinct regions of electrically charged particles (electrons and positively charged atoms and molecules), resulting from the ionisation of neutral gases by high energy (X-ray and U.V) solar radiation and cosmic rays.

The neutral atmosphere is subdivided into distinct regions defined by a temperature gradient within the region. The variation of temperature with altitude throughout the atmosphere is shown in Figure 1.1.1

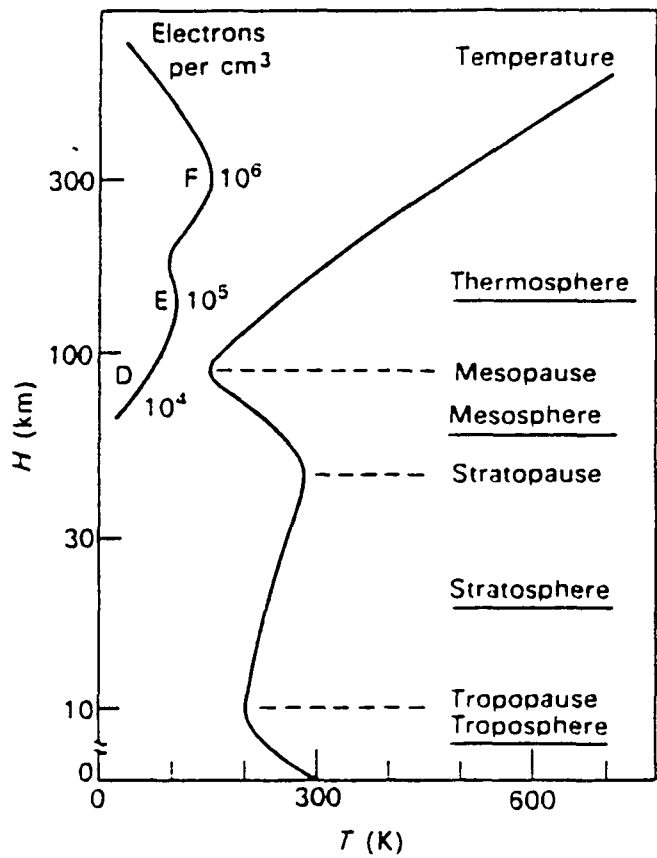


Figure 1.1.1
Temperature versus altitude profile of the earth's atmosphere [1].

About 80 - 85% of the total mass of the atmosphere resides in the troposphere [1] The troposphere is characterised by a steady decrease of temperature with increasing altitude which decreases from about 15°C at the earth's surface to about - 60°C at the tropopause (the region of the temperature minimum) It is maintained as a relatively distinct layer of the atmosphere by the cooler air of the stratosphere which lies above it. Within the troposphere the vertical decrease in temperature gives rise to relatively rapid circulation and vertical mixing of constituents because warmer air from near ground level tends to rise and be replaced by cooler air from above. Thus any pollutants released at the earth's surface can move to the top of the troposphere in a few days or less, depending on meteorological conditions. Essentially all of the water vapour, clouds and precipitation in the earth's atmosphere are found in this region, thus any pollutant gases released into the troposphere are quickly removed from the atmosphere provided they are either sufficiently soluble in water or can be converted to particulate form [2].

Most of the remaining mass of the atmosphere is found in the stratosphere, directly above the troposphere and extending to ~50 km. The stratosphere is a region of positive temperature gradient. The positive temperature gradient results from the absorption of solar U V. radiation (200 - 300nm) by ozone in the stratosphere. About 90% of the ozone in the atmosphere resides in the stratosphere, with the remainder found in the troposphere Above the stratosphere are the regions of the mesosphere (50 - 85km), thermosphere (85 - 500km) and the exosphere (an isothermal region beginning at ~500km [1] Most of the extreme U V solar radiation ($\lambda < 100\text{nm}$) is absorbed in the thermosphere above 100km Solar radiation between 100 and 200nm is absorbed by O_3 within the stratosphere Most of the solar visible and IR radiation traverses the entire atmosphere and reaches the surface of the earth [1]

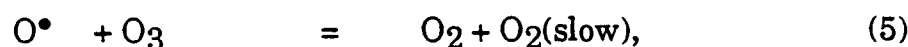
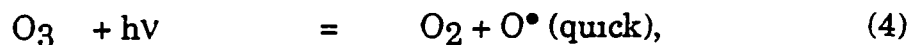
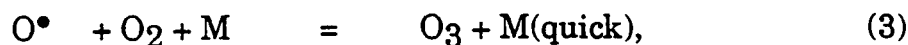
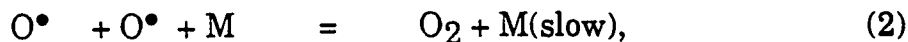
In addition to a significant body of information about physical characteristics of the atmosphere, our understanding of the atmosphere, its composition and its properties has been greatly expanded by efforts to build up a detailed picture of the chemistry of the atmosphere. Of all the chemicals found in the atmosphere, ozone is the one which has attracted most attention in recent decades.

The Ozone layer

Ozone is a natural trace constituent of the atmosphere and averages less than one part per million in the entire atmosphere. Although ozone can be found from ground level up to about 60km, the stratosphere contains approximately 90% of all ozone with a peak concentration at around 25km above the earth. This thin layer of ozone is involved in two important atmospheric phenomena. First, it intercepts much of the solar U.V. radiation between 240 - 300nm and prevents it from reaching the surface of the earth. Ozone is essentially the only atmospheric constituent acting as an absorber of solar radiation. Second, the absorption of this radiation plus some of the Visible and IR parts of the spectrum, raises the temperature of the stratosphere such that the 50km temperature is usually 60 - 70°C warmer than the temperatures characteristic of the 10 - 20km level (about 210°C). The resulting temperature structure is important in influencing the atmospheric circulation patterns for the stratosphere [3].

The stratospheric ozone layer is in a dynamic state, being continually formed and destroyed in a series of photochemically initiated reactions. Historically, the basic mechanism for the formation and removal of ozone was proposed by Chapman in 1930. Molecular oxygen is dissociated by light

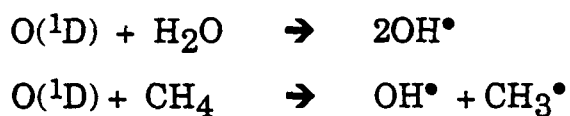
with wavelengths less than 242nm This is a slow process because light that is strongly absorbed by O₂ has been filtered out at higher altitudes



Of the subsequent processes, (2) is only significant in the mesosphere (above the stratosphere) where the lower density of oxygen limits the rate of formation of ozone by reaction (3). The ozone formed in reaction (3) absorbs light very strongly below 300nm and is also dissociated by visible light, the timescale of its decomposition by process (4) being about 1 minute by day. However, this process and reaction (3) merely interconvert the 'Odd Oxygen' species formed by process (1). In contrast, reaction (5) converts the odd oxygen species O and O₃ back to O₂ which can be regarded as even oxygen; this process is unusually slow for a highly exothermic reaction ($\Delta H = -390\text{kJ mol}^{-1}$) involving a free atom. Only in the last decade have laboratory measurements of the rates of these processes become accurate enough to show that reaction (5) accounts for the removal of only about one fifth of the 'odd oxygen' generated in the atmosphere by the photolysis of molecular oxygen [4]

The above scheme involves only species derived from oxygen and predicts considerably more ozone than is actually observed and consequently further ozone destruction pathways must be operative It is generally believed that the original Chapman mechanism accounts for approximately 20% of the total natural destruction rate for ozone A further

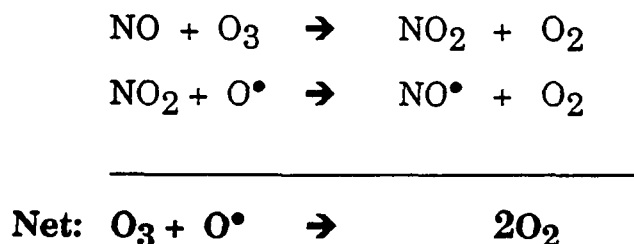
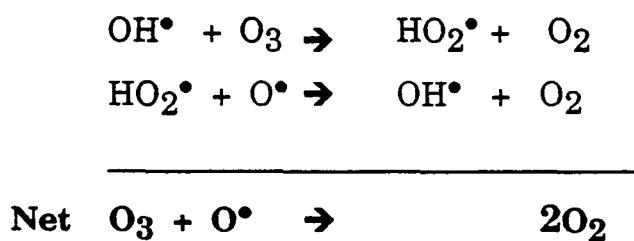
10% [2] of the natural ozone destruction rate is accounted for by catalytic cycles involving hydrogen-containing species, while the remaining 70% is accounted for by a catalytic cycle involving oxides of nitrogen [5,6] The electronically excited oxygen atoms $O(^1D)$, formed in the photodissociation of ozone (reaction 4), are responsible for the formation of odd hydrogen and odd nitrogen radicals in the atmosphere The hydroxyl radical is produced by the reaction of excited oxygen atoms with water vapour and methane, both of which are present at trace levels in the natural stratosphere:



While NO is produced as a result of the reaction of (O^1D) atoms with nitrous oxide which has a number of natural and anthropogenic sources:



The OH radical and NO then participate in catalytic cycles which account for the remaining 10% and 70% respectively, of the natural ozone destruction rate:



Because the atomic oxygen that reacts in the second reaction in each of these two cycles would otherwise have formed ozone, the net effect of each cycle is the destruction of two ozone molecules [2,5,6].

Rowland and Molina [7], Stolarski and Cicerone [8] and other research groups [9,10] were the first scientists to propose a chemical mechanism involving CFCs as a culprit in ozone depletion. CFCs, that is compounds containing chlorine, fluorine, carbon and possibly hydrogen, were developed by Thomas Midgley for Du Pont [11] in the 1930s and have been used extensively in the industrialised nations in the past decades primarily as propellants in aerosol spray cans, as refrigerants and as blowing agents, for example, for producing polyurethane foam. Their chemical characteristics have made them ideally suited for such uses in that they are generally non-toxic, non-flammable yet chemically inert [11,12]. The principal CFCs and HCFCs in use are CCl_3F , CCl_2F_2 and CHClF_2 . These are often referred to as CFC-11, CFC-12 and CFC-22, respectively after the Du Pont tradename, Freon. Although release rates of CFC-11, CFC-12 and CFC-22 temporarily levelled off in the mid 1970s, the concentrations in ambient air continued to rise because steady-state concentrations had not been reached in the atmosphere.

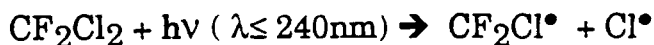
CFCs have very long lifetimes in the troposphere. This is a consequence of the fact that they do not absorb light of wavelengths above 290nm and do not react at significant rates with O_3 and OH . While rate constants for their reactions with NO_3 have not been determined, it is unlikely that these are significant either. In addition to the lack of chemical sinks, there do not appear to be substantial physical sinks, thus they are not very soluble in water and hence are not removed rapidly by

rainout [13] As a result, CFCs reside in the troposphere for years, slowly diffusing up across the tropopause into the stratosphere

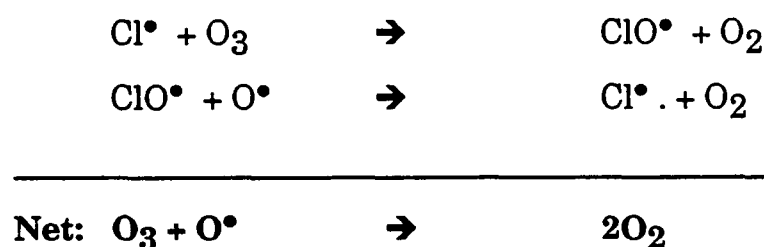
The lifetime of CFCs in the atmosphere can be estimated using a mass balance approach knowing the atmospheric concentrations of CFCs, one can calculate the total amount in the atmosphere. This amount must be the result of a balance between emissions into and loss from the atmosphere. If the emission rates are known, the loss rate required to give the observed atmospheric concentrations can be calculated, and from this, a lifetime obtained [14]. The two most common species CFC-11 and CFC-12 remain in the atmosphere for 75 and 100 years respectively

Approximately 8.1 million metric tons of CFC-11 and CFC-12 have been manufactured world-wide since 1931 and atmospheric measurements of their concentrations are in reasonable agreement with estimates of total emissions. There are two well-characterised processes for their breakdown in the stratosphere, photolysis by solar radiation of wavelengths less than 225nm and by reaction with excited oxygen atoms. The sun's radiation is effectively confined to wavelengths greater than 280nm in the troposphere and consequently photolysis of the chlorofluorocarbons is unimportant in this region [15]. The absorption spectra of the CFCs of greatest atmospheric interest show absorption maxima in the range 170-200nm. Both O₂ and O₃ absorb radiation in the ultraviolet, and there is a window in the overlapping O₂ and O₃ absorptions from approximately 185 to 210nm, that is, a region where the total light absorption is in a shallow minimum. By coincidence, this is the region in which the CFCs absorb light. Above 20km light is transmitted in the so-called 'solar window' which leads to the dissociation of the chlorofluorocarbons [16]

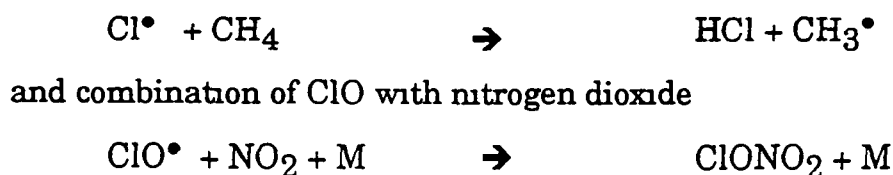
The C-Cl bond dissociation energy in CF_2Cl_2 is 318 kJmol^{-1} , whereas that for the strong C-F bond is 460 kJmol^{-1} . As a result upon light absorption the weaker C-Cl bond breaks [16].



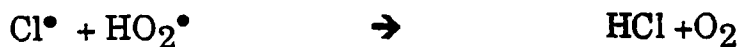
The chlorine atom released then reacts in a catalytic chain reaction which leads to the destruction of O_3



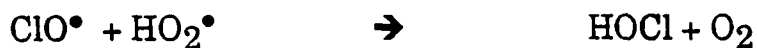
In the stratosphere, the chlorine catalytic step requires less than two minutes and will continue until the chain is temporarily terminated by the formation of HCl, or permanently ended by the downward diffusion of the chlorine species (HCl, ClO or Cl) into the weathering process of the troposphere [3]. This catalytic step may be interrupted by conversion of the highly reactive Cl and ClO into inactive forms that do not destroy ozone. The major processes identified to date are reactions with hydrogen-containing species, mainly methane to form hydrogen chloride.



In addition to interactions between ClO_x and NO_x chemistry, there are also important ClO_x - HO_x interactions.



The reactions of ClO with HO₂ forms HOCl which, along with HCl and ClONO₂ is another temporary reservoir for chlorine atoms:



However, like ClONO₂, HOCl photolyses to form chlorine atoms. Figure 1.1.2 summarises the interactions between ClO_x, NO_x and HO_x chemistry in the stratosphere.

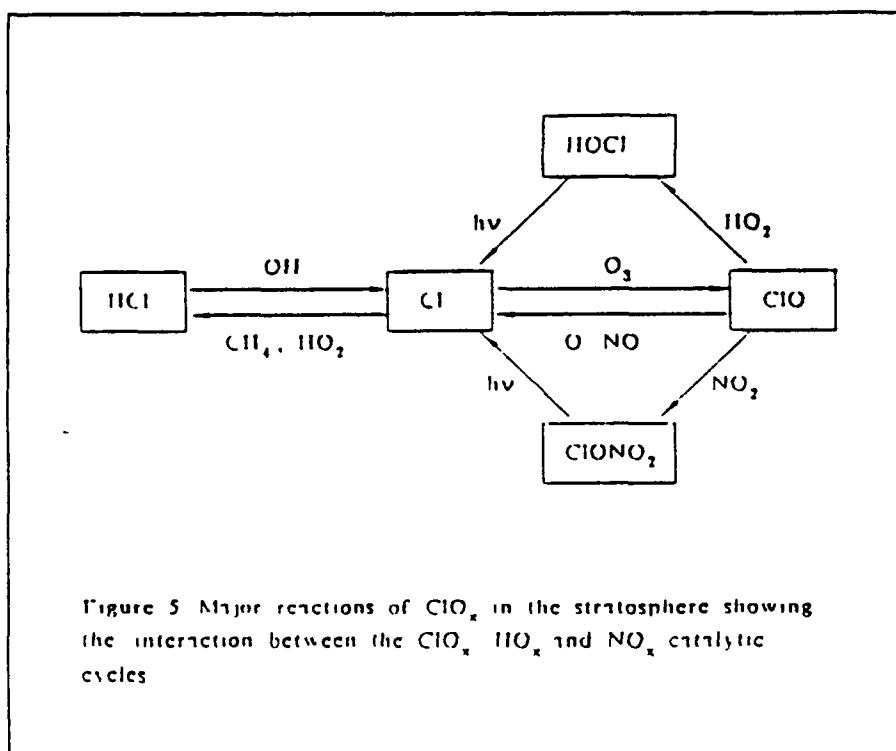


Figure 1.1.2

Major reactions of ClO_x in the stratosphere showing the interaction between the ClO_x, HO_x and NO_x catalytic cycles [16].

The second type of reaction believed to interfere with ozone destruction is the reaction of $\text{ClO}^\bullet$ with NO

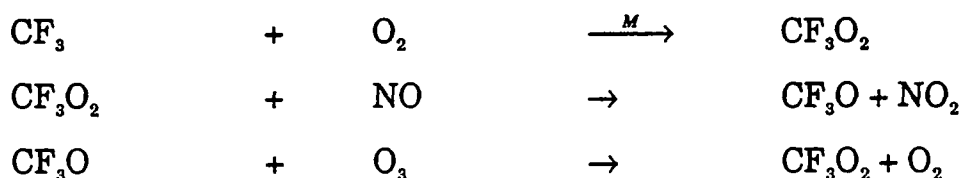


Nitrogen dioxide is photolysed in the reaction



regenerating the ozone originally destroyed in the formation of the ClO radical[15].

A major problem with “inert” C_2 halocarbons is that they often contain the CF_3 group. This is eventually released in the stratosphere. CF_3 then produces CF_3O_2 which can become involved in a catalytic chain cycle depleting O_3 .



The existence of interference reactions such as these suggest that CFCs should have a minimal impact on the global ozone layer, and this hypothesis is supported to a certain extent by historical data. However, the discovery and subsequent publication in 1985 of that data showed ozone concentrations in Antarctic regions were seriously depleted at certain times of the year prompted a renewed research effort aimed at elucidating mechanisms of atmospheric ozone depletion. This depletion in ozone concentrations over Antarctica - the so-called ozone “hole” - has been linked by many research groups to increased usage of CFCs in the western hemisphere since their introduction in the 1930s. Proponents of theories which implicate CFCs in this phenomenon have identified several different

processes which could minimise the effects of the interference reactions described above

For instance, the removal of nitrogen oxides from the stratosphere would facilitate the destruction of ozone. If the oxides were unavailable they could not combine with chlorine to form reservoir chlorine nitrate (ClNO_3). In addition some processes might alter chlorine reservoirs causing them to release active chlorine in the form of single atoms or ClO , that would destroy ozone [12]

Since 1957 the British Antarctic Survey had kept records of atmospheric composition at Halley Bay. In 1982, Joe Farman noted that these records were showing a progressive diminution in stratospheric ozone each summer above the Antarctic [17]. In October 1984 it became clear something dramatic was happening and in May 1985 [18] figures were released confirming that the ozone layer was rapidly being depleted. The average monthly level of ozone at Halley Bay for the previous 20 years or so were plotted, along with measurements of CFCs in the atmosphere of the southern hemisphere. The findings were such that the annual spring decrease in ozone was very marked and increasing. The growth in atmospheric CFCs was equally marked [17]

Scientists have put forward three possible theories to explain the continual ozone loss. Firstly a connection with the eleven year solar cycle was suggested. Periods of high sunspot activity, such as occurred around 1980, can produce large quantities of nitrogen oxides which catalyse ozone destruction.

However, measurements indicated that the concentration of nitrogen dioxide are abnormally low rather than abnormally high in the layer where ozone depletion occurs. Furthermore, the depletion occurs only quite low in the stratosphere, whereas the sunspot theory predicts that the ozone levels should continue to decrease at higher altitudes [6]

A second approach seeks to account for the "hole" in the ozone layer in terms of dynamical air motions near the pole. The mechanism of the "upwelling" of air would bring ozone-poor air from lower altitudes into the stratosphere above Antarctica. The theory predicts that all long-lived gases such as nitrogen oxides, methane and CFC-11 should be carried into the lower stratosphere by the upwelling, but observations from the Airborne Antarctic Ozone Experiment did not reflect the expected increase in concentrations there.

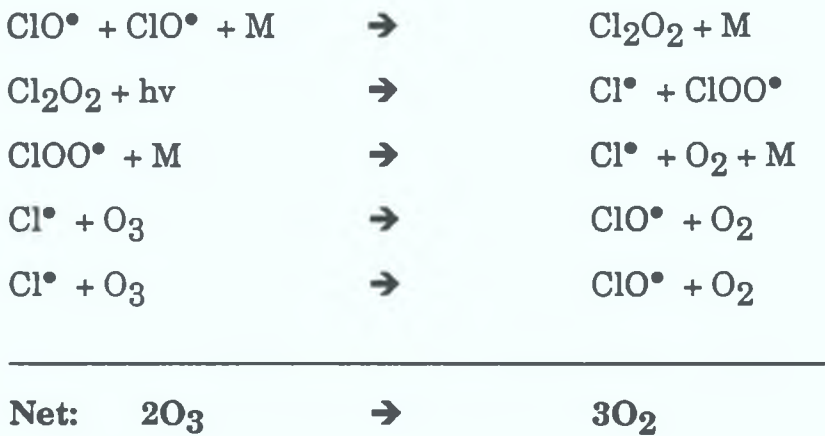
The third and now conclusive theory is that the ozone "hole" is caused by a chemical mechanism [19]. Even though many questions remain about the chemistry that drives ozone destruction, two major airborne experiments have been carried out to confirm that ozone depletion is in fact caused by a chemical mechanism [20].

Philip Solomon and colleagues at Stony Brook found the strongest evidence yet supporting the chemical destruction hypothesis [21]. The Stony Brook researchers had taken their millimetre wave spectrometer to McMurdo station, Antarctica as part of the 1986 National Ozone Expedition. Their primary objective was the measurement of microwave emissions from ClO because stratospheric chemists agreed that relatively larger amounts of the compound below 20km would be a clear sign that chemical reactions were ultimately responsible for the ozone loss in the "hole". Chlorine monoxide has been dubbed the "smoking gun" of ozone depletion, because chain reaction mechanisms proposed to destroy ozone depend on chlorine monoxide to carry the chain. Standard chemical theory called for more than 99% of the chlorine in the stratosphere to be tied up in inactive compounds such as ClONO₂ and HCl. The alternative to the inadequate Standard Chemistry was to free up chlorine through reactions of inactive compounds on the surfaces of natural aerosol particles, called Polar Stratospheric Clouds (PSCs) where the reactions are greatly accelerated.

compared with their rates when only gases are involved. Polar Stratospheric Clouds are thought to consist of water ice, nitric acid, and sulphuric acid.

Solomon and his group found high ClO in the lower stratosphere around 20 kilometres where aerosols are thickest and much of the ozone loss occurs. ClO was present at the right time and in sufficient concentrations to explain the Antarctic ozone “hole”. The single most convincing aircraft experiment was the measurement of huge amounts of chlorine monoxide by Harvard Chemistry Professor James G. Anderson and his research associate William H. Brune.

A chlorine chain first proposed by Mario J. Molina and co-workers, involving both chlorine monoxide and its dimer, is now thought to account for about 80% of the ozone loss:



Where M represents another molecule that is unchanged in the reaction. Anderson and co-workers also found evidence for a significant amount of chlorine monoxide dimer within the Antarctic ozone “hole”. Although chlorine chemistry is ultimately responsible for the ozone destruction, dynamics play a role in setting up the unique meteorology of Antarctica. Up in the stratosphere a stream of air known as the Polar vortex tends to circle Antarctica in winter. Air trapped within the vortex gets extremely cold during the Polar night because warm air from the mid-latitudes rarely

breaks through Stratospheric temperatures fall below -90°C , cold enough to form clouds even in the very dry stratosphere [22].

These high altitude clouds which are much commoner in the Antarctic region than the Arctic, form in the winter when the absence of sunlight and the isolation of the Antarctic region lead to stratospheric temperatures that often reach -80°C [12] It is likely that in the winter the nitrogen compounds condense and freeze becoming bound up in cloud particles They would then be unavailable to react with chlorine At the same time the cloud particles might facilitate the conversion of the chlorine reservoirs into active chlorine It is possible that the PCS's particles trap and slowly modify the major chlorine reservoirs preparing ClO to make a rapid "escape" when the sun shines [12,21,23].

The CFC theory of the ozone "hole" must explain not only how "normal" interferences to the Cl catalytic cycle are impeded during the Antarctic Spring but also how a uniquely polar phenomenon is overcome. In the polar spring the sun is still rather low on the horizon As a result, there is a reduction in the radiation-driven breakdown of ozone molecules and consequently a reduction in the amount of free oxygen atoms available for the chlorine catalytic cycle. The presence of a reasonable quantity of bromine (Br) in the Polar Stratosphere could help to compensate for this lack of free oxygens [12] Bromine atoms can react with ozone to form a bromine monoxide radical (BrO) and an oxygen molecule. The bromine monoxide in turn can react with chlorine monoxide forming another oxygen molecule and releasing free chlorine and bromine atoms (The net result is the conversion of ozone into oxygen) Such a combined chlorine-bromine catalytic cycle can operate smoothly even when free oxygen atoms are relatively scarce in the environment hence overcoming this Polar Phenomenon Figure 1.1 3 summarises the major bromine reactions in the stratosphere

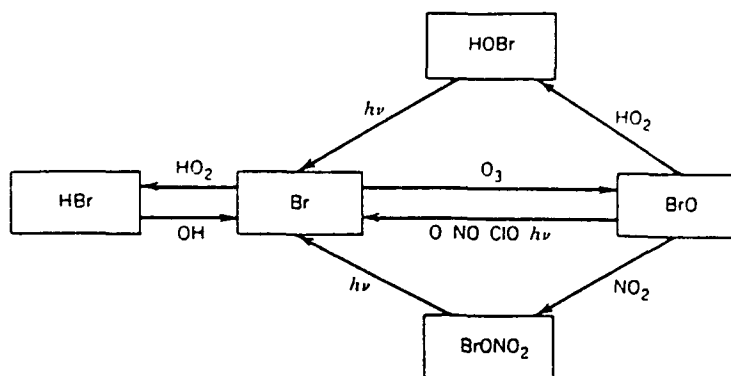


Figure 1.1.3

Schematic diagram showing the major reactions of bromine in the stratosphere [16].

Whether bromine also has an important function, as theory suggests, is not clear. Preliminary findings of the Airborne experiment indicate that the concentration of BrO, a few parts per trillion seems to argue against the proposed role in accelerating ozone destruction [23]. Theory requires a level of bromine significantly larger than this for bromine chemistry to be the dominant factor.

Chlorofluorocarbons may affect the environment in two ways, (1) in the stratosphere they are photolysed to provide chlorine atoms, which then react to destroy ozone as earlier discussed, and (2) since CFCs are strong infrared absorbers, they also act as greenhouse gases thus contributing to global warming. Each molecule of CFC gases traps 10,000 times more heat than a molecule of CO₂ [24].

Concern has been expressed over the use of halogenated anaesthetics: halothane (CF₃CHClBr), enflurane (CF₂HOCF₂CFCIH) and isoflurane (CF₂HOCCHClCF₃) because of their potential for stratospheric ozone

destruction [25]. These halogenated anaesthetic agents are the most widely used general anaesthetic agents in the Western World. At least 98% of the volume of anaesthetic agents actually used in the hospital is released into the atmosphere. Accurate figures for production and use of these compounds are not readily available, but a conservative estimate of the yearly emission rates of these species has been obtained from a survey carried out for the period Nov. 1987 to Nov. 1988 [26]. Because reaction with hydroxyl (OH) radicals is likely to be the main homogeneous sink for these species in the troposphere, Brown et al [27] have measured absolute rates of reaction with OH. Comparison with a one-dimensional model [28] indicates that the lifetimes of halothane, enflurane and isoflurane with respect to this reaction are 2,6 and 5 years respectively. The rates of emission of these halogenated anaesthetic agents are very low relative to other halogenated species such as methyl chloroform which has been identified as a major source of chlorine in the atmosphere. However, these anaesthetic agents were only introduced into clinical practice in the early 1960s and their rate of emission has increased dramatically since then [26]. The most important day-time degradation of the anaesthetic molecules [16] will be a reaction with OH radical.



Photolysis is another potential loss process, but the ultraviolet spectra of enflurane and isoflurane show absorption onsets at $\lambda < 290\text{nm}$ so that photolysis of these compounds does not occur in the troposphere, only in the stratosphere is there significant photolysis. For the bromine-containing species halothane, the onset of absorption seems to be similar; but there may be a long-wavelength tail as found for CF_2ClBr [29,30].

In addition to the small ozone depletion potentials, the global market for the anaesthetics 1,000,220 and 800 tonnes for halothane, enflurane and isoflurane [31], is much less than for CFC-11 and CFC-12, 350,000 and 400,000 tonnes [32]. It is unlikely therefore, that halothane can be responsible for any more than one thousandth of 1% of all ozone destruction [33]. While it is unlikely that the level of emissions of these anaesthetics will rise to that of methyl chloroform [26], it is possible that unchecked emissions of these and other species could lead to a situation arising where their significance could be much greater than is currently anticipated, creating a need therefore for increased environmental awareness and importance to the experimental work summarised in the following chapters.

Chapters 2 and 3 summarise findings obtained from a study of both the photooxidation and chlorine-atom sensitised oxidation of the routinely used anaesthetic, halothane. The aforementioned mechanisms are important reaction pathways for halothane and analogous compounds in the troposphere and stratosphere respectively.

Finally Chapter 4 summarises work carried out to determine tropospheric lifetimes for a series of brominated and chlorinated alkanes. The lifetimes of these compounds were calculated from their OH radical and Cl atom rate constants. However, for the purposes of this thesis only the Cl atoms rate constant are experimentally studied and the corresponding OH rate constants investigated by a colleague will be discussed later in that chapter.

1.2 REFERENCES

- [1] J S Levine, "Photochemistry of Atmospheres" Academic Press, London
- [2] D R Bates and M Nicolet, Geophys Res., **55** 301,(1950)
- [3] F.S Rowland, New Scientist, 717, December, (1974)
- [4] B A Thrush, Phil Trans R Soc (London), **A296**, 149, (1980).
- [5] P J. Crutzen, Quart. J. Roy Meteorol Soc **96**, 320, (1970)
- [6] H.S. Johnston, Science, **173**, 517, (1971)
- [7] M.J. Molina and F.S. Rowland, Nature **249**, 810 28 June, (1974).
- [8] R.J. Cicerone, R.S. Stolarski and S Walters, Science, **185**, 1165, (1974).
- [9] S.C. Wofsy and M.B McElroy, Can. J. Chem., **52**, 1510, (1974).
- [10] P.J. Crutzen, Can. J Chem., **52**, 1569 (1974).
- [11] R. Stevenson, Chemistry in Britain, **26** (8) 732 (1990)
- [12] R.S. Stolarski, Scientific American, **258** (1), 20 (1988).
- [13] National Research Council, Stratospheric Ozone Depletion by Halocarbons: Chemistry and Transport, National Academy of Sciences, Washington D C, (1979).
- [14] National Research Council, Causes and Effects of Changes in Stratospheric Ozone update 1983, National Academy Press, Washington D C., (1984)
- [15] H.W Sidebottom, Proceedings of Seminar Air Pollution - Impacts and Control, National Board for Science and Technology, 52, (1979)
- [16] B.J. Finlayson - Pitts and J.N. Pitts Jr. "Atmospheric Chemistry : Fundamentals and Experimental Techniques", Wiley, New York, (1984)

- [17] J.C Farman, New Scientist, **116** (1586), 50, (1987)
- [18] J.C. Farman, B Gardiner and J D Shanklin, Nature **315**, 207, (1985)
- [19] B.G Levi, Physics Today **41**(7), 17, (1988)
- [20] P.S. Zurer, Chemical and Engineering News, **65** (44), November 2, 22, (1987).
- [21] P Solomon, A. Parrish and R. deZafra, Spring Meeting of the American Geophysical Union, 18 to 21 May, Baltimore, Maryland, USA.
- [22] P.S. Zurer, Chemical and Engineering News, May 30, 16, (1988)
- [23] R.A. Kerr, Science **238**, 156, (1987).
- [24] United Nations Environment Programme "The Changing Atmosphere", Nairobi, Kenya UNEP Environment Brief No. 1.
- [25] J. Norreslet, S. Friberg, T.M. Neilsen and U. Romer, The Lancet, 719 April 1, 719, (1989).
- [26] P. McLoughlin, ph.D thesis, Dublin City University, (1992)
- [27] A.C. Brown, C.E. Canosa-Mas., A.D. Parr, J.M.T. Pierce and R.P. Wayne, Nature, **314** 635, (1989).
- [28] J.K. Hammitt, F Camm, P.S. Connell, W E. Mooz, K. A. Wolf, D J. Weubbles and A. Bamezai., Nature **330**, 711, (1987)
- [29] J.M Dumas, P Dupuis, G Pfister-Guillouzo and C Sandorfy, Can. J Spectrosc , **26** (3), 102, (1981)
- [30] B.R Lewis, L. Berzius and J M Carver, Appl Opt **25**, 2647, (1986).
- [31] R.C Rogers and J.A S Ross, The Lancet, 1209, May 27, (1989)

- [32] CMA Fluorocarbon Program Panel Production, Sales and Calculated Release of CFC-11 and CFC-12 through 1986 (Chemical Manufacturers Association, Washington D C , (1987)
- [33] J.M.T. Pierce and S P.K Linter, The Lancet, 1011, May 6th, (1989).

CHAPTER 2.0

KINETICS AND MECHANISM OF THE GAS PHASE PHOTOOXIDATION OF THE ANAESTHETIC, HALOTHANE

2.1 INTRODUCTION

Chapter one has been concerned primarily with a review of the environmental impact of chlorofluorocarbons (CFCs) on stratospheric ozone depletion and the importance of halogen atoms (chlorine and bromine) in the destruction of ozone

Halothane used extensively in the medical field world wide belongs to this class of compounds, chlorofluorocarbons CFCs may reside in the troposphere for years, slowly diffusing into the stratosphere where light of sufficient energy to break bonds is available and photodissociation can be an important removal mechanism

For the bromine-containing species, halothane, absorption onsets at $\lambda < 290 \text{ nm}$ [1], so that photolysis of these compounds does not occur in the troposphere, only in the stratosphere in there significant photolysis All anaesthetic agents except cyclopropane show broadly similar patterns of absorption with maxima in the range 188 - 204 nm [2] The absorption spectrum of halothane in the vapour state shows a maximum absorption at 204 nm with a tail extending as high as 290 nm [1], at 253.7 nm absorbance was only 5% of the maximum of 204 nm, in aqueous solution maximum absorption was at 200 nm but the tail was found to be unchanged When light of sufficient energy to break these bonds is available, then photodissociation can be an important mechanism thus resulting in



The free radical or haloalkyl radical in this study can react with O_2 to form oxidation products and these products may further react, eventually liberating all chlorine atoms to take effect on the ozone layer

The work carried out in these studies involve a preliminary investigation into the gas phase photooxidation of this halogenated alkane, at wavelengths < 290 nm and an attempt to elucidate a reaction mechanism

With the exception of some fluoromethanes absorption of light in the long wavelength region appears to result almost exclusively in dissociation at the weakest C-X bond. The primary products are thus an alkyl or haloalkyl radical and a halogen atom



In the absence of any direct evidence concerning the mechanism of oxidation of halothane, it is reasonable to consider published work on analogous compounds in an attempt to predict the atmospheric loss processes for halothane

Shanahan [3] has studied the kinetics and mechanism for the oxidation of methyl chloroform (CCl_3CH_3)

Release of methyl chloroform into the atmosphere yields CCl_3CH_2 radicals in the troposphere via hydroxyl radical attack. The principal recognised atmospheric sink for methyl chloroform is the reaction [4],



and $\text{CH}_3\text{CCl}_2^\bullet$ radicals in the stratosphere by photolysis



$$(\lambda = 170 - 240 \text{ nm})$$

An understanding of the oxidation reactions of the chloroethyl radicals generated in the above reactions is of some importance since they

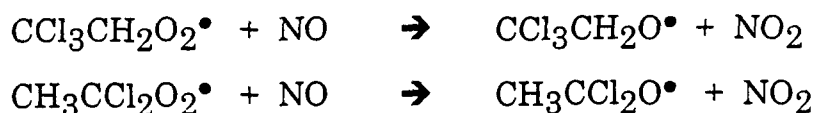
may liberate further chlorine atoms via reactions in the atmosphere. The removal mechanisms for these species has not been completely established, although it has been generally assumed that the remaining chlorine atoms will eventually be released.

Shanahan showed that $\text{CCl}_3\text{CH}_2\text{Cl}$ was the major product from the photolysis of chlorine in the presence of methyl chloroform. However, photolysis of chlorine/methyl chloroform mixtures at $26 \pm 3^\circ\text{C}$ in the presence of O_2 gave phosgene.

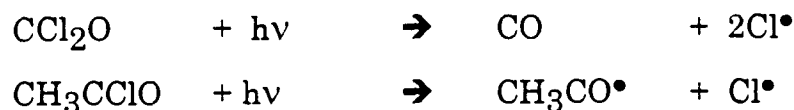
The primary products of $\text{CCl}_3\text{CH}_2^\bullet$ radical oxidation are dependent on the relative importance of the various reaction pathways for loss of 1,1,1 trichloroethoxy radicals ($\text{CCl}_3\text{CH}_2\text{O}^\bullet$). The removal rate of methyl chloroform in the presence of O_2 was found to be considerably increased compared to that observed when CH_3CCl_3 was photolysed in the presence of bromine. Thus it appears that photolysis in the presence of O_2 results in a chain reaction. To account for these observations, it is proposed that chlorine atoms produced in the initial and propagation steps lead to the photosensitised chain oxidation of methyl chloroform.

The products identified from the photolysis of methyl chloroform ($\text{CH}_3\text{CCl}_2^\bullet$) in the presence of O_2 gave phosgene as the major chlorine-containing oxidation product with smaller amounts of acetyl chloride, in good agreement with the work of Christiansen et al [5].

In the atmosphere it is predicted that the peroxy radicals will be converted to the corresponding chloroethoxy radicals by reaction with nitric oxide in reactions analogous to the use of alkyl peroxy radicals.



Further photolysis of phosgene and acetylchloride release the remaining chlorine atoms

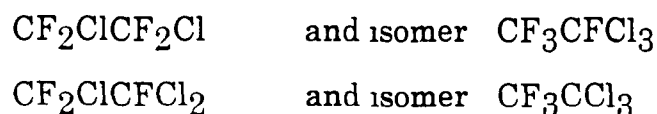


In the troposphere, the chlorine atoms will eventually be washed out as HCl, while in the stratosphere they can enter into the catalytic ozone destruction pathway [3]

While the photolysis of chlorofluoromethanes has received considerable attention mainly because of their behaviour in the atmosphere, photochemistry of the chlorofluoroethanes has never been studied systematically. Tominaga and co-workers [6], have recently observed that the rupture of bonds occurs more selectively in the photolysis than in the radiolysis of chlorofluoroethanes, only the C-Cl bonds are broken readily whereas the C-F, or C-C bonds are seldom broken in the photolysis

However, there appears to be a similarity in the mechanisms for the C-Cl bond rupture between the photolysis and radiolysis the rupture of two C-Cl bonds is favoured in the symmetrical or less asymmetrical isomers

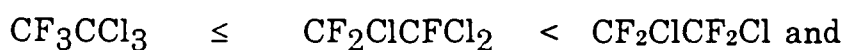
Two isomeric pairs of chlorofluoroethanes were studied,



Major products formed in photolysis of chlorofluoroethanes (with bromine as scavenger) are mono and dibromochlorofluoroethanes derived from the rupture of one or two C-Cl bonds of parent compounds, followed by scavenging with bromine

Product distribution reveals that the rupture of one or two C-Cl bonds occurs predominantly in the photolysis of chlorofluoroethanes than in the radiolysis whereas the yields of the photolysis products from the C-C or C-F rupture are far smaller than those observed in the radiolysis of similar compounds. This is not surprising if we consider the large energy difference involved in both types of reaction. The relative importance of the two models of C-Cl rupture (ie one C-Cl or two C-Cl) in the photolysis of these compounds largely depends upon the structure of their molecules (ie if symmetrical or asymmetrical). The ratio of the double C-Cl rupture is larger for the symmetrical or less asymmetrical than for asymmetrical and hence the proximity of chlorine atoms on one carbon atom favours the rupture of a single C-Cl bond, while two chlorine atoms or adjacent carbon atoms may be released simultaneously leaving an olefinic bond behind.

Fukumizu et al [7] found similar reactions to Tommaga et al [6], for the radiolysis of certain chlorofluoroethanes and chlorofluoropropanes. In addition they found that the G-value for the C-F bond rupture increases in the order



indicates the dependence on the number of C-F bonds in the molecules. It is worth mentioning that the C(1) - C(2) bond appears to be remarkably weaker than the C(2) - C(3) bond in the chlorofluorocarbons.

Another halogenated ethane to undergo photochemical investigation was 1,1,2 trichloro - 1,2,2 trifluoroethane. The radiation chemistry of such compounds presents an interesting study because of the three possible types of bond rupture i.e. the C-C, C-F and C-Cl bonds. Kananjian and Horrell [8] deduces a mechanism for the compound mentioned in the liquid phase from a knowledge of the final products, and product analyses was made using a combination of GC and Mass Spectrometry for distinguishing specific isomers. Previous investigations [9] has shown that radiolytic scission of the C-C bond is of the same order as the C-F bond break in the γ radiolysis of liquid hexafluoroethane and other reports of predominant C-F bond rupture have been made by Fallgatter and Hanrahan [10] and MacKenzie et al [11]. This however is not in accord with the results obtained in an ESR study by Fessenden et al [12] of the production of other than the CF_3 radical indicating little or no C-F bond scission and in agreement with Kananjian and Horrell. [8]

Haszeldine and Nyman [13] investigated the photolysis and photochemical oxidation of similar chlorofluoroethanes, namely CF_3CCl_3 , CF_3CHCl_2 and $\text{CF}_3\text{CH}_2\text{Cl}$. Light of wavelength >220 nm was used and molecular oxygen was added to effect photochemical oxidation. Oxidation of the compounds CF_3CHCl_2 and $\text{CF}_3\text{CH}_2\text{Cl}$ yielded trifluoroacetyl chloride and trifluoroacetic acid and yields were found to greatly increase when chlorine was used as initiator, by using bromine or chlorine as sensitiser, carbon-carbon bond cleavage could often be substantially prevented, and a free-radical mechanism was proposed again for these reactions.

The compound CF_3CCl_3 was oxidised to carbonyl fluoride. The results of this work establishes that their CH_2Cl , CHCl_2 or CCl_3 group can be oxidised to COCl or CO_2H in good or excellent yield.

Several workers [14-18] have extensively investigated the 147 nm photolysis of halogenated ethanes, particularly chlorinated and mixed halogenated ethanes

The 147nm photodecomposition of α,β disubstituted chloro and chlorofluoroethanes has shown that the formation of the major product olefins is associated primarily with dehalogenation processes. HCl elimination also occurs but not to the extent as found in the case of some α -substituted chloro and chlorofluoroethanes, where it is the principal reaction channel [14-16]. Tschuikow-Roux et al [14-17] postulated that dehalogenation occurs primarily via molecular elimination. However, in later studies of the 147 nm photolysis of $\text{CF}_2\text{ClCH}_2\text{Cl}$ [19], $\text{CF}_2\text{ClCHCl}_2$ [20] and CF_3CHCl_2 [21] they obtained evidence that the principal mode of decomposition to the corresponding olefins involves the production of Cl atoms, either by very rapid sequential (near simultaneous) C-Cl bond scission reactions or by the dissociation of an excited Cl_2^* molecule produced by molecular elimination in the primary process, further evidence on the two Cl-atom elimination was made by Yano et al [22] on the re-examination of $\text{CH}_2\text{ClCH}_2\text{Cl}$. The major primary process is the molecular production of ethylene ($\phi\text{C}_2\text{H}_4 = 0.67$) by two Cl-atom elimination. Other observed reaction products are $\text{C}_2\text{H}_3\text{Cl}$ and smaller quantities of C_2H_2 and $\text{CH}_2\text{ClCHCl}_2$. Approximately half of the vinyl chloride yield derives from primary molecular elimination of HCl, while the balance can be attributed to radical reactions.

Much research has been carried out on other fluorinated alkanes. In particular Phillips and Trotman-Dickinson [23] developed a chemically activated system which would permit a competitive comparison of the rates of HF and HCl elimination from the same energised fluoroalkane molecules,

formed by the combination of fluoromethyl (CF₃) radicals produced in the photolysis of the appropriate pure ketone or ketone mixtures.

The general reactions of an energised fluoroalkane A* can be written as:



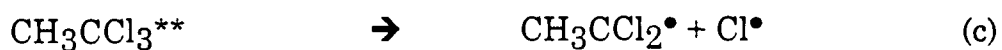
The initial vibrational energy content of the energised molecule is primarily a function of the strength of the C-C bond which is formed by radical combination and the temperatures of the system. There are several conflicting factors involved in the estimation of the C-C bond strength in the fluoroethanes. Thomarson and Pritchard [24] suggested that fluorination tends to weaken the C-C bonds in ethane in the same way as chlorination.

The primary process involved with the photooxidation of chlorinated ethanes has been investigated by another worker, Yuan [25]. 1,1,1, trichloroethane, and 1,1,2,2 tetrachloroethane were photolysed at near UV light 200-400 nm and in each case at least two excited states were found. For the CH₃CCl₃, the lower excited state which was produced mainly at λ>220 nm was found to decompose in the following manner.



Similar findings of equation (a) and (b) have been found previously with Calvert et al [26] and other workers [27, 28].

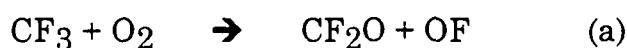
The higher excited $\text{CH}_3\text{CCl}_3^{**}$ molecule was produced predominantly at $\lambda < 220 \text{ nm}$ decomposes as follows



Reaction (d) may occur directly or via an excited $\text{C}_2\text{H}_3\text{Cl}_2^\bullet$ radical as intermediate

Peroxy radicals have long been postulated as intermediate chain carriers in numerous studies in the photooxidation of various halocarbons [29] and the major product of radiation and photochemical oxidation is the corresponding carboxyl halide [30], a reaction step currently envisaged for halothane photooxidation

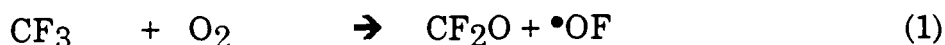
In a report on the photooxidation of CF_2I , Heicklen [31] proposed direct formation of CF_2O upon the reaction of CF_3 with oxygen



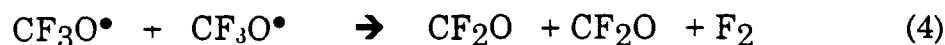
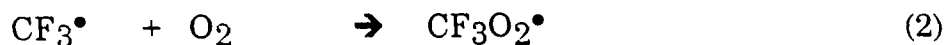
Several laboratory investigations [32-36] have probed kinetic and mechanistic determinations for oxidation by molecular oxygen of the trifluoromethyl radical $\text{CF}_3^\bullet$

A pioneering study by Frances and Hazeldine [30b] examined the gas phase photooxidation of trifluoromethane, trifluorobromomethane, and trifluoroiodomethane. In each case the primary product was carbonyl fluoride, CF_2O . These initial experimental observations were subsequently confirmed by Heicklen [31] who suggested two mechanisms capable of explaining the results

The first proposal centres on a direct transformation of CF₃ radicals



The second postulated mechanism involves the intermediacy of peroxy and oxyfluoromethyl radicals



Both of these mechanisms (1) and (2)-(4) are consistent with the recent quantum yield determinations for CF₂O production in which

$$\phi_{\text{COF}_2}^{184.9} = 1.02 \pm 0.10 \text{ and } \phi_{\text{CF}_2\text{O}}^{253.7} = 1.05 \pm 0.11$$

for the photooxidation of CF₃Br [37] and CF₃I respectively [38]

However, the two schemes above are subject to kinetic and thermochemical criticism. Self reactions of CF₃OO• and CF₃O• are endothermic and must remain doubtful on thermochemical grounds, however, verification of the participation of CF₃OO• and CF₃O• radicals in the mechanism of the oxidation of CF₃ radicals has been made for the first time in a CF₃X/O₂ photolysis system, under low-temperature matrix conditions employed, CF₂O is not formed by either of two previously proposed gasphase mechanisms involving •OF radicals or successive self reactions of CF₃OO• and CF₃O•. By contrast two types of CF₂O/IF molecular complexes are produced and these are suggested to originate from the unimolecular dissociation of CF₃OI, which is formed via the intermediary of CF₃OOI [39]

Finally one must look at the significance of photooxidation and (O¹D) atom reactions of fluorochlorocarbons and of OH radical reactions as halocarbon sinks in both the troposphere and the stratosphere was

investigated by Atkinson et al in 1976 [40] Based on product analysis they identified COF_2 as the photooxidation product from CHF_2Cl and CF_2Cl_2 , COFCl from CFCl_3 and COCl_2 and CO_2 from CCl_4 with quantum yields near unity measured for CCl_4 , CFCl_3 and CF_2Cl_2 These quantum yields were in good agreement with the value determined by Milstein and Rowland [41]

As in (O^1D) atom studies reactant loss and product formation were monitored by Infrared spectroscopy, similarly for our work with substituted ethanes the same technique was employed

The work carried out in this thesis involves a preliminary investigation into the gas phase photooxidation of halothane (CF_3CHClBr) at wavelengths $<290\text{nm}$, similar to the compounds investigated in this review. However, the introduction of halogens into the alkane structure shifts the absorption to higher wavelengths facilitating photooxidation at lower energy

Chapter two of this thesis involves an experimental investigation of the gas phase photooxidation using techniques available in order to elucidate the mechanism and kinetics of the reaction Preliminary experiments involved determining the major photooxidation products using IR spectroscopy These fundamental investigations were used to establish the initiation process and propagation steps as a guideline for further experiments Techniques used in the study included GC with FID detection and UV and IR spectroscopy

2.2 EXPERIMENTAL

2.2.1 Materials

2-bromo-2-chloro-1,1,1-trifluorethane (hospital grade, stated purity 99.99%) was supplied by Imperial Chemical Industries and Hoechst Ireland Ltd. Trifluoroacetyl chloride (98.0% min) and carbonyl fluoride (98.0%) were obtained from Fluorochem Ltd. All materials were degassed by the freeze-pump-thaw method and further purified by bulb-to-bulb distillation on the vacuum line prior to use. Carbonyl fluoride was stored in a blackened bulb to prevent decomposition. Oxygen (Ultra high purity) was supplied by B D H. Chemicals Ltd.

2.2.2 Apparatus

The apparatus shown in Figure 2.2.1 consisted of a conventional mercury-free, high-vacuum line, made of "Pyrex" glass. The vacuum was maintained by means of an Edwards silicone oil vapour diffusion pump (model E040/55), backed by an Edwards high-vacuum double stage rotary pump (model E2M2). Greaseless taps using "Teflon" o-rings, supplied by J Young Ltd, Acton was used. Reactant pressures in the 0-100 torr range were measured on a Pressure Transducer (MKS Baratron, 122 AA), while reactant pressures in the 0-750 torr range were measured on an Edwards EPS 10 Pressure Transducer. Vacuum Measurement was made by means of an Edwards Pirani Gauge, (Model PRE 10K), in conjunction with a Penning Gauge, (Model P25-EK). The volumes of bulbs A (1143cm^3), B (1174cm^3), C (1178cm^3) and D (325cm^3) were measured prior to attachment to the main line using a weight difference technique.

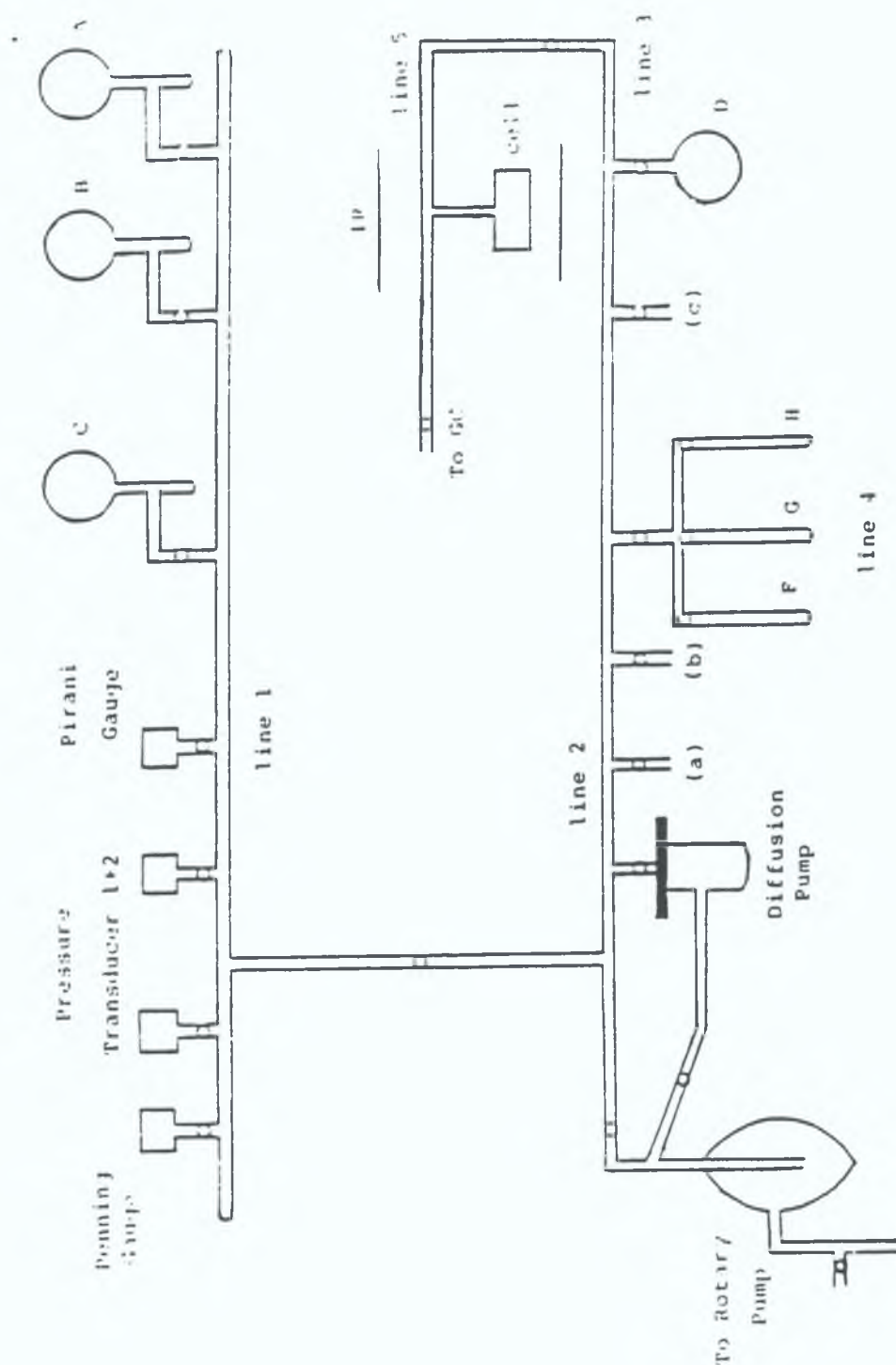


Figure 2.2.1
Diagrammatic representation of the conventional Mercury Free high vacuum line used in this work

The volumes of lines 1+PT1 (640cm³), line 1+PT2 (653cm³), 2 (680cm³), 3 (23cm³), 4 (49cm³), and 5 (85cm³) were measured by sharing known pressures of air into them from bulb D. Bulb D in Figure 2.2.1 was the primary volume from which each volume within the vacuum line was determined using Boyle's law,

$$\begin{array}{lcl} \text{Volume} & \propto & 1/\text{pressure} \\ P_1V_1 & = & P_2V_2 \end{array}$$

Gaseous reactants, including O₂, CF₃COCl and CF₂O were stored in bulbs A, B and C. 2-bromo-2chloro-1, 1,1-trifluoroethane was stored in reservoir F.

Reaction Vessel I, was cross-shaped with optically flat quartz windows at opposite ends (5.0cm diameter) and NaCl windows on the other arms. It had a volume of 235cm³. Reaction Vessel II was T-shaped with sodium chloride windows at each end (2.5cm diameter). The volume was 211cm³.

These reaction vessels on different occasions were housed in the sample compartment of a Perkin-Elmer Infrared Spectrophotometer (Model 297). Light entered the reaction vessel from the source positioned at right angles to the infrared beam. The light source was an "Applied Photophysics" medium pressure mercury lamp (400 watts) powered from its own intensity stabilised supply. The light intensity was varied by placing gauzes of different mesh-size between the lamp and reaction vessel. The gauze transmissions had previously been calibrated on a Pye Unicam UV-Visible Spectrophotometer (Model SP8-100).

2.2.3 Procedure

The apparatus was pumped down with liquid nitrogen placed around the traps to give a vacuum of 10^{-2} mBar (measured by the Pirani Gauge) and subsequently to a vacuum of 10^{-4} - 10^{-5} mBar (measured by the Penning Gauge). The required pressures of 2-bromo-2chloro-1, 1, 1-trifluoroethane, trifluoroacetyl chloride or carbonyl fluoride were measured (by means of the pressure transducer) into the system and frozen into bulb D. Oxygen and nitrogen were measured using the pressure difference technique (measured out excess of gas to ensure that when shared into a larger volume, the pressure drop matched that of required pressure in mixing bulb D). The reaction mixture was allowed to reach room temperature for at least 30 minutes before sharing into the reactant vessel. The water surrounding the lamp housing was turned on 1-2 minutes before turning on the lamp in order to avoid the lamp overheating. The lamp was allowed to stabilise for 10 minutes before the shutter was raised at the start of each run. The reaction time was recorded by means of a stop-clock and the temperature was found to remain constant to $\pm 1^{\circ}\text{C}$.

When the run was completed, the shutter was replaced and the irradiation time noted. The reaction mixtures were then analysed either by infrared spectroscopy or gas-liquid chromatography or a combination of both techniques.

2.2.4 Analysis

For earlier work, a Gow Mac Gas Chromatograph (Series 752) was used for the gas chromatographic analyses. Injector and column oven temperature shared the same control, but separate temperature controls were used for the detector and column oven. Later studies employed a Phillips Pye Unicam PU 4550 Gas chromatograph equipped with an F.I.D. Separate temperature controls were used for column oven, injector and detector. The carrier gas used was nitrogen (O.F.N. grade, from I.I.G.) with needle valve controls. Hydrogen H-10 (Murex) was used as carrier gas for the thermal conductivity detector, when in operation. The chromatograms were recorded on a Spectra-Physics integrator (Model SP 4270/4290).

The GC column packings and operating conditions were selected according to the compounds being identified. The chromatographic analyses of reaction mixtures containing 2-bromo-2-chloro-1, 1, 1-trifluoroethane and oxygen were carried out on a 2m stainless steel column packed with 10% SE-30 on chromosorb WHP 80-100 mesh. The column temperature was maintained at 35°C, while the injector and detector were operated at 50 and 200°C respectively. The carrier flow rate was 30cm³/min.

A Perkin Elmer (Model 297) Infrared Spectrophotometer was used for all spectroscopic analyses. The reaction was stopped at different irradiation times by placing a shutter in front of the light source. A complete infrared spectrum was then run from 4000cm⁻¹ to 600cm⁻¹. To convert optical density to pressure, it was necessary to perform calibrations by placing known pressures of reagents into the reaction vessel and recording the infrared spectra. Calibration curves relating the pressure of a particular

reagent to the optical density of a given characteristic band for the compound were obtained

The characteristic infrared absorption bands (cm^{-1}) used to identify the reactants and corresponding products are listed in Table 2.2.1

Table 2.2.1. Characteristic IR absorption Bands

COMPOUND	BANDS (cm^{-1})				
CF_3CHClBr	1307	1262			
CF_3COCl	1820	1280	1240	1200	940
CF_2O	1980	1250	980	775	
CO_2	2350	2290	1330	667.8	
SiF_4	1040				

When using gas chromatography to monitor the photooxidation profile for the anaesthetic, and corresponding photooxidation products, it proved useful to prepare standard calibration curves

Standard curves for the anaesthetic were established in the concentration range from 0 to 15 torr in N_2 with P_{Total} equal to 150 torr. These calibration mixtures were prepared on the vacuum line and transferred to the reaction cell by the same procedure as photolysis mixtures. After five minutes the cell contents were opened to the GC and injected onto the column using the automatic gas sampling valve. Similarly calibration curves using authentic samples of the photooxidation products, trifluoroacetyl chloride and carbonyl fluoride were prepared in the same manner.

Having established these curves, it was then possible to determine the concentration of the anaesthetic and photooxidation products at each photolysis time by extrapolation from standard curves

2.2.5 Identification of reaction products

Photolysis of $\text{CF}_3\text{CHClBr}/\text{O}_2$ mixtures at $<290\text{nm}$ and $20 \pm 2^\circ\text{C}$

Products and reactants were identified by comparison of their infrared spectra with those of authentic samples. The infrared spectrum of the reaction mixtures showed six main absorption bands (Figures 2.2.2 and 2.2.3). Two of the bands, centred at 1307cm^{-1} and 1262cm^{-1} were ascribed to halothane. Five of the absorption bands centred at 1820cm^{-1} , 1280cm^{-1} , 1240cm^{-1} , 1200cm^{-1} and 940cm^{-1} were ascribed to trifluoroacetyl chloride.

Pressure measurements were made from optical density measurements on the band centred at 1820cm^{-1} . Carbonyl fluoride was identified and pressure measurements made from its main band at 1980cm^{-1} . The band centred at 2350cm^{-1} was ascribed to carbon dioxide. Reactant concentration was determined from optical density measurements on the band centred at 1307cm^{-1} . The remaining band, centred at 1040cm^{-1} , was assigned to silicon tetrafluoride.

When infrared analyses were complete, the reaction mixtures were injected onto the chromatographic column. In cases where permanent gases CO_2 and CO were to be identified, a thermal conductivity detector was employed and hydrogen was used as carrier gas. Products and reactants were identified by comparison of retention times with authentic samples.

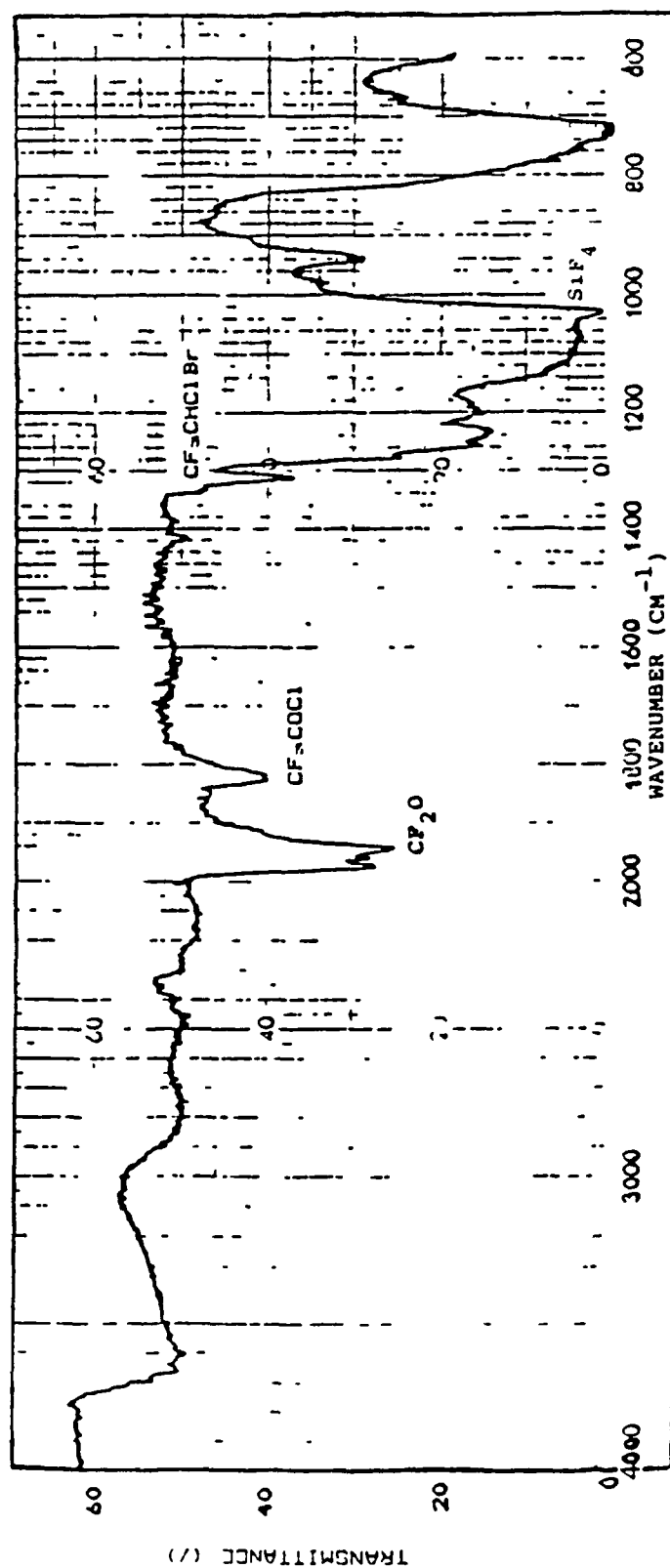


Figure 2.2.2
 Infrared spectrum of 4 torr CF3CHClBr and 50 torr O2 after 50 minutes photolysis; $\lambda < 290\text{nm}$ and 20°C

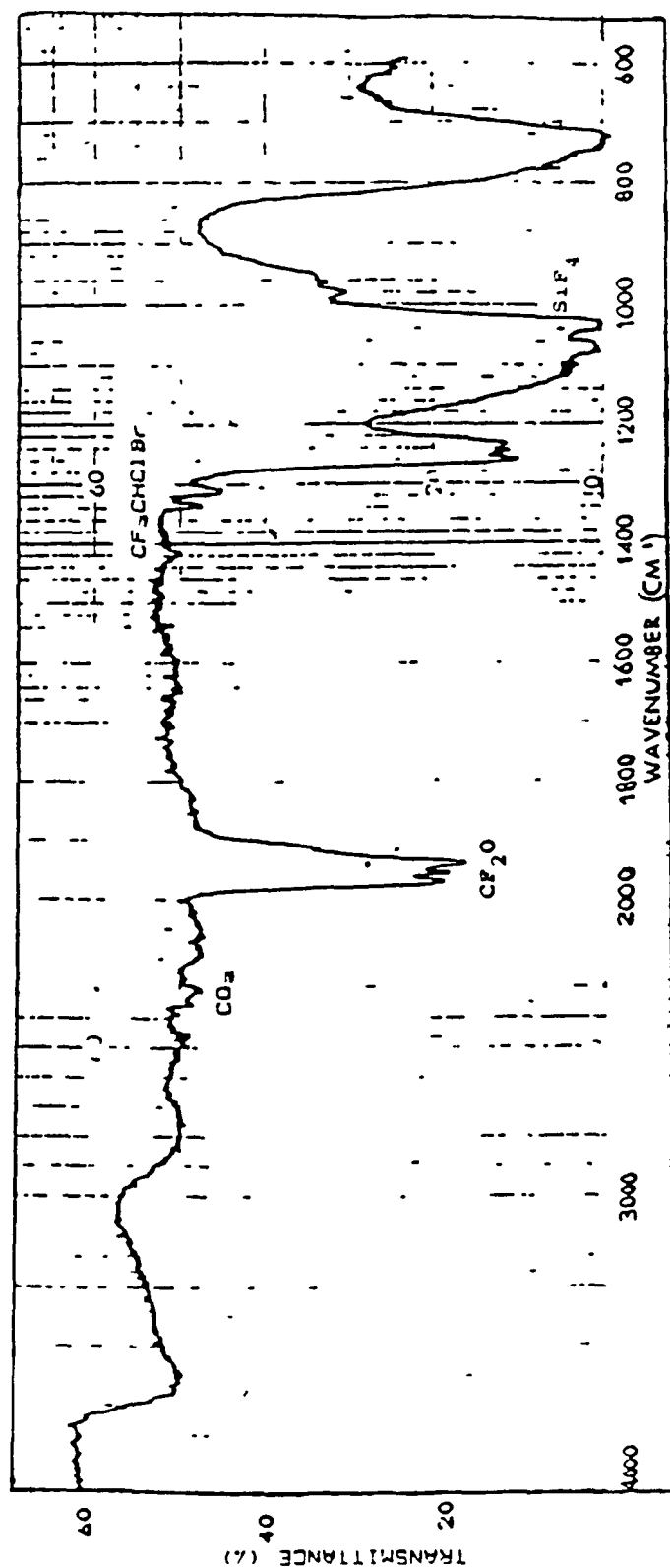


Figure 2.2.3
Infrared Spectrum of 4 torr CF_3CHClBr and 50 torr O_2 after 211 minutes photolysis; $\lambda < 290\text{nm}$ and 20°C

2.3 RESULTS

Photolysis of $\text{CF}_3\text{CHClBr}/\text{O}_2$ mixtures $\lambda < 290$ nm and $20 \pm 2^\circ\text{C}$

Preliminary reaction initiation studies:

To determine whether light was necessary for reaction to proceed, reaction mixtures of 30 torr halothane and 50 torr oxygen were monitored by GC in the presence and absence of light. The mixture was photolysed for two hours and then injected. It was found that no measurable loss of halothane took place in the absence of light.

Secondly to illustrate that light of certain wavelengths was responsible for photooxidation, and to narrow down the wavelengths responsible for reaction photolysis, photolysis of again 30 torr halothane in 50 torr oxygen was carried out for two hours with and without a Corning 0-52 optical filter (which excluded light < 335 nm). The reaction was monitored again by GC having photolysed with the CS-O52 filter, and no photolysis was found to have taken place as expected.

Photooxidation studies:

Initial work involved monitoring the decay of halothane and the appearance of reaction product IR bands over extended photolysis times and in the case of CF_3COCl by gas chromatography.

The output of the medium pressure lamp was unfiltered in these experiments. Figures 2.3.1 - 2.3.5 show the absorption bands produced during the photolysis of halothane in oxygen.

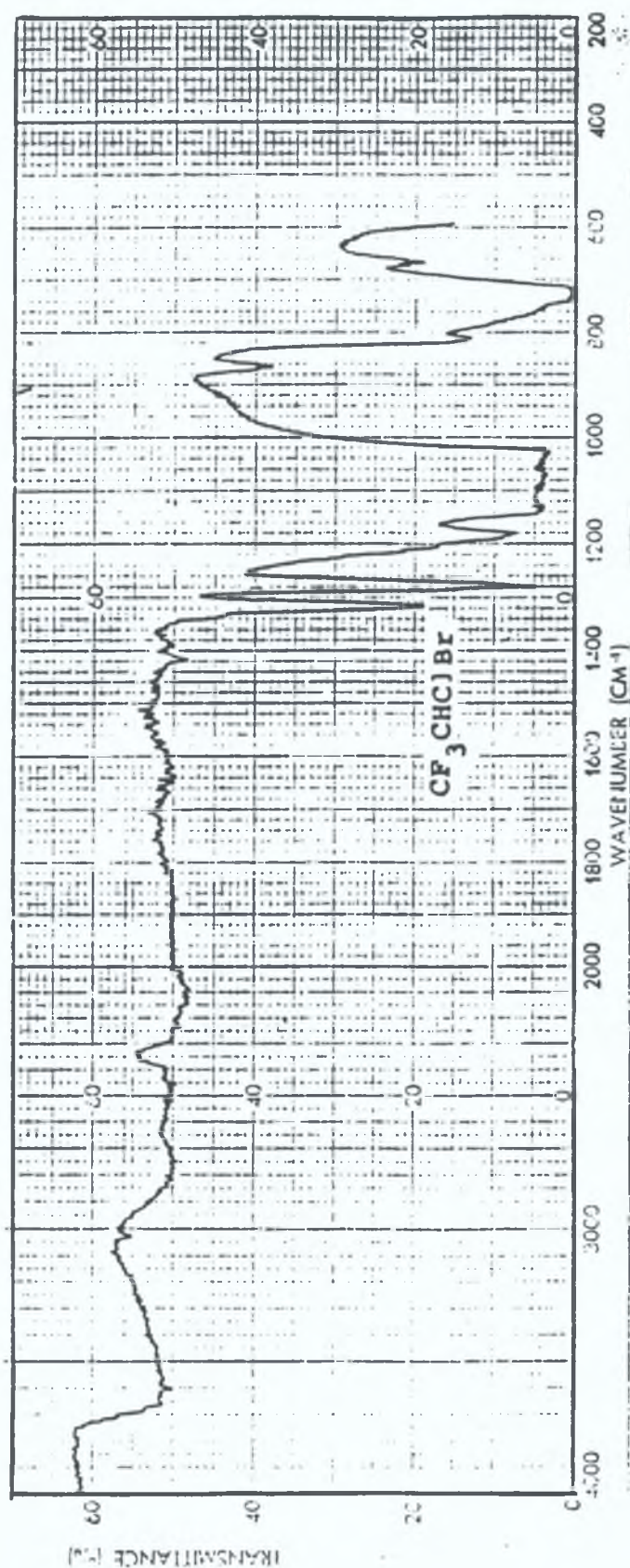


Figure 2.3.1
Infrared spectrum of 4 torr CF3CHClBr and 50 torr O2 prior to photolysis; $\lambda < 290$ nm, and 20°C

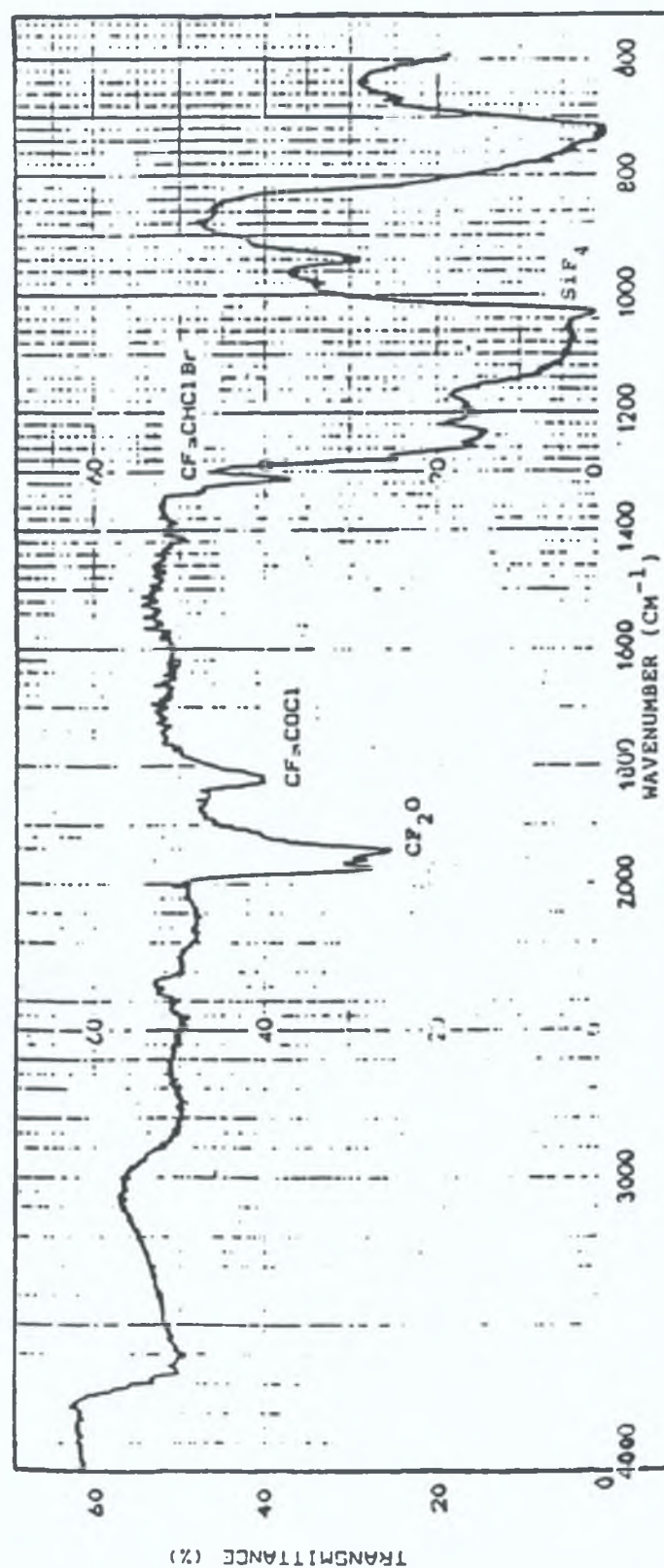


Figure 2.3.2
 Infrared spectrum of 4 torr CF_3CHClBr and 50 torr O_2 after
 50 minutes photolysis; $\lambda < 290 \text{ nm}$, and 20°C

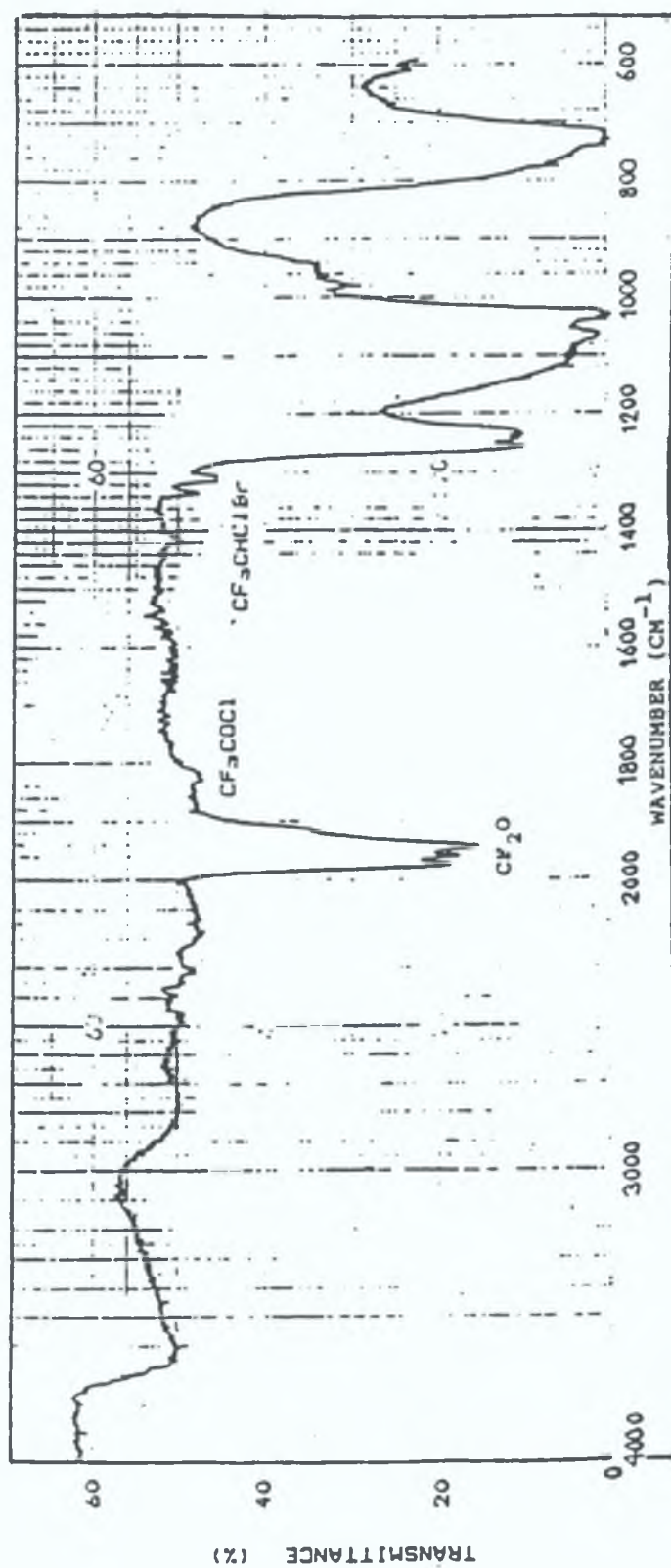


Figure 2.3.3
Infrared spectrum of 4 torr CF_3CHClBr and 50 torr O_2 after 154 minutes photolysis; $\lambda < 290 \text{ nm}$, and 20°C

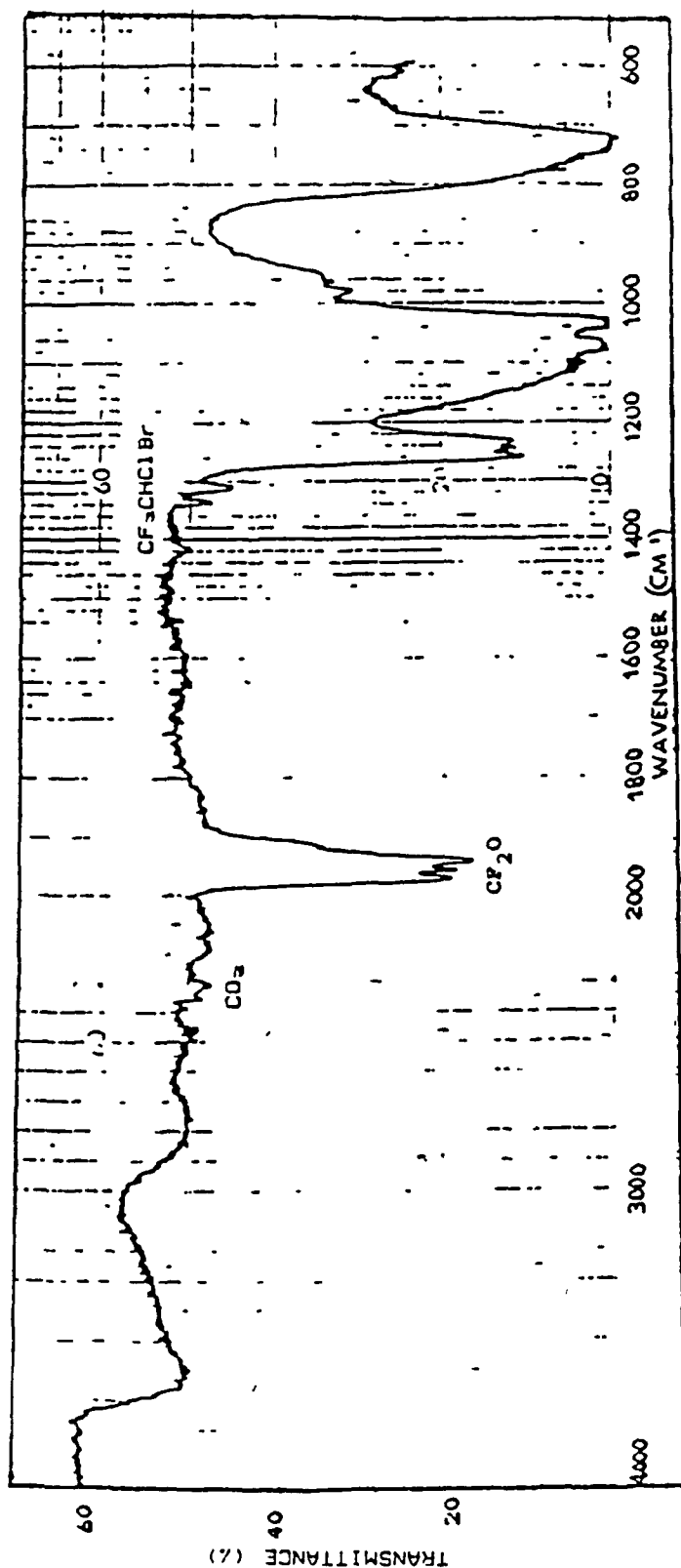


Figure 2.3.4
Infrared spectrum of 4 torr CF_3CHClBr and 50 torr O_2 after 211 minutes photolysis; $\lambda < 290 \text{ nm}$, and 20°C

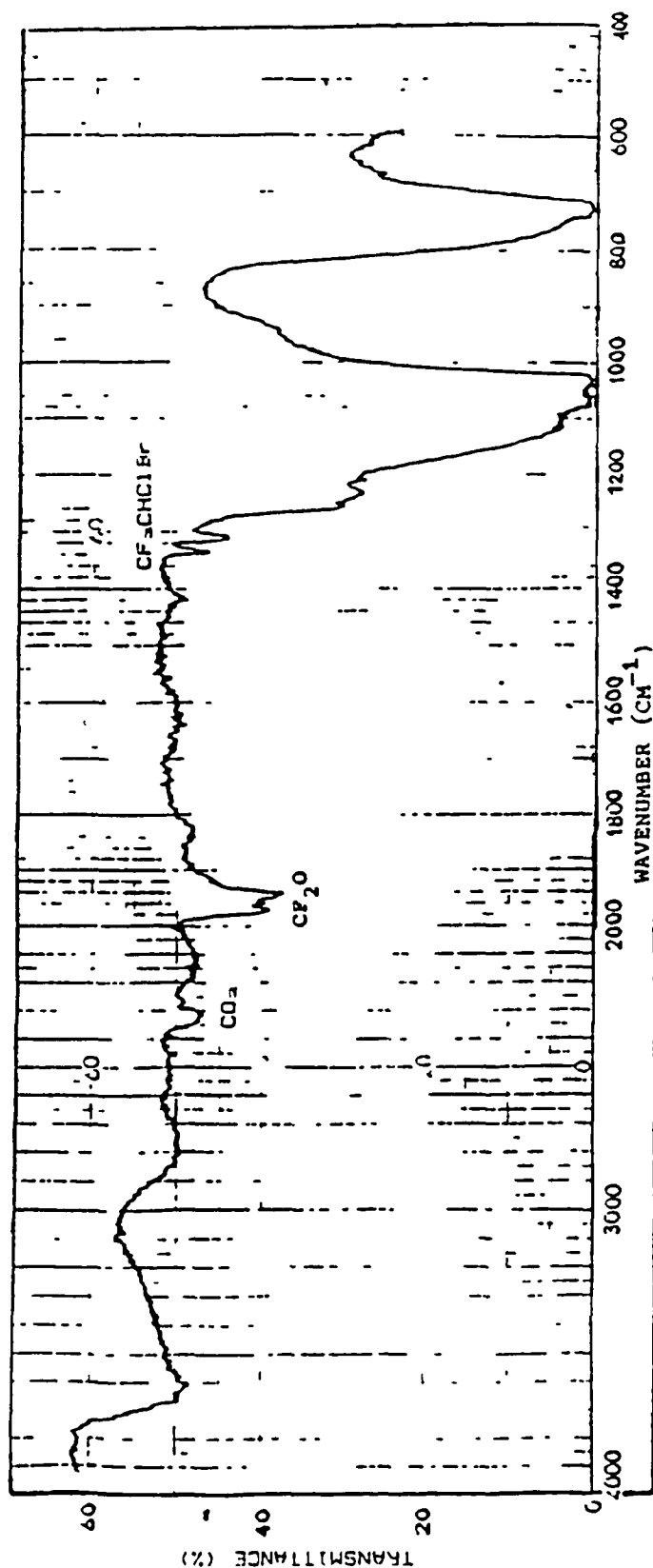


Figure 2.3.5
 Infrared spectrum of 4 torr CF_3CHClBr and 50 torr O_2 left in reaction cell overnight; $\lambda < 290 \text{ nm}$, and 20°C

The concentration of reactants and products were monitored spectroscopically as a function of time. Figure 2 3.2 and 2 3.3 show two major carbonyl peaks initially evident at 1820 cm^{-1} (CF_3COCl) and 1980 cm^{-1} (CF_2O). The concentration of both photooxidation products were observed to rise to a maximum and then fall off with increasing photolysis time. Figure 2 3 4. A third carbonyl band centred at 2350 cm^{-1} (CO_2) was also identified in the reaction mixture and its concentration also increased when the reaction mixture was stored in the reaction vessel overnight, Figure 2 3 5.

The significance of these bands are discussed later in the report, particularly with regard to the elucidation of possible reaction mechanisms.

Having completed preliminary IR investigations into the photooxidation of the anaesthetic, detailed reaction profiles were established with both the disappearance of reactant and the formation of products monitored.

Initially 4 torr halothane was photolysed in 9.92 torr oxygen with the resulting time history shown in Figure 2 3 6. The loss of halothane and the production of CF_3COCl was plotted against irradiation time. For a series of experiments the oxygen pressure was varied from 9.92 torr to 100 torr oxygen. the halothane pressure was maintained constant at 4 torr in all studies, as shown in Figure 2 3 6.

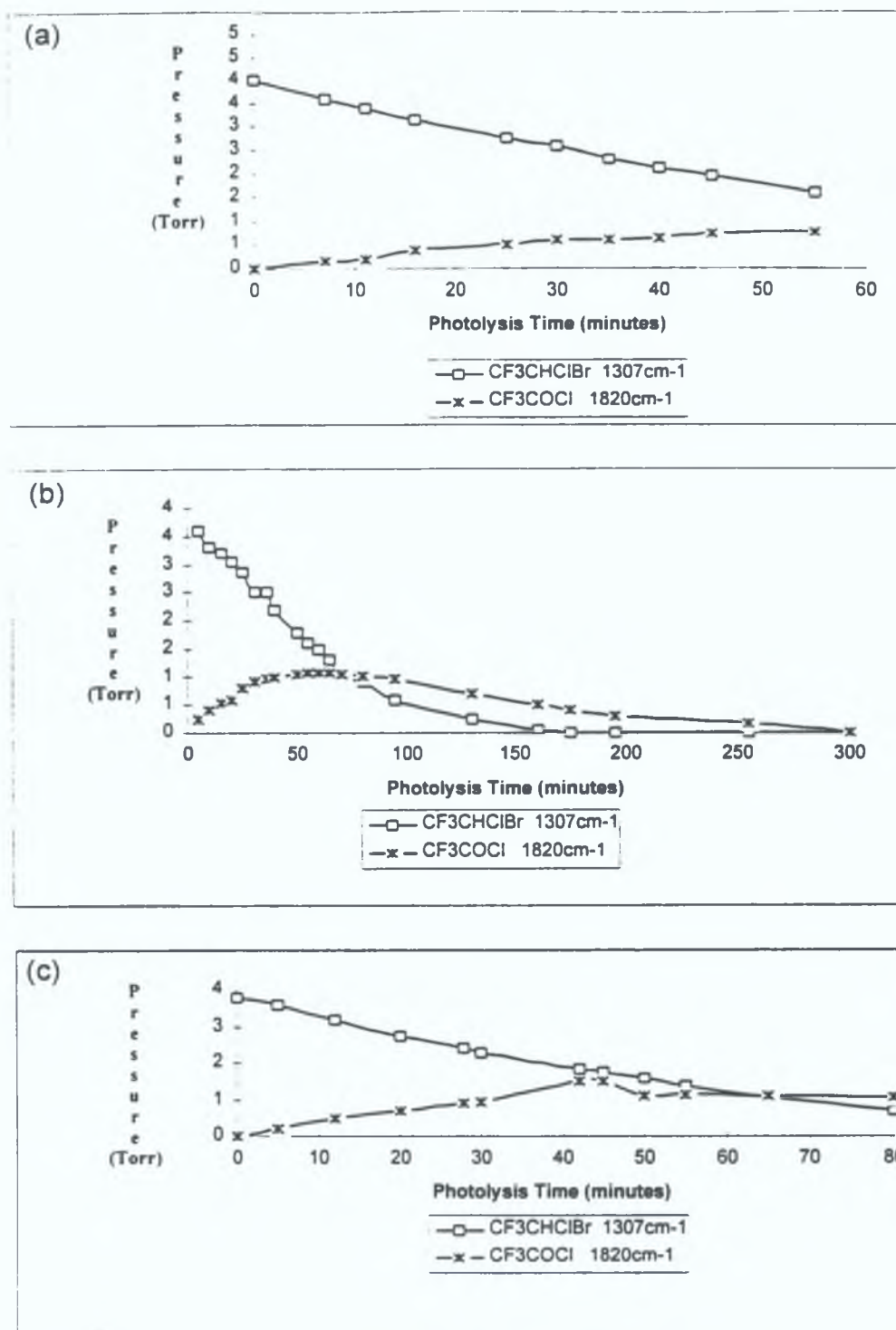


Figure 2.3.6

Photolysis profile for the photooxidation of 4 torr CF_3CHClBr in (a) 9.92 torr O_2 (b) 50 torr O_2 (c) 100 torr O_2 at wavelengths < 290 nm and at a temperature of $20 \pm 2^\circ\text{C}$.

The appearance of reaction product is also illustrated.

Effects of reaction parameters on the photooxidation of halothane

(a) Effect of light Intensity

Figures 2 3 7 and 2 3 8 illustrate the effect of light intensity I_a and $I_a^{0.5}$ on the rate loss of halothane and product formation. A constant halothane pressure of 4 torr in 51 torr oxygen was monitored at 4, 14, 45 and 100% transmittance. The 4, 14 and 45% transmission filters were fashioned from wire mesh and their transmittance determined by monitoring their UV/Visible spectrum from 190-800 nm.

Rate loss of halothane and rate of product formation were calculated using the following equations

$$PV = nRT \quad (1)$$

Rearranging

$$n = \frac{PV}{RT} \quad (2)$$

Where

$$R = 0.08205 \text{ dm}^3 \text{ atm} \cdot \text{mol}^{-1} \text{K}^{-1}$$

T = Temperature in kelvin

Pressure (P) must be expressed in atmospheres

$$\text{ie } P = \frac{\text{Torr}}{760} = \text{atm} \quad (3)$$

Inserting equation (3) into equation (2) derives

$$n = \frac{P(\text{torr}) / 760(\text{torr} / \text{atm}) \cdot V(\text{dm}^3)}{(0.08205) \left(\frac{\text{dm}^3 \text{ atm}}{\text{mol deg}} \right) \cdot T(\text{K})} = \text{mol}$$

where volume (V) is expressed in dm^3

$$\frac{n(\text{mol})}{V(\text{dm}^3 - \text{Volume of cell})} = \text{mol dm}^{-3}$$

and

$$\frac{\text{mol dm}^{-3}}{\text{photolysis time, (seconds)}} = R_p / \text{mol dm}^{-3} \text{sec}^{-1}$$

Where R_p = rate of formation of product in $\text{mol dm}^{-3} \text{sec}^{-1}$

and $-R_X$ = rate of loss of reactant X in $\text{mol dm}^{-3} \text{sec}^{-1}$

The results of varying light intensity on the rate of loss of reactant and rate of product formation are tabulated in Table 2.3.1

Table 2.3.1

Effect of varying light intensity on the photolysis of CF_3CHClBr in the presence of oxygen, $\lambda < 290 \text{ nm}$ and $20 \pm 2^\circ\text{C}$

$I_a^{0.5}$ (%)	I_a (%)	$\text{PCF}_3\text{CHClBr}$ (torr)	P O_2 (torr)	Phot Time (secs)	$-\text{RCF}_3\text{CHClBr}, \text{RCF}_3\text{COCl}, \text{RCF}_2\text{O}$ $\text{mol dm}^{-3} \text{sec}^{-1}$ ($\times 10^8$)		
10	100	4.0	51	300	5.49	3.66	1.37
6.7	45	4.0	51	600	2.75	1.37	0.23
3.74	14	3.9	51	1680	0.65	0.49	0.25
2	4	4.0	51	2100	0.52	0.26	0.07

The relationship between the rate of reaction, I_a , and $I_a^{0.5}$ are shown in Figures 2.3.7 and 2.3.8 respectively

The intensity of light incident on the reaction mixtures affected the loss of halothane and the concentration of its main photooxidation product in a linear fashion for I_a , Figure 2.3.7 and in a non-linear fashion for $I_a^{0.5}$, Figure 2.3.8.

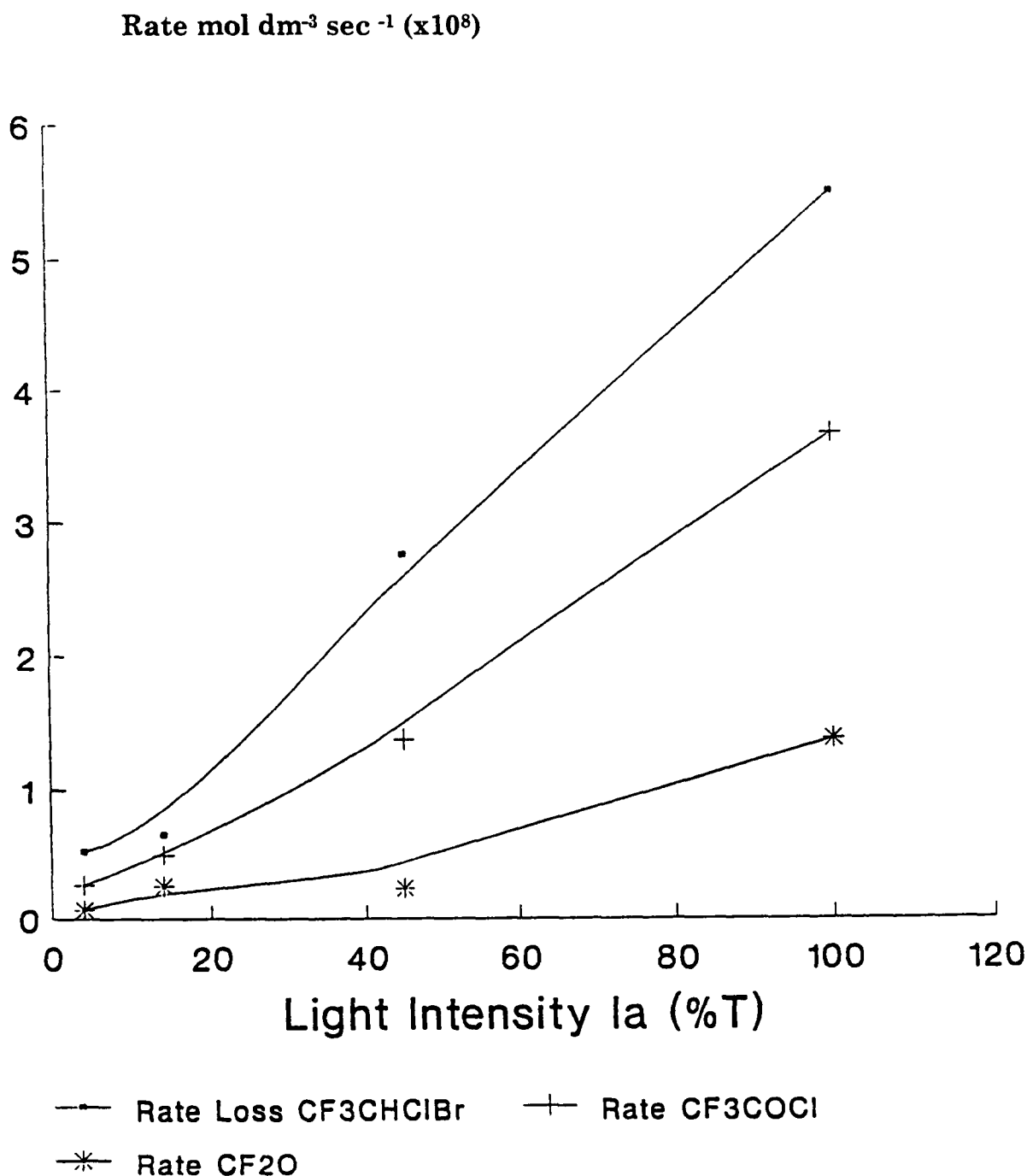


Figure 2.3.7

Effects of light intensity (I_a) on the rate of loss of CF_3CHClBr and on levels of photooxidation products. Reactions were carried out at a temperature of $20 \pm 2^\circ\text{C}$, in the presence of oxygen and using wavelengths < 290 nm

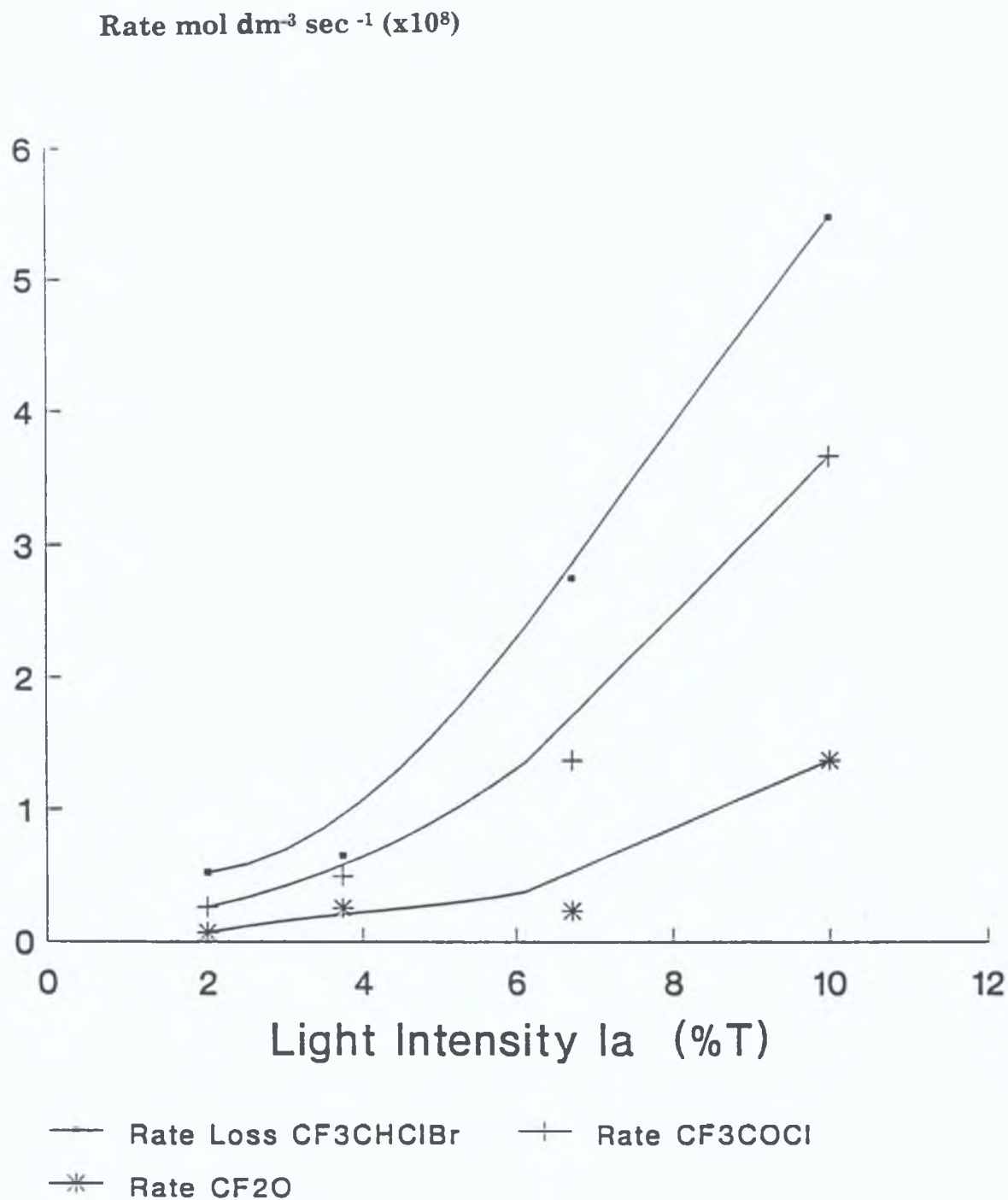


Figure 2.3.8
 Effects of light intensity ($I_a^{0.5}$) on the rate of loss of CF₃CHClBr and on levels of photooxidation products. Reactions were carried out at a temperature of 20 ± 2°C, in the presence of oxygen using wavelengths < 290 nm.

(b) The effect of halothane concentration

Similar experiments were carried out to observe the relationship between halothane concentration and rate of reactant loss

Concentrations of halothane varying from 2 to 7.2 torr were prepared in 50 torr oxygen and irradiated for five minutes in order to have a 5-10% conversion of reactant. The results are tabulated in Table 2.3.2

Figure 2.3.9 shows the linear relationship between the rate of loss of halothane, and the concentration of halothane added to the initial reaction mixture

(c) The effect of oxygen concentration

In this set of experiments, 4 torr halothane was mixed with concentrations of oxygen varying from 9.92 to 101.33 torr. The rate of product formation was constantly measured at 5-10% conversion. The data is shown in Table 2.3.3. Figure 2.3.10 illustrates the effect which oxygen concentration exerted on the reaction rate of the anaesthetic, halothane

For both the anaesthetic, halothane, the rate loss and the concentration of the photooxidation products remained essentially constant over the oxygen range investigated

Table 2.3.2

Effects of varying CF_3CHClBr concentration on the photolysis of CF_3CHClBr in the presence of oxygen, $\lambda < 290 \text{ nm}$ and $20 \pm 2^\circ\text{C}$

PERCENTAGE TRANSMISSION (%)	REACTANT PRESSURE (TORR)		PHOTOLYSIS TIME (SECONDS)	-R CF_3CHClBr $\text{mol dm}^{-3} \text{sec}^{-1}$ ($\times 10^8$)
	CF_3CHClBr	O_2		
100	2 0	50	300	2 75
100	4 0	50	300	3 66
100	5 7	50	300	5 49
100	7 2	50	300	7 32

Table 2.3.3

Effects of varying oxygen concentration on the photolysis of CF_3CHClBr in the presence of oxygen, $\lambda < 290 \text{ nm}$ and $20 \pm 2^\circ\text{C}$

$\text{P}_{\text{CF}_3\text{CHClBr}}$ (TORR)	P_{O_2} (TORR)	PHOTOLYSIS TIME (SECONDS)	-R CF_3CHClBr R CF_3COCl R CF_2O $\text{mol dm}^{-3} \text{sec}^{-1}$ ($\times 10^8$)		
4 0	10 28	300	3 66	4 58	-
4 0	49 93	300	3 66	4 58	-
4 0	101 33	300	3 66	4 58	-

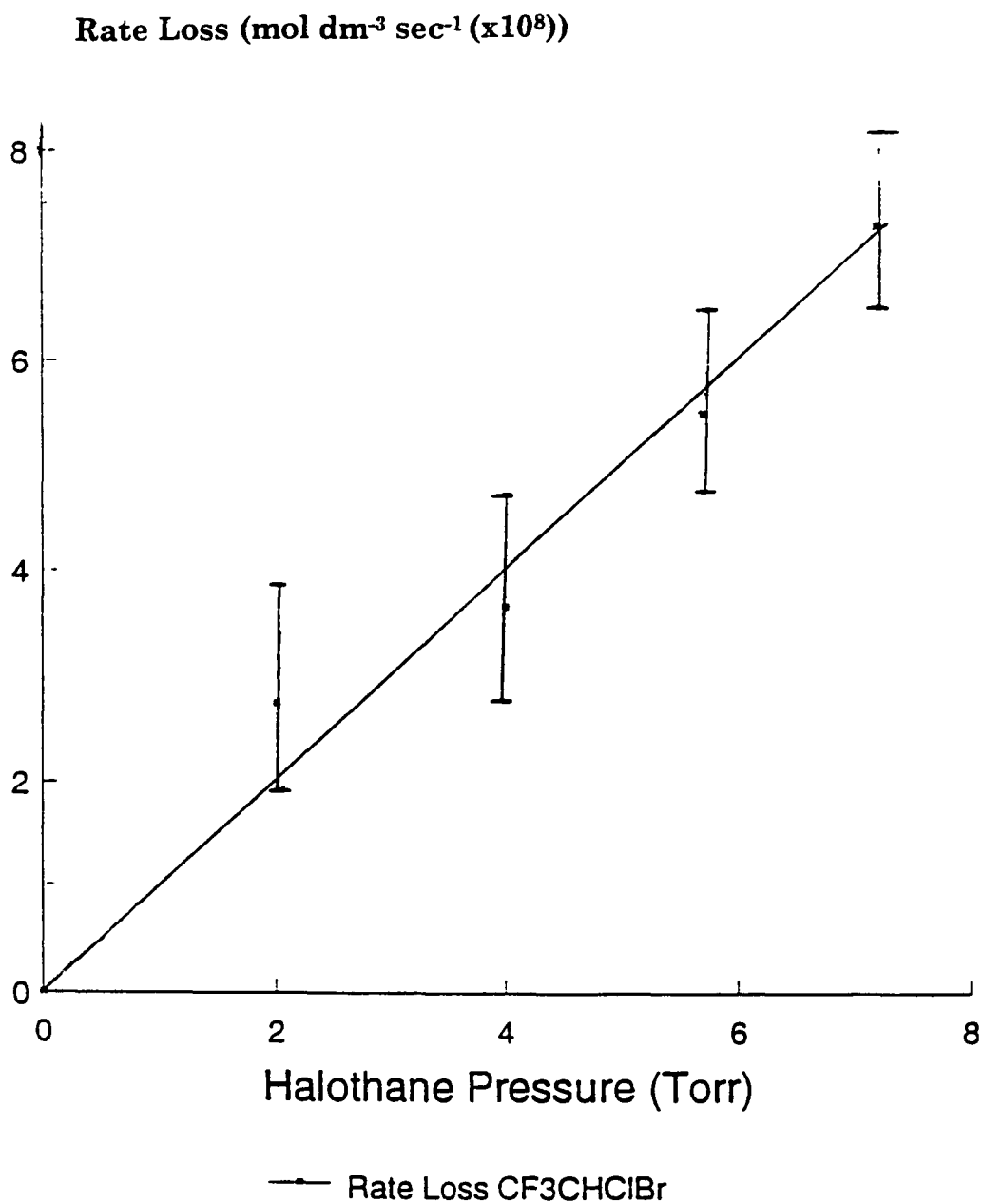


Figure 2.3.9
Effects of halothane concentration on the rate loss of halothane, Reactions were carried out in the presence of 50 torr oxygen at wavelengths $< 290 \text{ nm}$ and $20 \pm 2^\circ\text{C}$.

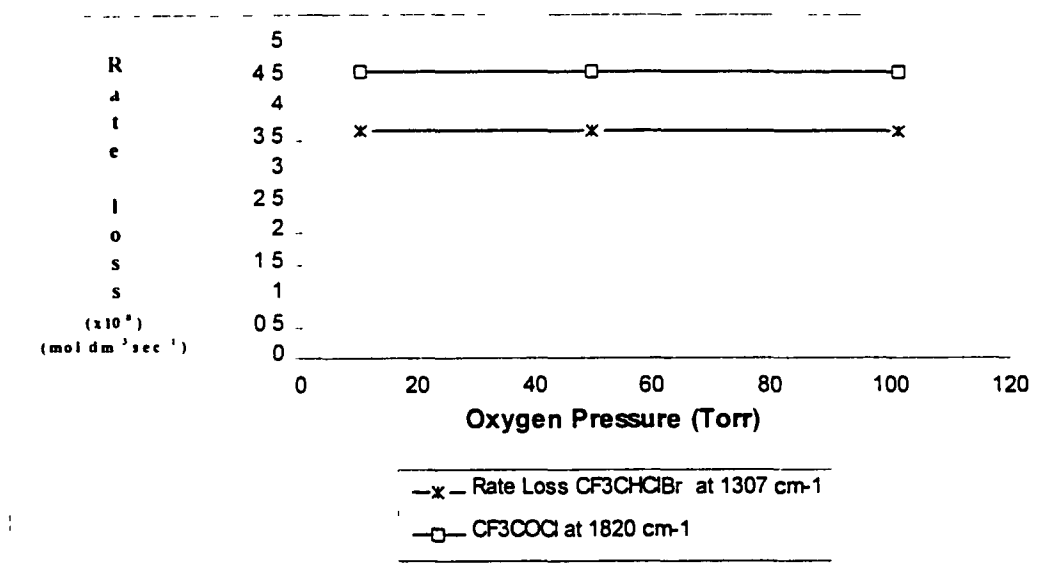
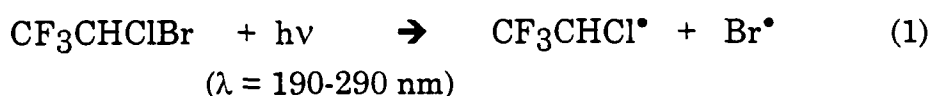


Figure 2.3.10
Effects of oxygen concentration on the rate of loss of halothane and on the formation of its photooxidation product. Reactions were carried out in the presence of 4 torr halothane at wavelengths < 290 nm and $20 \pm 2^\circ\text{C}$.

2.4 DISCUSSION

Photolysis of halothane (CF_3CHClBr) in the presence of oxygen in the wavelength range 190-290 nm yielded CF_3COCl (1820 cm^{-1}) CF_2O (1980 cm^{-1}) and CO_2 (2350 cm^{-1})

The formation of these products was rationalised in terms of the following reaction mechanism



Although the intensity of output from the medium pressure mercury lamp is low below 240 nm (in the region where anaesthetics have maximum absorption) tail end absorption by anaesthetics has been demonstrated as being an important process [1,2] in their photooxidation

For mixtures of halothane plus O_2 , no dark reactions at $20 \pm 2^\circ\text{C}$ were observed. Furthermore no reaction occurred when gas mixtures were irradiated at wavelengths $>335\text{ nm}$ (radiation was attenuated by a Corning

CS-O52 optical filter) The results from the initial photooxidation studies followed by IR spectroscopy are given in Figures 2.3 1-2 3 5 The photooxidation of halothane resulted in the formation of three products identified by the appearance of IR bands at 1980 cm^{-1} , 1820 cm^{-1} and 2350 cm^{-1}

A strong band at 1980 cm^{-1} was attributed to CF_2O and was confirmed by comparison with a standard spectrum, Figure 2.3 2 Another peak assigned to CF_2O at 1250 cm^{-1} was attributed to the stretching $\nu_{\text{C-F}}$ for difluorocompounds

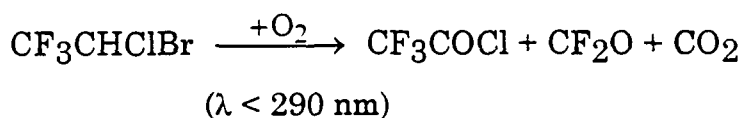
The band at 1820 cm^{-1} was due to the formation of CF_3COCl and was confirmed by comparison with a standard spectrum, Figure 2.3.2.

The influence of a halogen (Cl) attached directly to the carbonyl C=O causes the C=O stretch absorption to appear around 1820 cm^{-1} This absorption may be split especially when there is α - carbon substitution Conjugation of the C=O shifts the absorption in the usual manner to a slightly higher λ position A band also associated with the acid halide is found in the vicinity $1000\text{-}910\text{ cm}^{-1}$ and is quite broad The band at 2350 cm^{-1} was due to the formation of CO_2 , Figure 2 3 4

CO_2 has three vibration modes, an antisymmetric stretch at 2350 cm^{-1} , a symmetric stretch at 1330 cm^{-1} and a bending stretch at 667 cm^{-1} For linear triatomic molecules we would expect four vibrational models ie $3N-5 = 4$ instead of three Bending consists of 2 vibrations, the two sorts of motion are termed degenerate and it is always in the degeneracy of a bending mode that the extra vibration of a linear molecule over a non-linear one is found Carbon dioxide was observed after prolonged

photolysis in the reaction vessel overnight, Figure 2 3 5 CHClO was not identified with the analytical techniques used in this study, but it is reasonable to assume that it was formed during the reaction

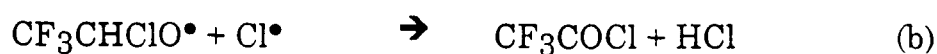
At this stage of analysis, results indicated that the photooxidation of the anaesthetics could be summarised as follows



The proposed mechanism indicates that it is possible that bromine atoms produced in the initiation step may abstract a hydrogen from CF₃CHClBr to yield the CF₃CClBr radical. The oxidation products of this radical could include CF₃COCl and /or CF₂O and possibly CClBrO. It was not possible to distinguish between the reactions leading to formation of CF₃COCl and CF₂O in this system, so our data does not rule in/out this possibility. However, it is expected that bromine atoms produced in the initiation step was removed from the system by bromine atom combination in reaction (9) as the main radical loss process

Steps (4-6) of the proposed mechanism are well established reaction pathways for the CF₃CHClO radical [13]

The CF₃CHClO radical could either give trifluoroacetyl chloride by the loss of its hydrogen atom in several ways



Step (4) of the proposed mechanism is the same reaction as (a) and step (5) proposes the same reaction as (b) except Br radicals and not Cl radicals are available in our system to react with CF_3CHClO to form CF_3COCl as products studies have shown and HBr.

Step (6) of the mechanism proposes that the CF_3CHClO radical breaks down by carbon-carbon bond fission, a third well established reaction [13].



The trifluoromethyl radical (CF_3) would then react with O_2 in the reaction type.

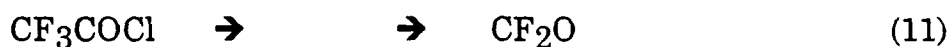


Alternatively the interaction of the perfluoroalkyl radical CF_3 with O_2 leads to the formation of CF_2O [31] as proposed to occur in step (7). CO_2 is known to be formed from the oxidation of CF_2O step (8) and SiF_4 formed presumably by decomposition of CF_2O on the glass surfaces [30b].

The presence of carbonyl fluoride in the reaction mixture supports this proposal, and the formation of carbon dioxide after storing the reaction mixtures overnight in the dark, Figure 2.3.5 is also consistent with this proposal [37]. CO_2 was detected only by IR spectroscopy and not GC. The use of GC with a flame ionisation detector limited the number of reaction products determined. CF_2O was broken down on the column to CO_2 [37] as CO_2 is completely oxidised it elicited no response from the flame ionisation detector. Carbonyl fluoride is not a primary product of the reaction as shown by the marked induction period prior to its formation (Figure 2.4.1) and trifluoroacetyl chloride was detected in all reaction mixtures; even after short photolysis times. For further studies, confirmation that CF_3COCl is a

primary product of the reaction could be obtained by measuring the quantum yields for the loss of halothane and formation of CF_3COCl . Accurate knowledge of the quantum yields of end product formation is an essential first step in the determination of a photochemical mechanism and to complement our studies of intermediates involved in the photooxidation reactions.

As discussed photolysis and/or decomposition of CF_3COCl as it is formed leads to the production of CF_2O (Figures 2.3.2 - 2.3.5). From the time history for the photolysis of halothane in the presence of oxygen, Figure 2.3.6 (b) it is clear that the concentration of CF_3COCl initially rises, reaches a maximum and then falls off to zero. This suggests that CF_2O is a secondary product arising from photolysis of CF_3COCl is entirely consistent with the experimental data. Thus reactions (6) and (7) may not be the major source of CF_2O in the reaction mixture, and the complex reaction (11) must be considered as a source of this product.



There is insufficient data from this work to suggest a plausible mechanism for formation of CF_2O from CF_3COCl in the reaction mixtures.

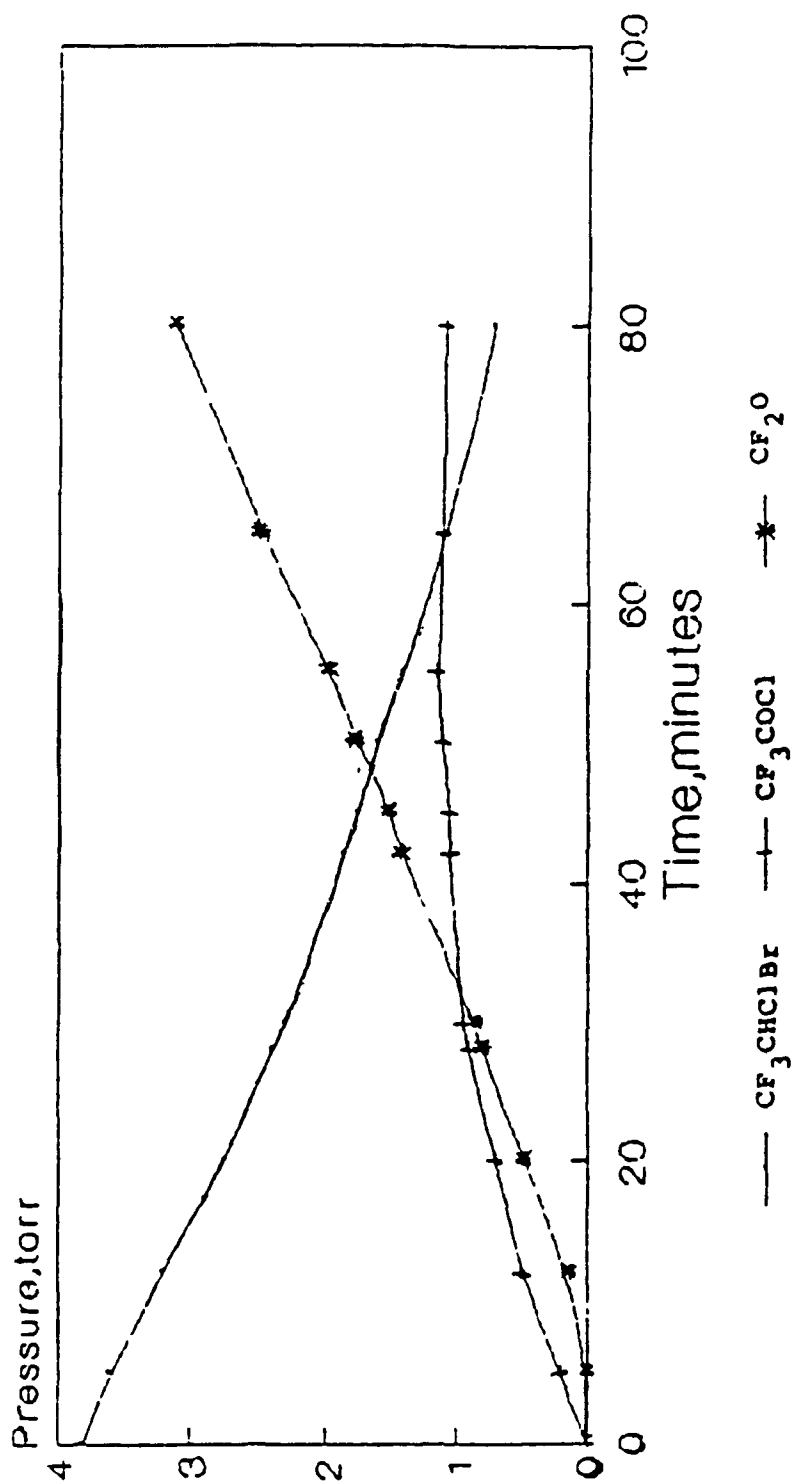


Figure 2.4.1

Photolysis profile for the photooxidation of 4 torr CF_3CHClBr in 100 torr O_2 at wavelengths < 290 nm and $20 \pm 2^\circ\text{C}$. The appearance of reaction products is also illustrated.

The formation of CF_2O from the photolysis of CF_3COCl has been confirmed experimentally as seen in Figure 2.4.2. It is possible that reactions (6) and (7) may represent a minor pathway to CF_2O , but our results do not allow us to confirm or rule out this possibility. The rate of formation of CF_3COCl in the photolysis of $\text{CF}_3\text{CHClBr}/\text{O}_2$ mixture will be given by

$$R_{\text{CF}_3\text{COCl}} = \phi_p I_a$$

where ϕ_p is the quantum yield of decomposition of CF_3CHClBr in the primary process and I_a is the absorbed light intensity

The effect on $R_{\text{CF}_3\text{COCl}}$ of varying the incident light intensity, I_0 , is shown in Figure 2.3.7. I_0 is related to the absorbed light intensity, I_a , if the Beer-Lambert Law is obeyed

I_a is always small and proportional to I_0 .

$$I_a = I_0 \epsilon C L$$

where L is the cell length in cm and ϵ is the molar extinction of CF_3CHClBr

The rate of CF_3COCl formation should be proportional to the first power of the incident light intensity. This is confirmed by the data in Table 2.3.1

Figure 2.3.7 demonstrates the linear relationship that was shown between the intensity of the light energy incident on the reaction mixtures and the formation of photooxidation products. As the intensity of light decreased from 100% down to 4%, so also did the rate of reaction which is consistent with the proposed C-Br bond breakage mechanism. When the intensity of light was reduced, thus the extent of photooxidation was similarly reduced.

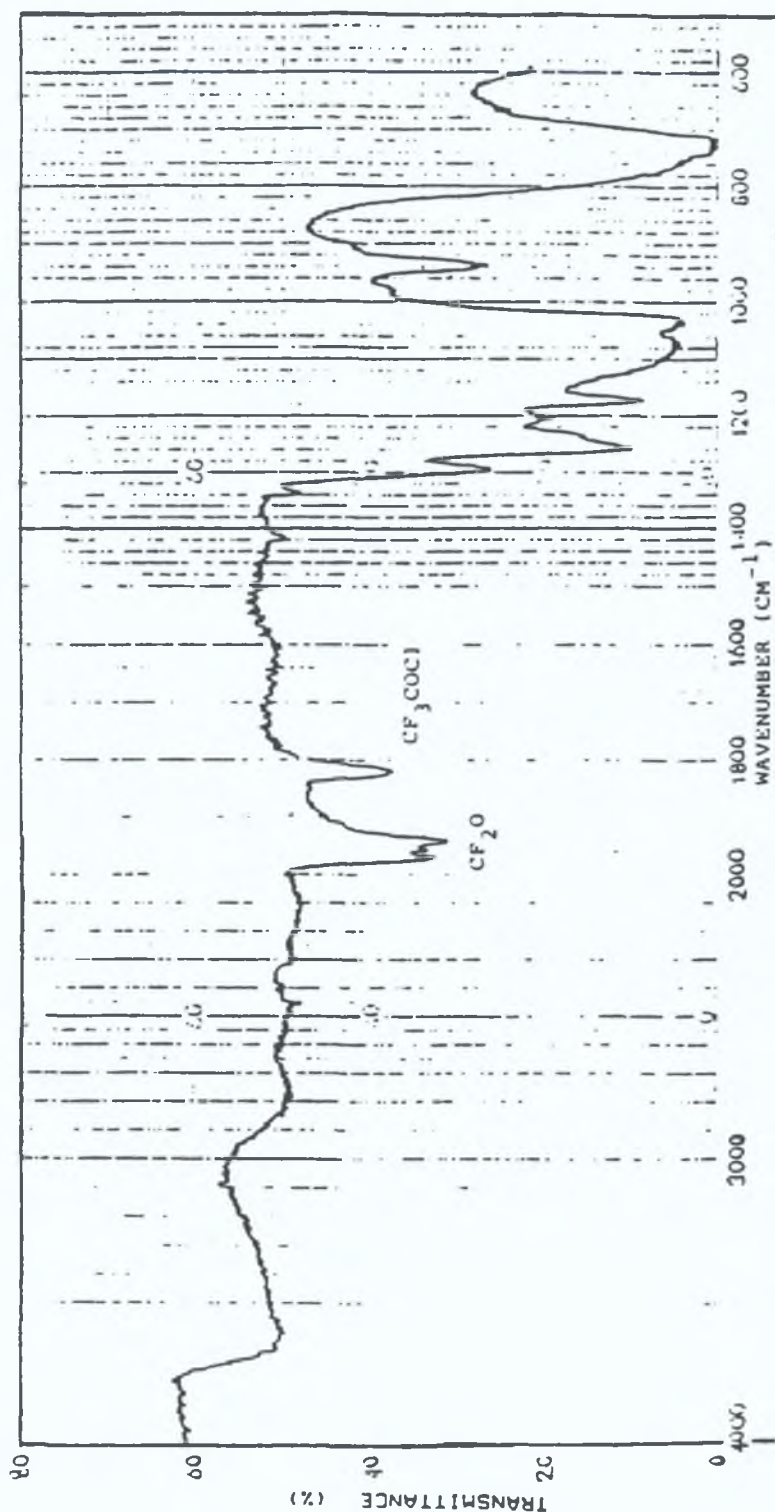


Figure 2.4.2
Infrared spectrum of 4 torr CF_3COCl in 50 torr O_2 after 45 minutes photolysis at wavelengths < 290 nm and $20 \pm 2^\circ\text{C}$

The fact that the rate of formation of CF_2O appears to be independent of absorbed light intensity confirms that CF_2O is not a primary product of the reaction

Effect of anaesthetic concentration on the rate of loss of this compound is illustrated in Figure 2.3.9. As expected as the concentration of halothane is increased from 2 to 7.2 torr, the rate of loss increases. This observation is consistent with the fundamental rate expression

$$\frac{-d[\text{halothane}]}{dt} = k_r [\text{halothane}]^n$$

where n = order of reaction

k_r = rate loss of halothane

$[\text{halothane}]$ = halothane concentration

The results presented in Figure 2.3.10 demonstrates the effect which the oxygen pressure in the reaction mixture exhibited on the rate of loss on halothane and the levels of the monitored product. The data presented in Figure 2.3.10 show the rate of CF_3COCl formation is independent of oxygen pressure in the range of these studies 10.28 - 101.33 torr. Hence step (2) is in the pressure - independent range under these experimental conditions. Halothane reaction does not vary either over the pressure range as the mechanism proposes.

The mechanisms proposed in this work for the photooxidation of halothane are by no means conclusive. Further work in this area needs to be carried out to produce a more comprehensive reaction mechanism.

It would be interesting to carry out quantum yield studies on the reaction products and on halothane itself. Techniques such as GC-Mass spectrometry in addition to FTIR studies could be used in order to determine reaction products with more certainty, than with the limitation of these studies.

2.5 CONCLUSION

From the results obtained in this work, photodissociation is the primary loss process for halothane under simulated stratospheric conditions

For the bromine-containing species, halothane, absorption onsets at $\lambda < 290$ nm. Using wavelengths of light in this region enabled photooxidation to proceed via C-Br bond breakage (the C-Br bond is the weakest in these molecules) within the halothane molecule

Photolysis of these compounds does not occur in the troposphere, only in the stratosphere. The conditions used in this work simulate atmospheric conditions typical of those in the stratosphere ie high energy light $\lambda < 290$ nm and low pressures (100 torr).

The proposed mechanism for photooxidation in these studies is by no means conclusive, however the formation of carbonyl fluoride, trifluoroacetyl chloride and carbon dioxide found experimentally using IR spectroscopy and GC techniques support this mechanism. As discussed in chapter one, chlorofluorocarbons such as halothane when released into the atmosphere undergo stratospheric and tropospheric reactions

In the stratosphere, the molecule's bromine and chlorine atoms are released and can participate in reaction pathways, ultimately leading to ozone depletion in a manner analogous to all CFC molecules

2.6 REFERENCES

- [1] J M Dumas, P Dupuis, G Pfischer-Guillouzo and C Sandorfy, *Can J of Spectrosc* , **26** (3), 102 (1981)
- [2] A M Barrett, J F Nunn *Brit J of Anaesth* , **44**, 306, (1972)
- [3] I Shanahan, "Oxidation of Haloalkyl Radicals", Ph D Thesis, (1984)
- [4] L Nelson, I Shanahan, H Sidebottom, J Treacy and O J Nielsen, *Int J chem Kinet* , **22**, 577 (1990)
- [5] V O Christiansen, J A Dahlberg, H F Anderson, *Acta Chem Scand* , **26**, 3319 (1972)
- [6] T Tominaga, T Aoyama, Y Makide, *Radiochem Radioanal Lett* , **28**(1), 27 (1977).
- [7] T Fukumizu, Y Makide, T Tominaga, *Radiochem Radioanal Lett* , **23**, 353 (1975)
- [8] A. R Kazanjian, D R Horrell, *J. Phys Chem.*, **75** (14) 2217-19 (1971).
- [9] A Sokolowska and L. Kevan, *J Phys Chem.*, **71**, 2220 (1967)
- [10] M. B Fallgatter and R J Hanrahan, *J Phys Chem.*, **69**, 2059 (1965).
- [11] D R MacKenzie, F W Block, and R. H Wisall, Jr , *J Phys Chem* , **69**, 2526 (1965)
- [12] R W Fessenden and R H Schuler, *J Chem Phys* , **43**, 2704 (1965)
- [13] R N Haszeldine and F Nyman, *J Chem Soc Part II*, 387 (1959)
- [14] T Ichimura, A W Kirk, and E Tschuikow-Roux, *Int J Chem Kinet.*, **9**, 473 (1977)
- [15] D Salomon, A W Kirk and E Tschuikow-Roux, *J Phys Chem* , **83**, 2569 (1979)
- [16] D Salomon, A W Kirk and E Tschuikow-Roux, *Int J Chem Kinet* , **9**, 619 (1977)
- [17] D Salomon, A W Kirk and E Tschuikow-Roux, *J Photochem* **7**, 345 (1977)

- [18] T Ichimura, A W Kirk and E Tschuikow-Roux, *Int J Chem Kinet* ,
9, 697 (1977)
- [19] T Yano and E Tschuikow-Roux, *J Phys Chem* , 83, 2572 (1979)
- [20] T Yano and E Tschuikow-Roux, *J Phys Chem* 72, 3401 (1980)
- [21] T Yano, K H Yung and E Tschuikow-Roux, *J Chem Phys* , 84,
2146 (1980)
- [22] T Yano and E Tschuikow-Roux, *J Phys Chem* , 84, 3372 (1980)
- [23] D C Phillips, A F Trotman-Dickenson, *J Chem Soc A* , 7, 1667
(1968)
- [24] R L Thomarson and G O Pritchard, *J Phys Chem* , 70, 2307
(1966)
- [25] T S Yuan, *Diss Abstr Int B.*, 39(8), 3861 (1979)
- [26] J G Calvert, J N Pitts, *Photochemistry*, Wiley, New York, 394
(1966)
- [27] G O. Pritchard, M J Perona, *J Phys Chem.* 73(9), 2944 (1969).
- [28] D W Sester, *J Amer Chem Soc.*, 90, 582 (1968)
- [29] E H Lyons, Jr , and G Dickenson, *J Amer Chem Soc* , 57, 443
(1935)
- [30] (a) J Banus, H. T Emeleus and R N Haszeldine, *J. Chem Soc.*,
3041 (1965)
- (b) W C Francis and R N Haszeldine, *J Chem Soc* , 2151 (1955)
- (c) D G Marsh and J Heicklen, *J Phys Chem* , 69, 4410 (1965)
- [31] J Heicklen, *J Phys Chem* , 70, 112 (1966)
- [32] K R Ryan, I C Plumb, *J Phys Chem.*, 86, 4678 (1982)
- [33] A M Dognon F Caralp, R Lesclaux. *J Chim Phys Phys Chim
Biol* , 82, 349 (1985)

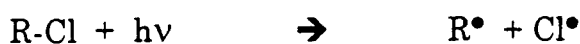
- [34] (a) V E Vedeneev, M A Teitelboim, A A Shoikhet, *Izv Akad Nauk , SSSR, Ser Khim* , 8, 1757 (1977)
- (b) V E Vedeneev, M A Teitelboim, A A Shoikhet, *Izv Akad Nauk SSSR, Ser Khim.*, 12, 2663 (1979)
- [35] F Caralp R Lesclaux, A M Dognon, *Chem Phys Lett* , 129, 2663 (1986)
- [36] L Batt and R Walsh, *Int J Chem. Kinet* , 15 605 (1983)
- [37] R Withnall, J R Sodeau, *J Photochem.*, 33, 1 (1986)
- [38] K C Clemitshaw, Ph D Thesis, University of East Anglia, Norwich, 173, (1986)
- [39] K. C Clemitshaw and J R Sodeau, *J Phys Chem* , 93, 3552, (1989)
- [40] R Atkinson, G M. Breur, J N Pitts Jr., H. L Sandoval, *J Geophys Res.*, 81(33), 5765 (1976)
- [41] R Milstein, F S Rowland, *J Phys Chem* , 79, 669 (1975)

CHAPTER 3.0

KINETICS AND MECHANISM FOR THE GAS PHASE CHLORINE-SENSITISED PHOTOOXIDATION OF HALOTHANE

3.1 INTRODUCTION

Chapter two investigated the main stratospheric loss process for halogenated alkanes, photodissociation. When light of sufficient energy to break the bonds is available, then photodissociation can be an important mechanism resulting in



the free radical or haloalkyl radical in this study can then react with O_2 to form oxidation products and as discussed in Chapter two, eventually liberating all chlorine atoms to take effect on the ozone layer

It is now well established that organic chemicals emitted into the troposphere are removed by reaction with a number of reactive intermediates including OH, HO_2 , and NO_3 radicals, O_3 by photolysis and by wet and dry deposition[1]

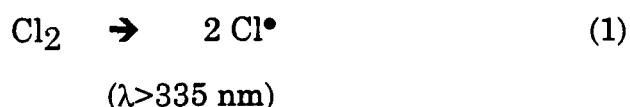
The role of chlorine chemistry in the troposphere has received little attention because Cl atoms are sufficiently scarce that they could not compete with OH radicals as a dominant loss mechanism for hydrocarbons in the troposphere [2]

This scenario is supported by the fact that the reaction of Cl atoms with CH_4 is only 13 times faster than the corresponding radical reaction whereas OH radicals are nearly 1000 times more abundant in the lower troposphere. However, by comparison, typical reaction rates of non-methane hydrocarbons (NMHCS) with Cl atoms are nearly 100-1000 times faster than the corresponding OH radical rates [3-5], because of their greater reactivity towards NMHCS, Cl atoms may play an important role in NMHC oxidation at all latitudes

For the majority of organic compounds present in the troposphere, reaction with OH radicals during daylight hours is expected to be the

dominant removal process [1,6,7] due to the H-abstraction power of the hydroxyl radical and its high electrophilicity leading to addition reactions

In order to simulate OH reactions with various halogenated alkanes, for purposes of gaining information on the mechanism and kinetics of these reactions, the initial step, generation of OH radicals, however proved experimentally difficult to do and for this reason chlorine gas is photolysed at $\lambda > 335$ nm to produce Cl atoms which mimic tropospheric reactions in the same way as OH radicals



to abstract a hydrogen resulting in the formation of an alkyl or haloalkyl radical and HCl.

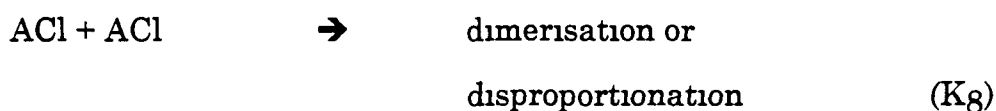
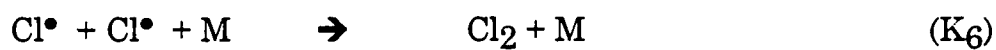
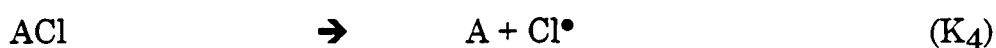
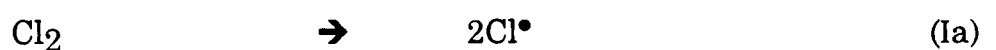
As mentioned earlier, this chapter is concerned with the elucidation of the tropospheric loss process for halothane but in the absence of any direct information concerning the mechanism, it is reasonable to consider published work on analogous compounds in an attempt once again to predict the atmospheric loss process in the troposphere

Back in the thirties, it was clearly understood that light absorbed by chlorine molecules leads to photodissociation to atoms and that the subsequent reactions, recognised as chain reactions proceed with involvement of these atoms. Bodenstein and his group [8] assumed that a chlorine atom abstracts a hydrogen atom from a saturated hydrocarbon or adds to a double bond forming in both cases a hydrocarbon or chlorinated hydrocarbon radical. In the phosgene synthesis the corresponding radical is

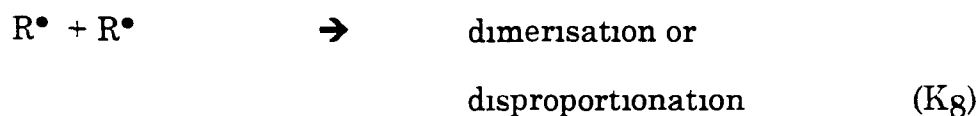
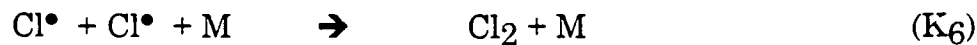
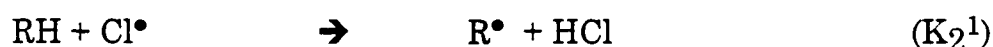
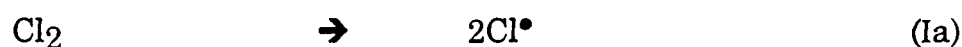
COCl The reaction chain should proceed alternately by a chlorine atom and a free radical

Rollefson, on the other hand, showed that the observed kinetic properties could equally well be explained by a chain mechanism in which the chain carriers are Cl and Cl₃ [9,10,11]

Using either the Bodenstein or the Rollefson mechanism similar reaction steps have been proposed for different substances but in none of these earlier studies [10,12] was an attempt made to put forward a general reaction scheme Such a general scheme [13] may be written for addition as



and for substitution reactions



Whatever ethylenic hydrocarbon A or saturated hydrocarbon RH reacts with a mixture of chlorine atoms and chlorine molecules, this scheme is supposed to be valid

The effects of substituents on the reactivities of C-H bonds in an aliphatic chain to photochlorination have received considerable study. The results have traditionally been accounted for in terms of the inductive and resonance effects of the substituents[14-21]

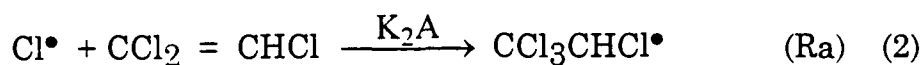
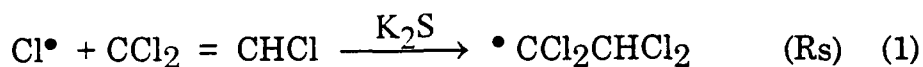
Thus a chlorine substituent always deactivates the β position toward chlorination by induction but its effect on the α -position seems to vary from compound to compound due to the intervention of the resonance stabilisation of the radical intermediate. Tedder and his coworkers [16][18] found that a chlorine substituent retards the reactivities of the α -positions of primary and secondary butyl chlorides. On the otherhand, the rate enhancement by an α -chlorine substituent has been reported by several workers. For example, a C-H bond in methyl chloride has been found to be more reactive than that of methane [22]. Henne and Renoll also found that the chlorination of 1,1,1 trifluoroethane affords only the dichlorination product [23]

Migita et al [24] carried out a comprehensive study of the influences of substituents upon reactivity of each position in aliphatic chains toward the homolytic chlorination. The effect of the structure on the rate of hydrogen abstraction from chloroalkanes by a chlorine atom has been investigated by carrying out the competitive photochlorination of eight different chloroethanes in the presence of 2,2, dichloropropane to which the relative activities have been referred

This would be of interest in our studies of halothane, where substitution is high in the molecule. The results show that the successive interaction of a chlorine substituent at the 1-position decreases the reactivity of the 2-position, but that, in some cases, it increases that of the 1-position.

Martens, Franklin et al [25] observed the H abstraction from chlorinated ethanes by chlorine atoms relative to a common competitor and to compare the results with the corresponding data in the gas phase [26]. From the results obtained, it can be seen that the activation energy differences and the frequency factor ratios for tertiary hydrogen abstraction are very similar in the liquid and gas phase. Compared to hydrogen abstraction from chloroform the reactivities of secondary and primary hydrogens are all enhanced, and particularly those of the less chlorinated compounds, on passing from the gas to the liquid phase [25]. The increased effect of a change of phase on passing from tertiary to primary hydrogen atoms shows up in the decreased selectivity in the chlorination of unsymmetric chloroethanes [27] in the liquid phase compared to that in the gas phase. Though the reactivity scale for different primary, secondary and tertiary C-H bonds is broader in the liquid phase.

Bertrand et al [28] carried out further work on determining the point of attack of a chlorine atom on a particular alkene, trichloroethylene. The photochlorination [29-32], the oxygen inhibited photochlorination [33] and the chlorine-photosensitised oxidation [34] of trichloroethylene have been investigated earlier. All of these reactions involve the addition of a chlorine atom to trichloroethylene as a chain propagation step. Both symmetric (Rs) and asymmetric (Ra) tetrachloroethyl radicals may be formed simultaneously.



Both radicals form C_2HCl_5 on reaction with Cl_2 , but in the presence of oxygen they may yield different oxidation products, as is suggested by results on the chlorine photosensitised oxidation of trichloroethylene [34] Results show that the chlorine-photosensitised oxidations of C_2HCl_3 , 1,1,1,2 - $\text{C}_2\text{H}_2\text{Cl}_4$ and 1,1,2,2 - $\text{C}_2\text{H}_2\text{CCl}_4$ studied at 357°K have long chain reactions and the products formed are

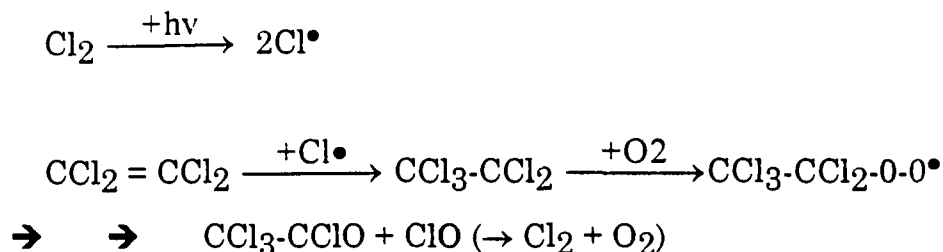
For the chlorine photosensitised oxidation of 1,1,1,2 $\text{C}_2\text{H}_2\text{Cl}_4$ the following products were found COCl_2 , HCl , CO_2 and 1,1,1,2 $\text{C}_2\text{H}_2\text{Cl}_4$, and the reaction products for chlorine-photosensitised oxidation of C_2HCl_3 were found to be HCl , CO_2 together with traces of C_2HCl_3 , C_2Cl_4 , C_2HCl_5 , C_2Cl_6 , CCl_3COCl , trichloroethylene epoxide, CHCl_3 and CCl_4 .

The reaction products of 1,1,2,2 $\text{C}_2\text{H}_2\text{CCl}_4$ after about 98% tetrachloroethane consumption were $\text{CH}_3\text{Cl}_2\text{COCl}$, COCl_2 , HCl and CO_2 , 1,1,2,2 - $\text{C}_2\text{H}_2\text{CCl}_4$, CCl_3COCl and traces of C_2HCl_3 and C_2HCl_5 .

It can be concluded from these results that the rate constant for the addition of a chlorine atom to the less chlorinated carbon atom in trichloroethylene is at least eight times greater than that for addition to the more chlorinated one [28]

Further work by Yasnitski [35] on deducing a mechanism of the migration of halogen and hydrogen atoms in the oxidation of haloethylenes was studied and for the chlorine-sensitised photooxidation of

tetrachloroethylene, Schaumacher and co-workers [36-38] and later Miller and Dittman [39] proposed a mechanism according to which the reaction is initiated by sensitised atoms, which can explain observed migration of chlorine in this case

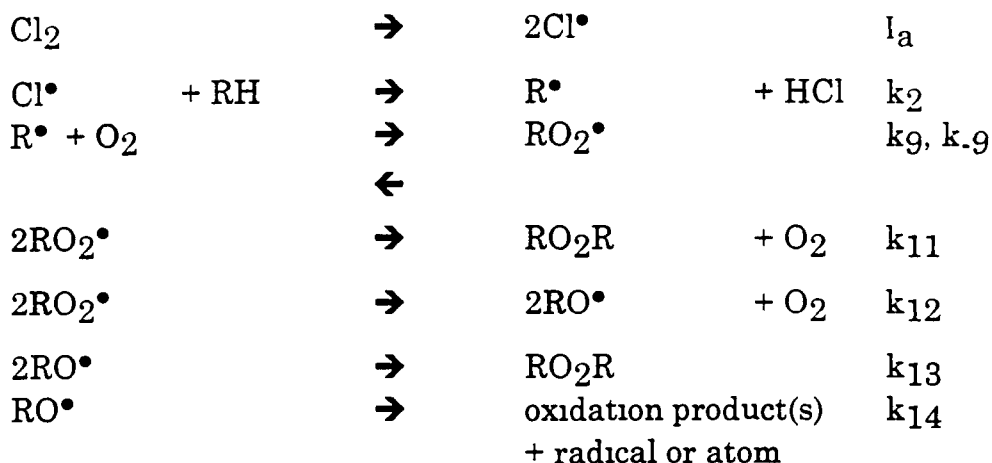


This mechanism was in agreement with certain experimental data and found that chlorine-sensitised oxidation can be initiated by radiation absorbed only by chlorine ($\lambda = 435.8 \text{ nm}$)[40]

Further work by Bertrand, Olbregts et al [41] reported on long-chain chlorine photosensitised oxidations that had been observed in the gas phase at about 335 K for a number of chloroethanes and chloroethylenes namely 1,1,2,2- and 1,1,1,2-C₂H₂Cl₄, C₂Cl₄ and C₂HCl₅ but not for 1,2-C₂H₂Cl₂, C₂H₄, 1,2-C₂H₄Cl₂, 1,1,1-C₂H₃Cl₃ and C₂H₆

Bertrand et al investigated all chlorinated ethanes and ethylenes that yield only one type of radical by the attack of Cl atoms and put forward an explanation of why oxidation occurs in certain cases and not in others. Gaseous mixtures of Cl₂, O₂ and halogenated ethane/ethylene were irradiated with light of 436 nm used to initiate the reactions and the reactions were followed by means of one or more of the following techniques: (1) pressure measurement of pressure changes, (2) product analysis, (3) Mass Spectroscopy.

A reaction mechanism had been proposed by Meyers and Huybrechts in conjunction with Goldfinger [42] based on their earlier work which reduces to the following steps for high O₂ pressures



The formation of oxidation products in reaction 14 was proposed to occur via the rupture of a C-H, C-Cl or C-C bond in the RO radical. The corresponding bond energies, were obtained from known and estimated heats of formation. Based on bond energies for the loss of H or Cl, respectively, from the oxygen bearing carbon atom would lead to the formation of an aldehyde or acid chloride

Loss of H or Cl from the adjacent carbon atom with the formation of an epoxide was not considered since this path would be more endothermic and in addition no epoxides had been found experimentally. A C-C rupture would result in the formation of an oxidation product (CH₂O, CO and HCl, or COCl₂) and a radical (CH₃, CH₂Cl, CHCl₂ or CCl₃)

Experimental results show that the bond energies in the less chlorinated RO radicals differ greatly from those in the more chlorinated ones. It was thus more probable that k_{14} increased considerably with increasing chlorine content of the RO radicals. Hence ϕ_{ox} would be greatest

for the highly chlorinated ethanes and ethylenes, found to be in agreement with experiment [41]

From a comparison of the experimental results and the bond energies, it appeared that long-chain oxidation occurs when the decomposition of the radical is exothermic by at least about 63 kJ/mol. Taking this into account enables one to explain the nature of the primary reaction products of the long-chain oxidations of 1,1,1,2- and 1,1,2,2- $\text{C}_2\text{H}_2\text{Cl}_4$, C_2Cl_4 and C_2HCl_5 . Thus 1,1,1,2- $\text{C}_2\text{H}_2\text{Cl}_4$ yields only COCl_2 , CO and HCl by C-C rupture, while 1,1,2,2- $\text{C}_2\text{H}_2\text{Cl}_4$ gives only CHCl_2COCl by C-Cl rupture. C_2Cl_4 and C_2HCl_5 lead to the formation of both CCl_3COCl and COCl_2 by C-Cl and C-C rupture.

Bertrand et al [41] therefore have provided evidence from their studies that those chlorinated ethanes and ethylenes that yield only one type of radical by attack of a chlorine atom, it is thus possible to explain why some oxidise and others don't and also to explain the type of oxidation products.

It is a reasonable assumption that photochlorination or chlorine atom sensitised oxidation of halothane will proceed in a manner analogous to the established mechanisms discussed in this chapter for similar species. The formation of products generated from both photochlorination and chlorine atom sensitised oxidation of halothane in the presence of oxygen could be rationalised in terms of two reaction mechanisms and will be investigated experimentally in this chapter.

3.2 EXPERIMENTAL

3.2.1 Materials

Chlorine (Argo International Ltd , stated purity 99.5%) was degassed by repeated freeze-pump-thaw cycles at liquid nitrogen temperatures. It was trap-to-trap distilled on the vacuum line using an acetone slush bath to remove volatile impurities and an ethyl acetate slush bath to remove involatile contaminants until no further impurities could be detected chromatographically. It was stored in a blackened bulb to prevent decomposition. Nitrogen (O.F.N. grade, Air Products Ltd ,) was used as a diluent gas for the reaction mixtures. All other materials were used as described in section 2.2.1.

3.2.2. Apparatus

The apparatus used is described in section 2.2.2. For those experiments in which chlorine was present, bulb D, line 3 and 5, the sample compartment of the infrared spectrophotometer and the teflon tubing connected to the gas sampling valve were covered with black cloth to prevent photolysis by the room lights. A Corning glass filter 0-52, (Figure 3.2.1) was used to isolate light of approximate wavelength before entering the reaction vessel, eliminating all wavelengths in the region $190 < \lambda < 330$ nm and transmitting only in the visible region of the spectrum.

3.2.3 Procedure

The procedure was identical to that described in section 2.2.3.

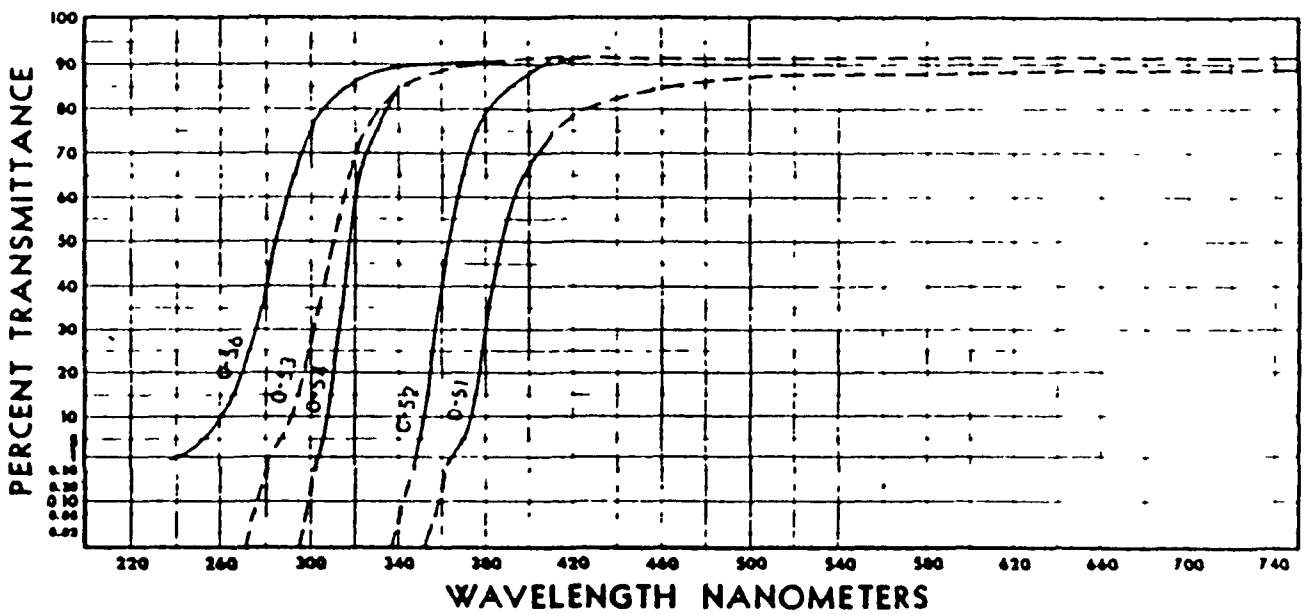


Figure 3.2.1
Spectral transmittance of Corning glass filters

3.2.4 Analysis

The analyses were carried out by infrared spectroscopy and gas liquid chromatography as previously described in section 2.2.4. For those experiments in which 2-bromo-2-chloro-1,1,1-trifluoroethane and chlorine was present, the column packing and operating parameters were identical to those described in section 2.2.4. For experiments in which chlorine and oxygen were present in the reaction mixture, a 2m glass column packed with 3% OV-17 on chromosorb WHP 80-100 mesh was used for analysis. The operating conditions again were identical to those previously described. The characteristic infrared absorption bands (cm^{-1}) used to identify the reactants and products and measure their concentrations are listed in Table 3.2.1.

Table 3.2.1 Characteristic IR absorption bands

Compound	Bands (cm^{-1})
CF_3CHClBr	1307, 1262
$(\text{CF}_3\text{CCl}_2\text{Br})_2$	1250, 1230, 860

3.2.5 Identification of reaction products

Photolysis of $\text{CF}_3\text{CHClBr}/\text{Cl}_2$ mixtures at $\lambda > 335 \text{ nm}$ and 20°C

CF_3CHClBr was identified by comparison of the infrared spectrum with that of an authentic sample and pressure measurements were made from the band centred at 1307 cm^{-1} as shown in Figure 3.2 2

Product identifications were made by infrared spectroscopy and when the infrared analyses were complete, the reaction mixtures were injected onto the chromatographic column as described earlier. Product identities were confirmed by gas-liquid chromatographic-coupled mass spectroscopy

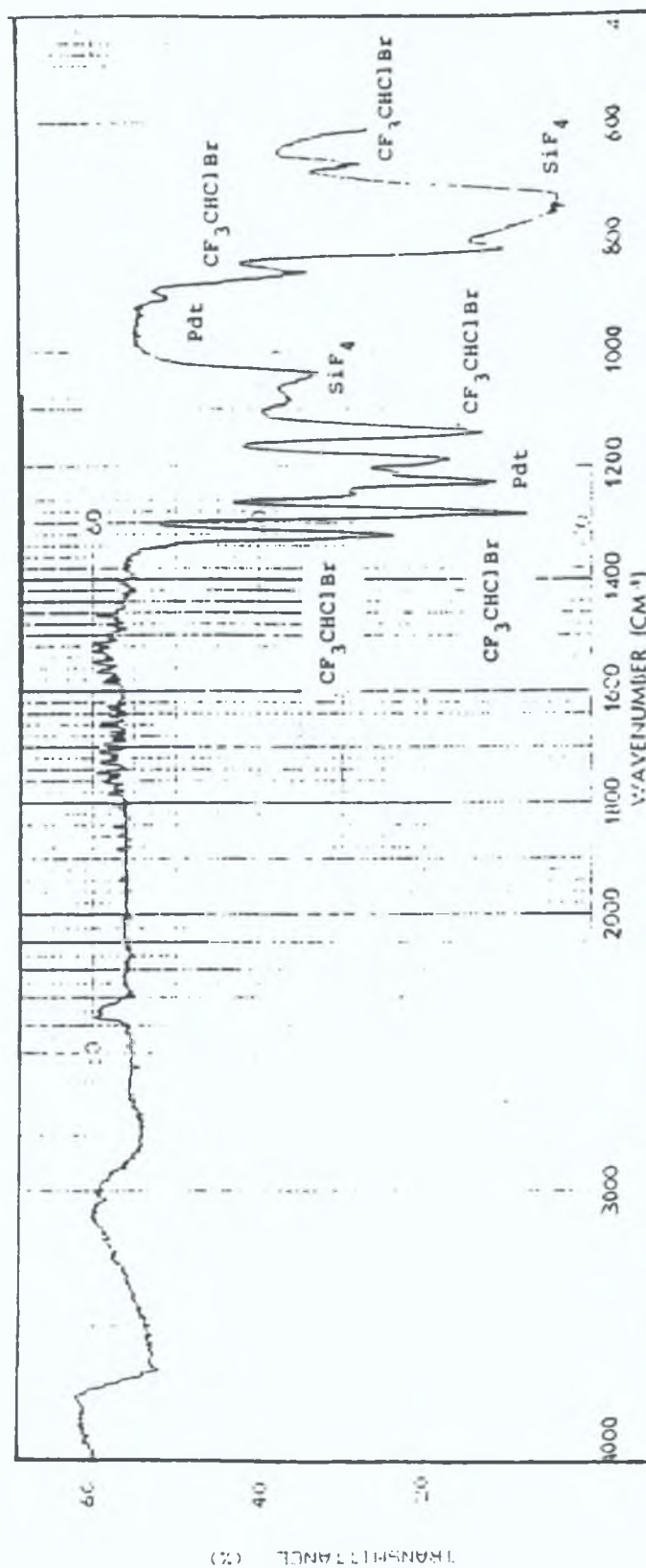
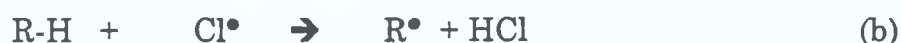


Figure 3.2.2
Infrared Spectrum of 5 torr CF_3CHClBr and 10 torr Cl_2 after 5 minutes photolysis $\lambda > 355 \text{ nm}$ and 20°C

3.3 RESULTS

To investigate the initiation reaction for oxidation of halothane (CF_3CHClBr) involves H abstraction by OH radicals which is a well established reaction, but OH radicals are difficult to generate experimentally and for the purpose of this work chlorine gas was photolysed to generate Cl atoms which react by the same initiation step with halothane.



Photolysis of chlorine in the wavelength range 290-420 nm (using Corning CS-O52 glass filter $\lambda > 335$ nm) in the presence of halothane was investigated in order to determine the reaction mechanism for oxidation of the radical produced in this process.

Preliminary work to product studies:

(a) Setting up analytical conditions for product identification.

The initial work was concerned with setting up analytical parameters for product identification and quantitation by gas chromatography. Quantitative analysis of gaseous samples containing low concentrations of halothane gave non-reproducible results. This lack of reproducibility was attributed to loss of halothane from the gas phase by adsorption in the gas sampling valve. It was found that no adsorptive losses were sustained when gas mixtures containing halothane and nitrogen were analysed, and the

quantitative results of these analyses were highly reproducible. Consequently, all experiments were carried out in the presence of at least 100 torr oxygen free nitrogen.

The response of the FID to the compounds of interest was established on a daily basis. The resulting calibration curves were linear with typical correlation coefficients of $r = 0.999$.

A halothane calibration curve was prepared in the range of 1-12 torr and made up to a total pressure of 100 torr in nitrogen. A representative halothane calibration curve is given in Figure 3.3.1 with calibration results from two consecutive days plotted on the same graph. The slopes of the calibration curves for the compounds of interest remained constant over extended periods of time. Hence it was not necessary to perform a complete calibration each day.

Product analysis was obtained in relation to the photooxidation products of halothane using gas chromatography, having optimised the analytical parameters.

Initially 3 torr halothane and 30 torr Cl_2 were prepared to a total pressure of 100 torr in N_2 and photolysed with a resulting time history shown in Figure 3.3.2 using the CS-O52 optical filter ($\lambda > 335 \text{ nm}$). The loss of halothane was monitored against time, Figure 3.3.2. A gas chromatogram of the products formed after 7 minutes photolysis resulting from photolysis of the same reaction mixture is given in Figure 3.3.3 for qualitative purposes.

Gas Chromatography Analyses

Using the chromatographic conditions outlined in section 2.2.4, after 7 minutes photolysis, two peaks were measured and assigned as product peaks

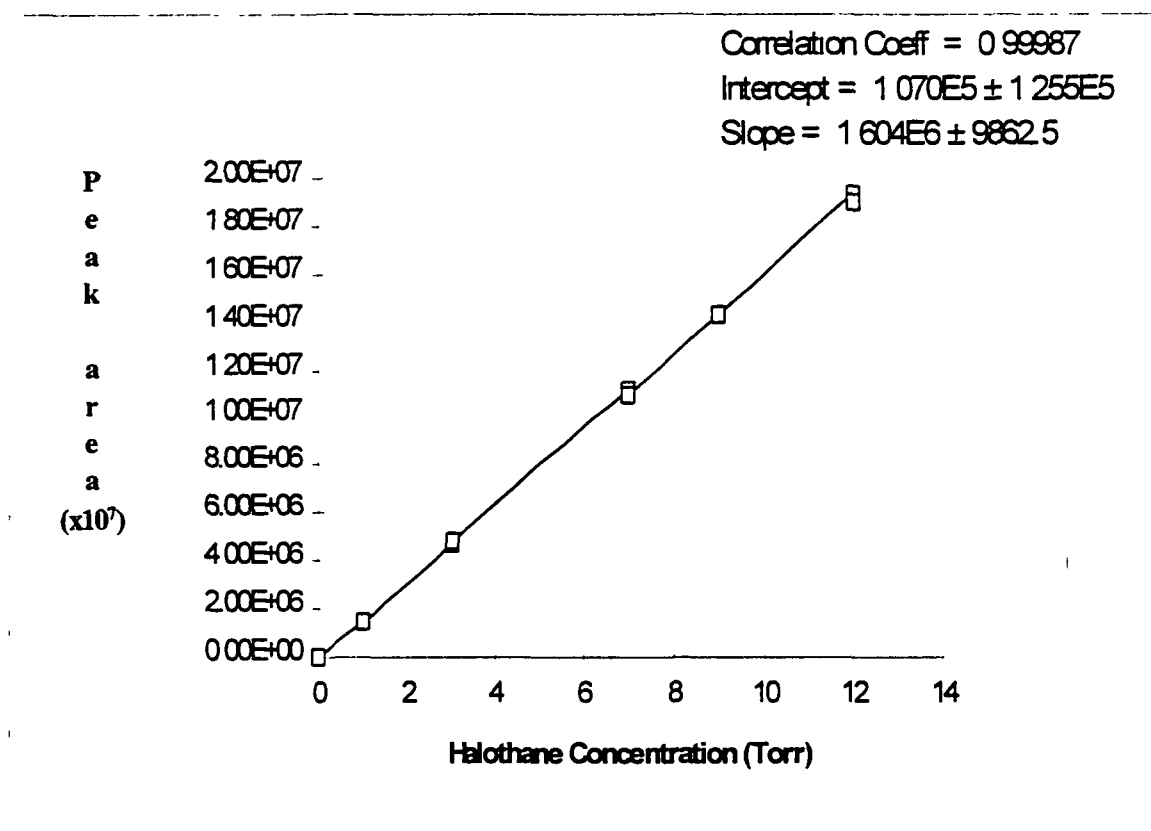


Figure 3.3.1
CF₃CHClBr standard curve in 100 torr N₂ determined by GC.

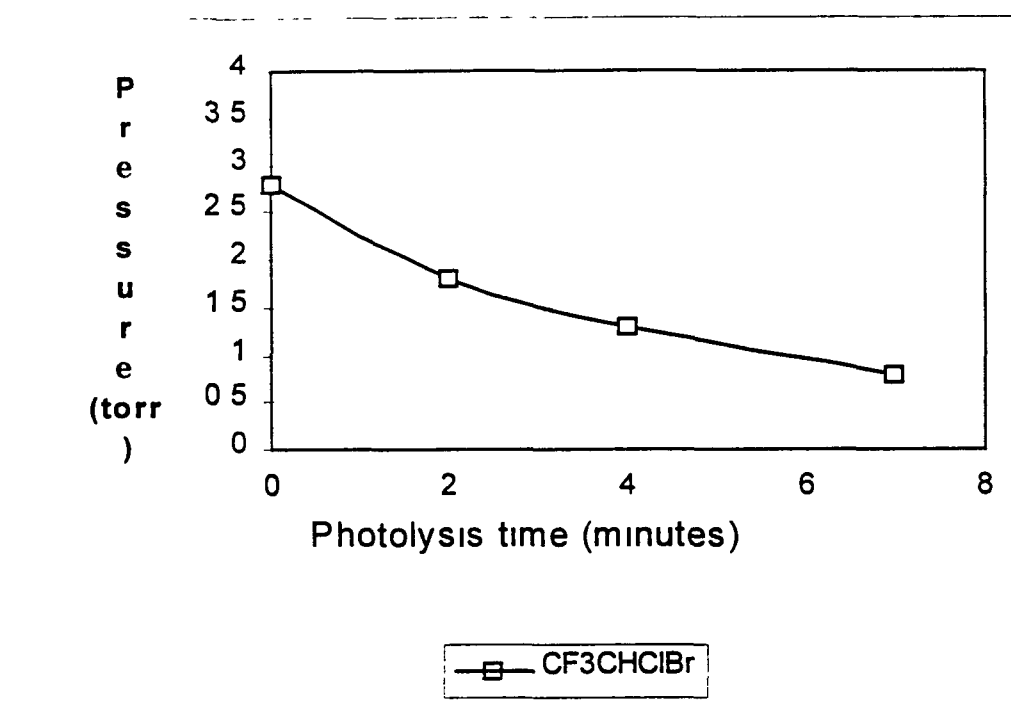


Figure 3.3.2
Photolysis profile for the photolysis of 3 torr CF_3CHClBr , 30 torr, Cl_2 in 67 torr N_2 at wavelengths > 335 nm and $20 \pm 2^\circ\text{C}$

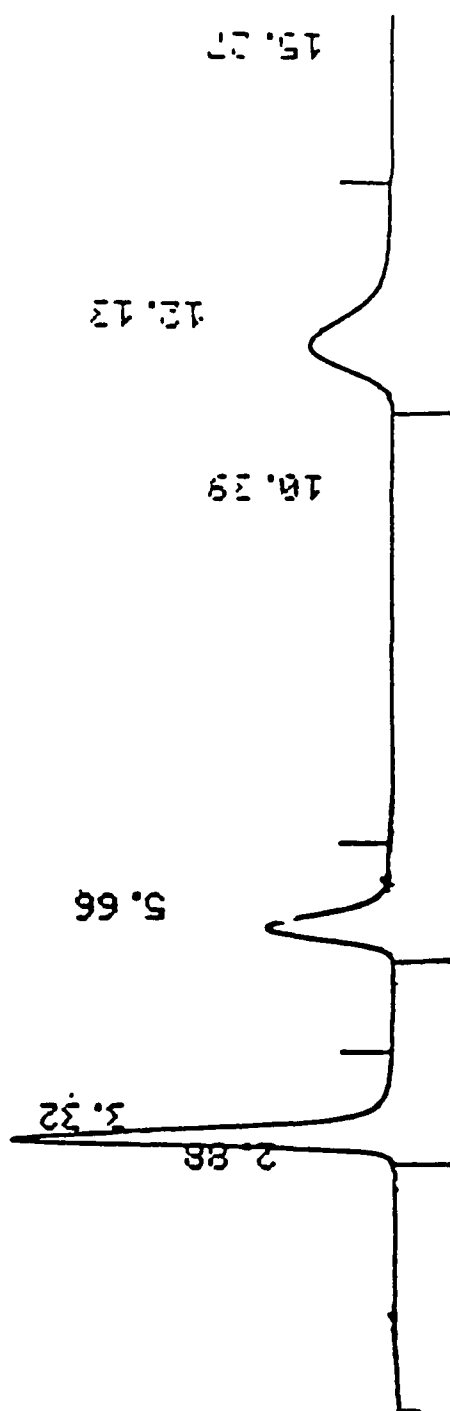


Figure 3.3.3

**Photolysis of 3 torr CF_3CHClBr , 30 torr Cl_2 in 67 torr N_2 ,
wavelengths > 335 nm, and $20 \pm 2^\circ\text{C}$.**

**The spectrum represents the reaction mixture after 7 minutes
photolysis.**

Although products were visible using the GC/FID no information could be obtained as to their nature. As it was possible to separate these reaction products from halothane using gas chromatography, it was decided to carry out off-line GC/mass spectroscopy work on the reacted gas mixtures in an attempt to elucidate these product components.

Gas mixtures containing 3 torr halothane, 30 torr Cl₂ and 67 torr N₂ were prepared on the vacuum line and transferred to the reaction cell and photolysed using a CS-O52 filter for 4 hours in order to allow reaction to go to completion. The reaction mixture was transferred to a gas tight sample holder with self-sealing rubber septa attached for sample withdrawal.

Figure 3.3.4 shows a chromatogram achieved for the reaction products of halothane using these reaction conditions prior to GC-Mass spectroscopy, chromatographic conditions as outlined in Section 2.2.4. An RIC trace obtained for the reaction is given in Figure 3.3.5. Reaction mixture components visible in the RIC trace were fragmented by electron impact to give the mass spectra in Figures 3.3.6 and 3.3.7.

Figure 3.3.6 is the mass spectra obtained from the fragmentation of component one, two and three visible in the RIC trace for the chlorine-sensitised oxidation of halothane. The first spectrum (a) yielded very little information. The fragment at $\left(\frac{m}{z} = 28\right)$ is probably due to Air/CO in the system. The spectrum of the second eluent (b) shows the presence of a CF₃ group $\left(\frac{m}{z} = 69\right)$, a CCl₃ group $\left(\frac{m}{z} = 117\right)$ and a CF₃CCl₂ group $\left(\frac{m}{z} = 151\right)$ and the component was confirmed against a library search to be CF₃CCl₃.

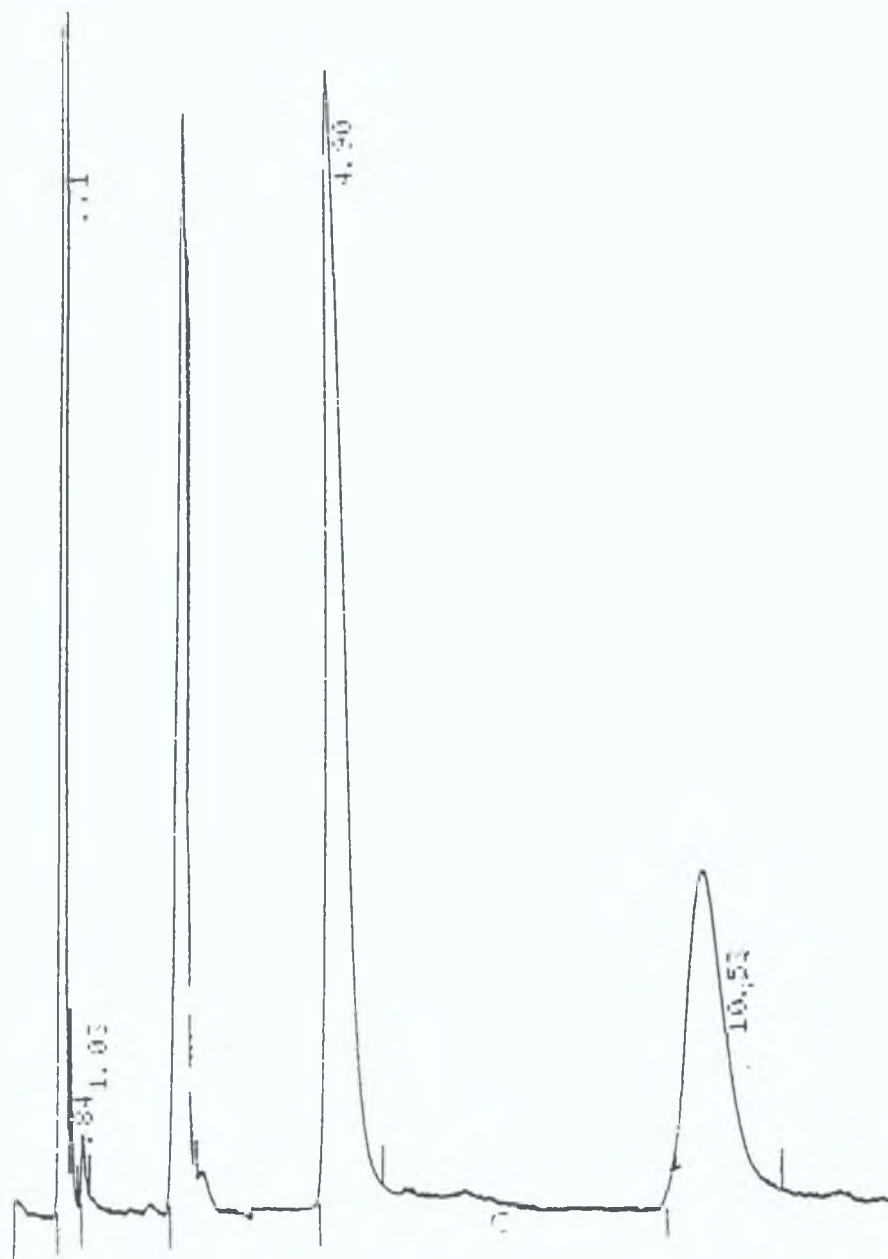


Figure 3.3.4
3 torr CF_3CHClBr , 30 torr Cl_2 in 67 torr N_2 , photolysed for 4 hours using wavelengths >335 nm and $20 \pm 2^\circ\text{C}$ and injected onto the GC using conditions as outlined in Section 2.2.4 prior to GC-Mass spectroscopy

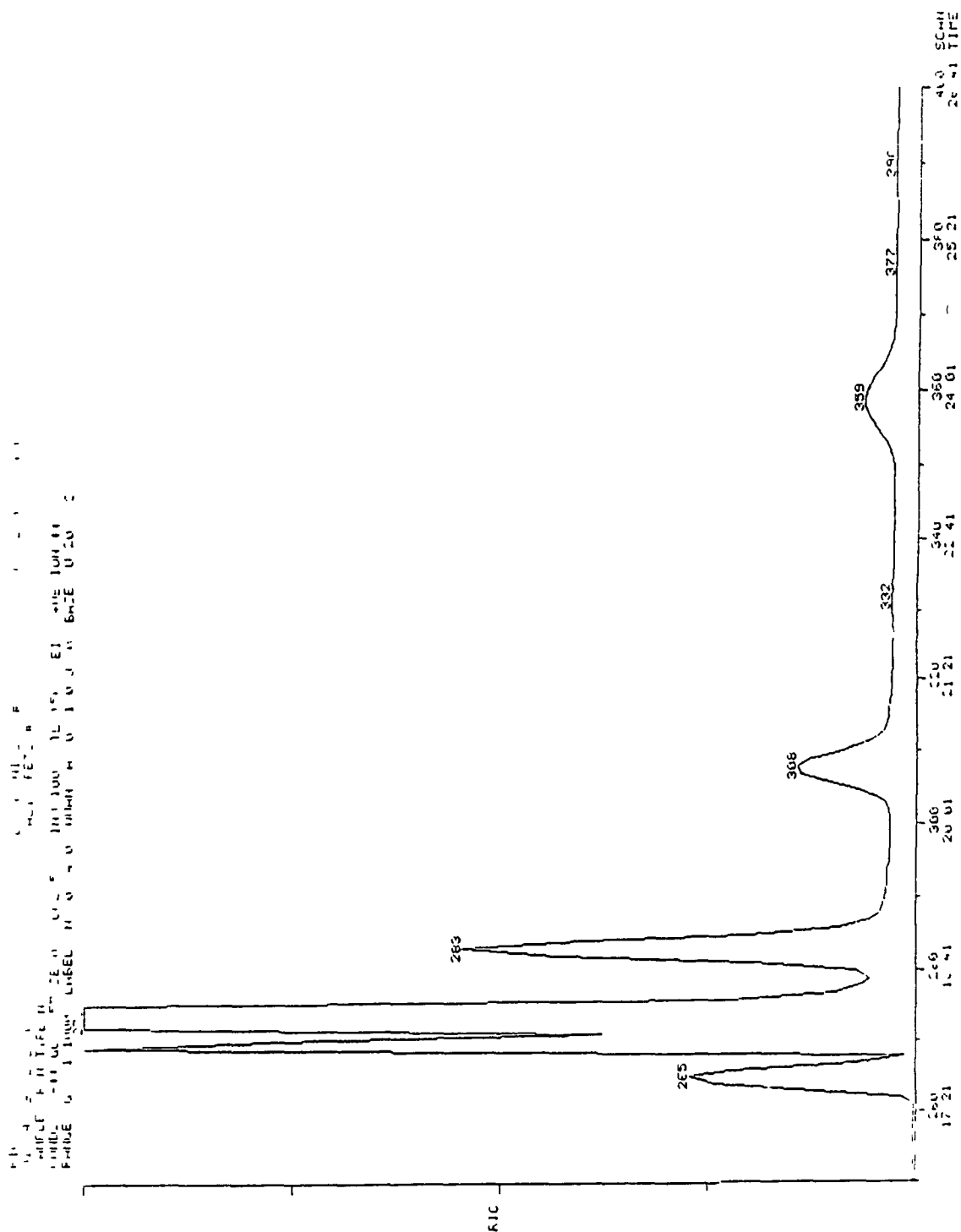


Figure 3.3.5
The off-line RIC trace for CF₃CHClBr oxidation mixture.
3 torr CF₃CHClBr, 30 torr Cl₂ in 67 torr N₂, photolysed for 4 hours
using wavelengths >335 nm and 20 ± 2°C .

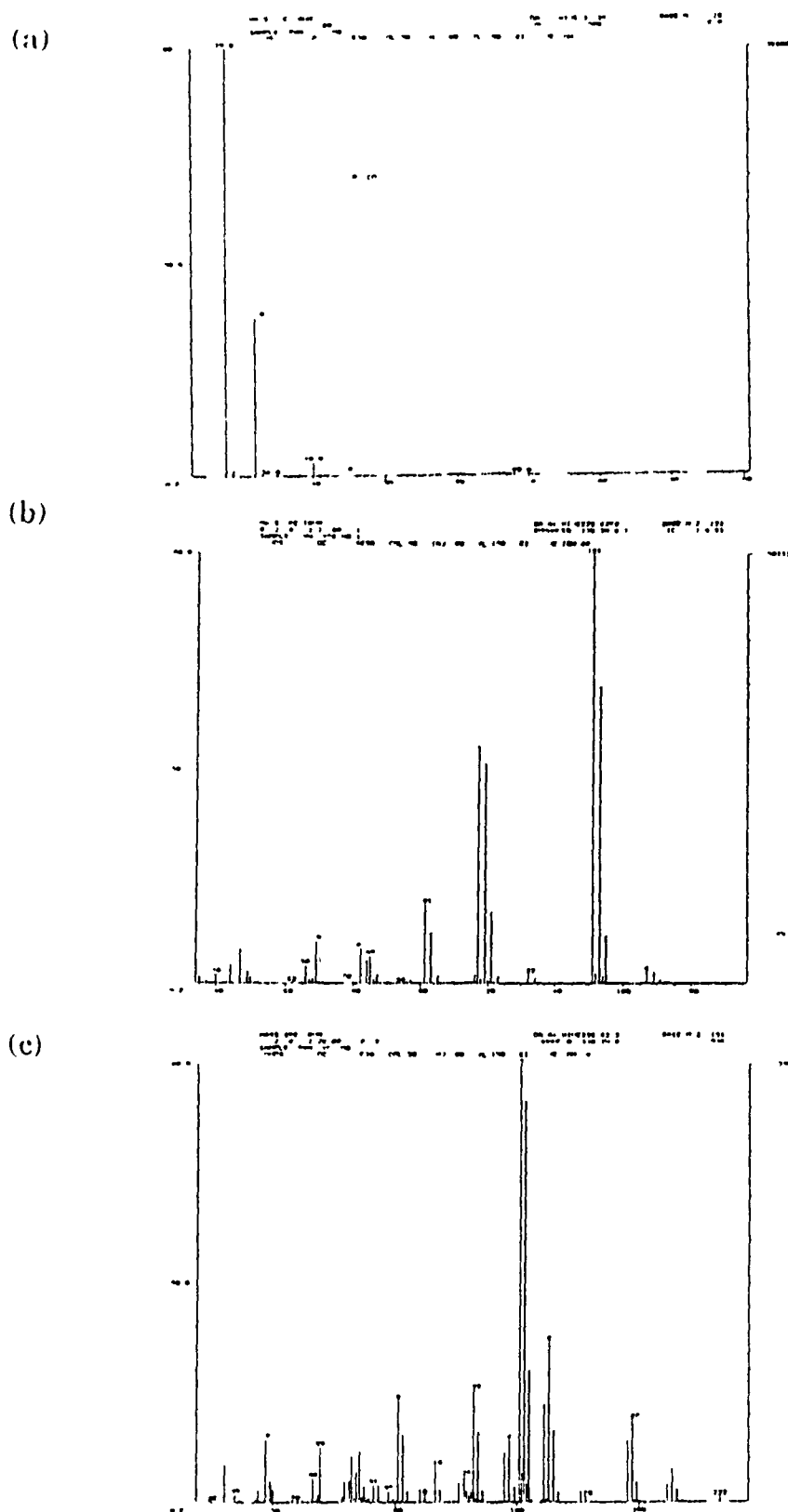


Figure 3.3.6

The mass spectra obtained from the fragmentation of (a) the first eluent, (b) the second eluent and (c) third eluent visible in Figure 3.3.5.

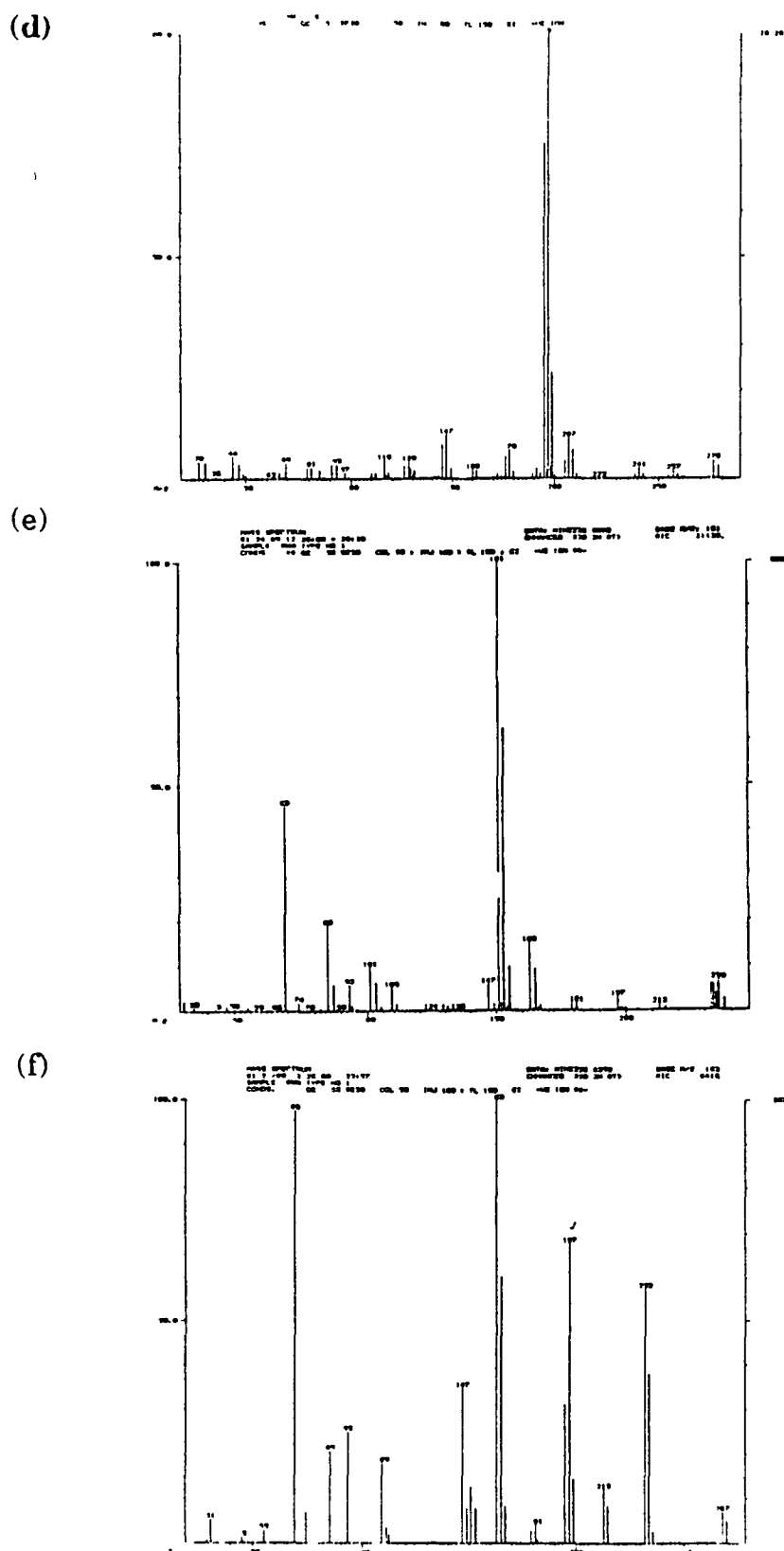


Figure 3.3.7
The mass spectra obtained from the fragmentation of (d) fourth eluent, (e) fifth eluent and (f) sixth eluent in Figure 3.3.5

The third mass spectrum (c) obtained from fragmentation of component three visible in the RIC trace shows the presence of a CF_3CCl_2 fragment $\left(\frac{m}{z} = 151\right)$, CF_3 $\left(\frac{m}{z} = 69\right)$, CCl_2 $\left(\frac{m}{z} = 82\right)$, $\text{CCl}_2\text{Br}^{81}$ $\left(\frac{m}{z} = 163\right)$ and may be contributed to $\text{CF}_3\text{CCl}_2\text{Br}$.

Figure 3.3.7 is the mass spectra of component four (d), five (e) and six (f) eluted from the same reaction mixture.

The spectrum resulting from the fragmentation of component four (d) visible in the RIC trace shows a CF_3CClBr (M) peak, $\left(\frac{m}{z} = 195\right)$ (M+2) peak $\left(\frac{m}{z} = 197\right)$ and (M+4) peak $\left(\frac{m}{z} = 199\right)$. The mass range covered in the spectrum is too small for definite identification but may be attributed to the oxidation product $(\text{CF}_3\text{CClBr})_2$ dimer.

The spectrum resulting from the fragmentation of component five (e) visible in the RIC trace, shows the presence of a CF_3 group $\left(\frac{m}{z} = 69\right)$ and CF_3CCl_2 group $\left(\frac{m}{z} = 151\right)$. The mass spectrum was confirmed against a library search to be $(\text{CF}_3\text{CCl}_2)_2$ dimer. The spectrum obtained from fragmentation of component six (f) visible in the RIC trace shows the presence of a CF_3 group $\left(\frac{m}{z} = 69\right)$ CF_3CClBr (M) peak $\left(\frac{m}{z} = 195\right)$, (M+2) peak $\text{CF}_3\text{CCl}^{37}\text{Br}$ $\left(\frac{m}{z} = 197\right)$ and (M+4) peak $\text{CF}_3\text{CCl}^{35}\text{Br}^{81}$ $\left(\frac{m}{z} = 199\right)$ a $\text{CCl}_2\text{Br}^{81}$ group $\left(\frac{m}{z} = 163\right)$ and CBr^{81} group $\left(\frac{m}{z} = 93\right)$. The mass spectrum did not have definite identification but may be contributed to $(\text{CF}_3\text{CCl}_2\text{Br})$. Having established the reproducibility of the overall system in the laboratory, a number of experiments were carried out in which the effect of varying the $[\text{Cl}_2][\text{CF}_3\text{CHClBr}]$ ratio on the ratio of product concentrations was investigated.

The CF_3CHClBr concentration was maintained constant at 3 torr and the chlorine concentration was varied from 3 torr to 30 torr with the total pressure maintained at 100 torr in all experiments by the addition of nitrogen

In an additional series of experiments, the concentration of chlorine was kept constant at 1 torr while the halothane pressure varied from 10 to 80 torr. In all cases for both sets of experiments, two major products were identified but the relative concentrations of these products varied as the $[\text{Cl}_2][\text{CF}_3\text{CHClBr}]$ varied. The results are given in Table 3.3.1

Further experiments were carried out with the same reactant pressures of chlorine, halothane and nitrogen and photolysed until the reaction was complete. No additional products were identified.

(c) Photolysis of Cl_2 / CF_3CHClBr / O_2 mixtures

Further studies on the effect of oxygen on the Cl atom sensitised oxidation of halothane was investigated. A reaction mixture of 3 torr halothane and 10 torr chlorine in the presence of 30 torr oxygen was photolysed for three hours using a CS-052 filter ($\lambda > 335 \text{ nm}$), chromatographic conditions are outlined in Section 3.2.4.

Although products were visible using the GC/FID no information could be attained as to their nature, Figure 3.3.8. As it was possible again to separate the reaction products using gas chromatography, off-line GC-mass spectroscopy was carried out in a similar procedure to the halothane and chlorine reaction mixture.

Table 3.3.1

Photolysis of CF_3CHClBr / Cl_2 mixtures at wavelengths >335 nm and $20 \pm 2^\circ\text{C}$.

Pressure (torr)			P_{Total} (Torr)	P_{Cl_2} : P_{Hal}	Phot. Time (Secs)	Products	Ratio
Hal	Cl_2	N_2					
3	30	-	33	10.1	15	$\text{CF}_3\text{CCl}_2\text{Br}$, $(\text{CF}_3\text{CClBr})_2$	14 1
3	30	-	33	10 1	60	"	4 1
3	30	67	100	10 1	15	"	*
3	30	67	100	10.1	15	"	2.1
3	30	67	100	10.1	15	"	6 1
3	3	94	100	1 1	180	$\text{CF}_3\text{CCl}_2\text{Br}$, $(\text{CF}_3\text{CClBr})_2$	*
3	60	94	157	20.1	60	"	*
10	1	-	11	1.10	300	$\text{CF}_3\text{CCl}_2\text{Br}$, $(\text{CF}_3\text{CClBr})_2$	2.1
20	1	-	21	1 20	15	$\text{CF}_3\text{CCl}_2\text{Br}$,	*
20	1	-	21	1 20	30	"	*
20	1	-	21	1 20	60	"	*
20	1	-	21	1.20	120	$\text{CF}_3\text{CCl}_2\text{Br}$, $(\text{CF}_3\text{CClBr})_2$	*
20	1	-	21	1 20	300	"	*
40	1	-	41	1 40	60	"	*
60	1	-	61	1 60	300	"	*
80	1	-	81	1 80	300	"	15 1

N B *Indicates that a quantitative determination was not possible in addition to a qualitative analysis

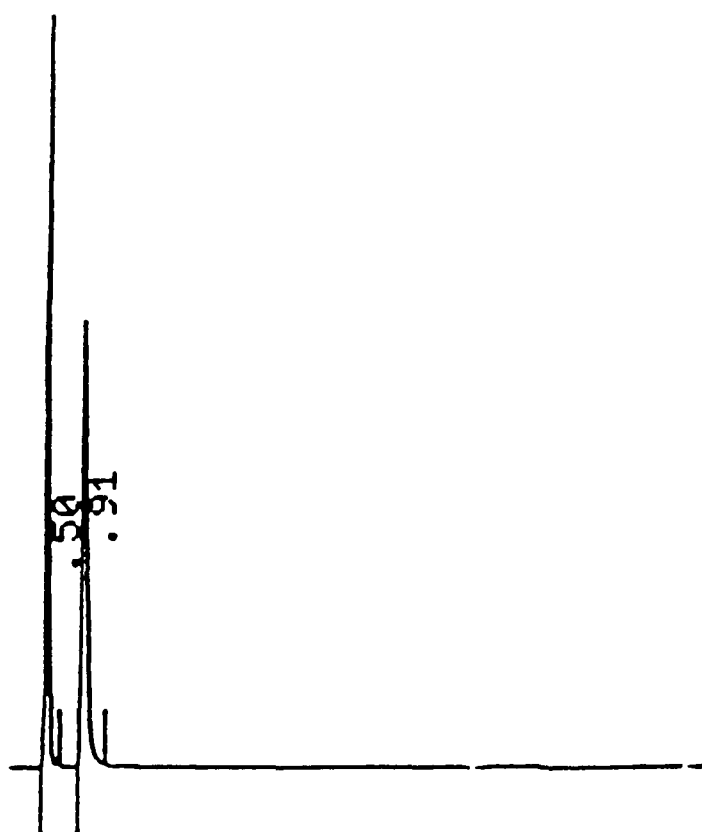


Figure 3.3.8
3 torr CF_3CHClBr , 10 torr Cl_2 and 30 torr O_2 photolysed for 3 hours using a CS-052 filter, at wavelength >335 nm and $20 \pm 2^\circ\text{C}$ and injected onto the GC. Chromatographic conditions as outlined in Section 3.2.4

An RIC trace obtained for the reaction mixture is given in Figure 3 3 9 Reaction mixture components visible in the RIC trace were fragmented by electron impact to give mass spectra in Figure 3 3 10

Figure 3 3 10 is the mass spectra obtained from the fragmentation of component one and two The spectrum of component one eluent (a) indicates the presence of a CO group $\left(\frac{m}{z} = 28\right)$ The mass range covered in the spectrum is too small for definite identification The spectrum of component two eluent (b) can be attributed to unreacted halothane The mass spectrum for halothane indicates a CF_3 fragment $\left(\frac{m}{z} = 69\right)$ a $\text{CHClBr}^{79} (\text{M})$ peak, $\left(\frac{m}{z} = 127\right)$, (M+2) peak $\text{CHClBr}^{81} \left(\frac{m}{z} = 129\right)$ and (M+4) peak $\text{CHCl}^{37}\text{Br}^{81} \left(\frac{m}{z} = 131\right)$

Very little information was obtained in relation to identification of photooxidation products from the halothane, chlorine and oxygen reaction using GC-Mass Spectroscopy

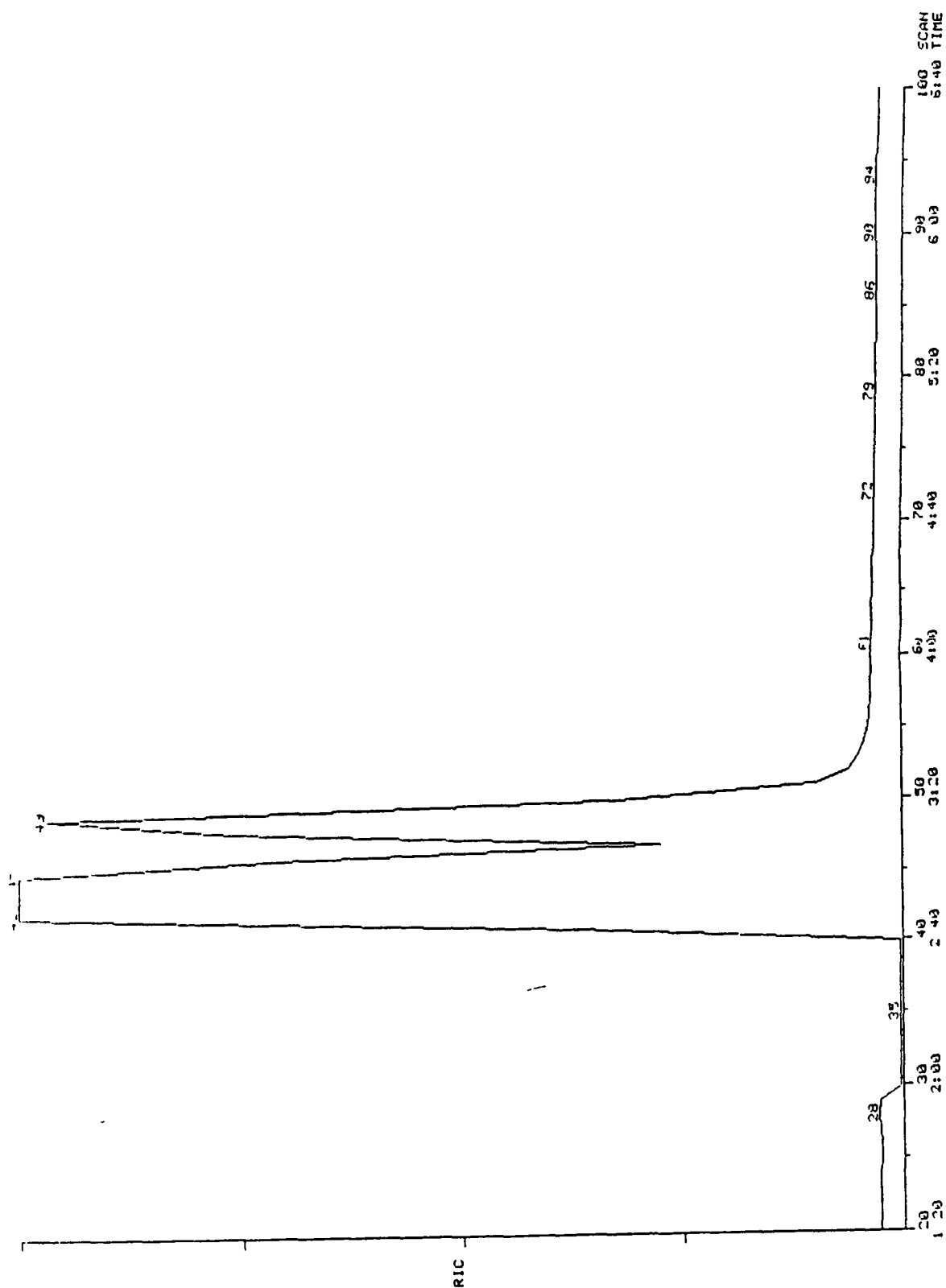
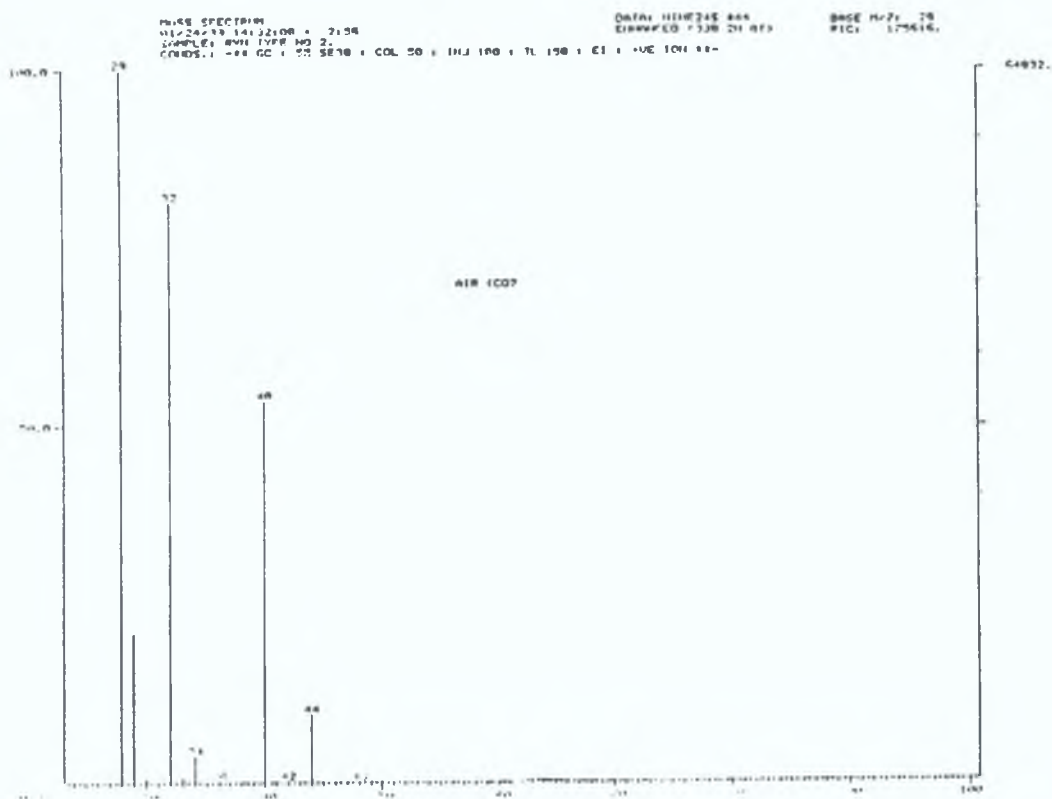


Figure 3.3.9

The off-line RIC trace for CF_3CHClBr photooxidation mixture, 3 torr CF_3CHClBr , 10 torr Cl_2 and 30 torr O_2 was photolysed for three hours using wavelengths $>335 \text{ nm}$ and $20 \pm 2^\circ\text{C}$

(a)



(b)

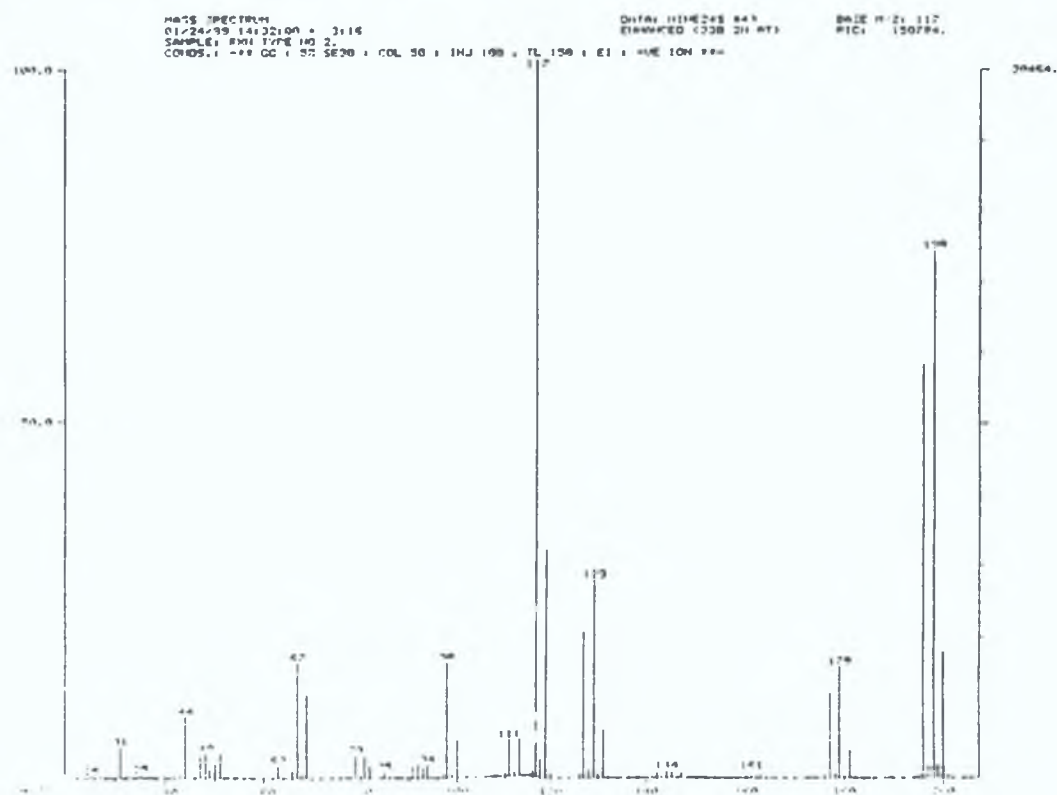
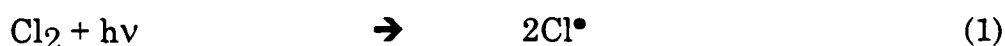


Figure 3.3.10

The mass spectra obtained from the fragmentation of (a) first eluent and (b) second eluent visible in Figure 3.3.9.

3.4 DISCUSSION

The chlorine atom sensitised oxidation of halothane at wavelengths >335 nm was assumed to yield $\text{CF}_3\text{CCl}_2\text{Br}$ and $(\text{CF}_3\text{CClBr})_2$ as the two major products. HCl was not observed with the analytical technique used in this study, but it is reasonable to assume that it was formed during the reaction. The formation of these products was rationalised in terms of the following reaction mechanism



Although the intensity of output from the medium pressure mercury lamp is low above 240 nm, a CS-052 optical filter was used to ensure that only light of wavelengths >335 nm irradiated the reaction vessel to initiate the reaction process.

From the mechanism reaction 5 is unlikely to occur since radical recombination depends on such factors as collision frequency, concentration of radical species and rate of reaction

Product studies in relation to the chlorine atom sensitised oxidation of halothane were carried out using a combination of IR and GC spectroscopy. For quantitative GC work, the problem of halothane loss from the gas phase by adsorption onto the gas sampling valve was overcome by

ensuring that all experiments were carried out with a total pressure of at least 100 torr in oxygen free Nitrogen as diluent gas

Having used IR spectroscopy to establish the appearance of oxidation product peaks, for halothane, similar work was carried out using gas chromatography to follow the progress of the reaction

To determine the concentration of halothane at each photolysis time, standard curves were prepared as shown in Figure 3.3.1. High correlation coefficients and low intercepts were obtained over the concentration range studied. These standard curves also illustrate the accuracy of the procedure used for the preparation of gas mixtures on the vacuum line and the reproducibility of the GC injection apparatus outlined in Figure 2.2.1

Initially 3 torr halothane and 30 torr Cl_2 prepared to a total pressure of 100 torr in Nitrogen was photolysed and the reaction monitored by IR. No information as to the nature of the reaction products was established at this point.

The results from the initial chlorine atom sensitised oxidation studies followed by GC is given in Figure 3.3.2 and the formation of two peaks were noted as expected for the proposed mechanism

Based on the fact that chlorine atoms are readily involved in reaction (2) and CF_3CHClBr was present in low concentrations makes it possible to assume that reaction 5 does not occur to any great extent

The proposed mechanism would suggest that at high $[\text{Cl}_2]/[\text{CF}_3\text{CHClBr}]$ ratios chain termination is expected to be exclusively by

chlorine atom combination To verify this, the reaction was carried out and monitored by GC Spectroscopy under varying $[\text{Cl}_2]/[\text{CF}_3\text{CHClBr}]$ ratios to determine the kinetic behaviour of the aforementioned reaction pathways

The results shown in Table 3.3.1 indicate that at both high and low $[\text{Cl}_2]/[\text{CF}_3\text{CHClBr}]$ ratios, two major products, presumed to be $\text{CF}_3\text{CCl}_2\text{Br}$ and $(\text{CF}_3\text{CClBr})_2$ were formed although the ratio of products varied significantly from 2:1 to 15:1

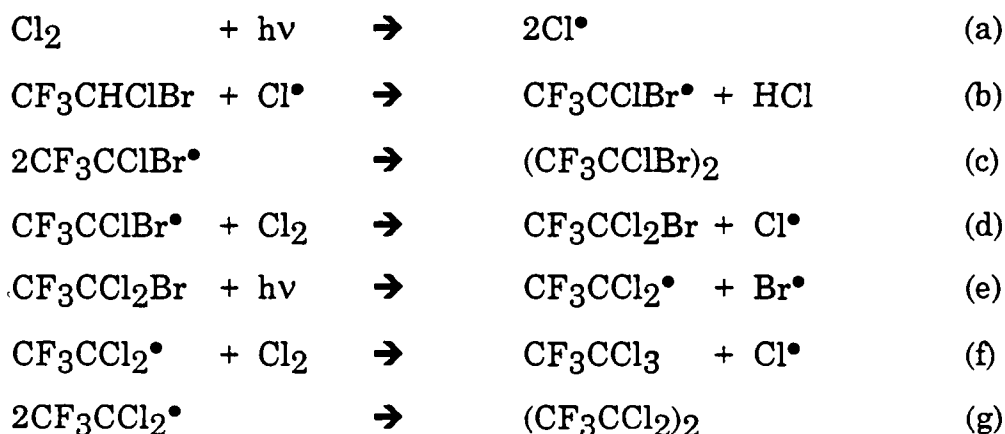
The first proposed peak with retention time equal to 5.66 minutes was identified as the only major product for some low $[\text{Cl}_2]/[\text{CF}_3\text{CHClBr}]$ ratios, but it is reasonable to assume that the second major product may have been formed but has not been identified within the limits of detection used. As can be seen from the results of the four experiments which utilised a $[\text{Cl}_2]/[\text{CF}_3\text{CHClBr}]$ of 1:20, $(\text{CF}_3\text{CClBr})_2$, the second peak with retention time equal to 12.13 minutes was only identified at longer photolysis times. It is reasonable to assume that this product was also formed at shorter photolysis times but its concentration was below the limit of detection of the flame ionisation detector. The other possibility which should be considered is that $(\text{CF}_3\text{CClBr})_2$, the second peak is a secondary product of the reaction. $\text{CF}_3\text{CCl}_2\text{Br}$ does not absorb radiation in the wavelength range used for this study and there is no other apparent secondary source of $(\text{CF}_3\text{CClBr})_2$. Hence it is most unlikely that this is not a primary product.

Since the products were visible using GC/FID, and it was possible to separate these reaction products from halothane using GC, it was therefore decided to switch from IR/GC to GC-Mass spectroscopy, since the photooxidation products were separated from the parent compound, halothane, their identification by Mass spectroscopy was possible.

Gas mixtures containing 3 torr halothane, 30 torr Cl₂ and 67 torr N₂ were prepared and photolysed for four hours in order to allow the reaction to go to completion and analysed by GC, Figure 3 3 4 before taking off-line to analyse by GC-Mass spectroscopy

The GC-Mass spectroscopy results proved inconclusive and the proposed mechanism is now in question. The results of the RIC trace showed six peaks in which two peaks were identified as CF₃CCl₃ and (CF₃CCl₂)₂, three other peaks were proposed to be CF₃CCl₂Br, (CF₃CClBr)₂ and (CF₃CCl₂Br) according to fragmentation patterns and the sixth peak was assumed to be Air/Co in the system

Based on this information the proposed mechanism could now be rationalised as follows



Step (e) in the newly proposed mechanism will probably not occur. From both a photochemical and thermochemical point of view, light in the wavelength range 190-290 nm is necessary to break the C-Br bond (the weakest bond in the halothane molecule) and since light >335 nm irradiates the system, it therefore makes this reaction most probable not to occur.

Further studies on the effect of oxygen on the chlorine atom sensitised oxidation of halothane was investigated, similarly the reaction was analysed off-line by GC-MS and the RIC trace and mass fragmentation patterns identified halothane as the major peak, the second peak was attributed to Air/Co in the system

The photooxidation mechanisms proposed in this thesis for halothane are by no means conclusive. Further work is required in order to conclusively identify the products formed and generate a more comprehensive oxidation reaction mechanism to take into account product formation. Increased use of GC-Mass spectroscopy combined with techniques such as FTIR and NMR spectroscopy as analytical tools for product identification and an accurate knowledge of the quantum yields of end product formation is an essential step in the determination of a photochemical mechanism and to complement our studies of intermediates involved in the photooxidation reactions

3.5 CONCLUSION

It is now well established that organic compounds emitted into the troposphere may be removed by reaction with a number of reactive intermediates including OH radicals

For the purpose of gaining information on the mechanism and kinetics of reactions of this type, the chlorine atom sensitised oxidation of halothane using light of wavelength >335 nm was studied. The reaction was found to proceed via a hydrogen atom abstraction from the molecule by a chlorine atom, this process is analogous to the OH radical abstraction reaction which is expected to occur under tropospheric conditions. As the lamp emits radiation above 335 nm, bond breakage within the halothane molecule was not possible, therefore the only source of chlorine atoms in these reaction mixtures resulted from the photodecomposition of molecular chlorine added to the reaction mixture. The reaction products were not the same as those found for photooxidation of halothane under simulated conditions (Chapter 2)

Lack of time and analytical limitations did not allow us to unambiguously identify the products formed. Other techniques such as GC/MS, FTIR and NMR spectroscopy would provide more information which would allow formulation of a comprehensive and conclusive reaction mechanism for oxidation of halothane under simulated tropospheric conditions

3.6 REFERENCES

- [1] B J Finlayson-Pitts and J N Pitts Jr , "Atmospheric chemistry Fundamentals and Experimental Techniques", Wiley and Sons Publishers. (1986)
- [2] S C Wofsy and M B McElroy, Can J Chem , **52**, 1582 (1974)
- [3] H B Singh, Geophys Res Lett , **4**, 101, (1977)
- [4] J Rudolph and D H Enhalt, J Geophys Res , **86**, (C12) 11959 (1981)
- [5] W. L Chameides and R J Cicerone, J Geophys. Res , **83** (C2) 947 (1978)
- [6] R Atkinson, W P L Carter, Chem. Rev , **84** 437 (1984)
- [7] R. Atkinson, Chem Rev., **86** (69) (1986).
- [8] M Bodenstein, Z physik Chem., **13**, 56 (1894), Ibid , **22** 1 (1897), Ibid., **29**, 295 (1898)
- [9] J C Ghosh, S K Bhattacharyya and S C Bhattacharyya, Z Physik Chem , **B32**, 145 (1636)
- [10] G K Rollefson, "The Photochemistry of Halogens", Hermen et cie, Paris, (1936)
- [11] G K Rollefson and H Eyring, J Am Chem Soc , **54**, 170, (1932)
- [12] H J Schaumacher, Z Angew, Chem , **50**, 483 (1937)
- [13] P A Gosselaim, J Adam and P Goldfinger, Bull Soc Chem Belges, **65**, 533 (1956)
- [14] C Walling "Free Radicals in Solution", John Wiley & Sons, New York, 356, (1957)

- [15] C Walling and M F Mayahi, J Am Chem Soc , **81**, 1485 (1959)
- [16] P C Anson, P S Fredericks and J M Tedder, J Chem Soc , 918 (1959)
- [17] P S Fredericks and J M Tedder, J Chem Soc , 144 (1960)
- [18] P S. Fredericks and J M Tedder, J Chem Soc , 3520, (1961)
- [19] H Singh and J M Tedder, J Chem Soc , 4737 (1964)
- [20] E Muller and E W Schmidt, Chem Ber , **97**, 2614 (1964)
- [21] N. Colebourne and E S Stern, J Chem Soc , 3599, (1965)
- [22] H O Pritchard, J B Pyke and A F Trotman-Dickenson, J Am Chem Soc , **77**, 2629, (1955).
- [23] A L. Henne and M W. Renoll, J Am Chem. Soc., **58**, 889, (1936)
- [24] Toshihiko Migita, Mansanori Kosugi and Yoichiro Nagai, Bulletin of the Chemical Society of Japan, **40**, 920, (1967)
- [25] G. J Martens, J A. Franklin, M Godfroid, M. Delvaux and J Verbeyst, Int J Chem Kinet , **5**, 539, (1973)
- [26] C Cillien, P Goldfinger, G Huybrechts and G Martens, Trans Faraday Soc , **63**, 1631 (1967)
- [27] G J Martens, M Godfroid and J Vebeyst, Bull. Soc Chim Belg , **81**, 57 (1972)
- [28] L Bertrand, J A Franklin, P Goldfinger and G Huybrechts, Journal of Physical Chemistry, **72**, 3926 (1968)
- [29] K L Muller and H J Schaumacher Z Physik, Chem , **B35**, 455, (1937)

- [30] F S Dainton, D A Lomax and M Weston, Trans Faraday Soc , **53**, 460 (1957)
- [31] G Chiltz, S Dusoleil, P Goldfinger, G Huybrechts, A M Mahieu, and D Van der Auwera, Bull Soc Chim, Belges, **68**, 5, (1959)
- [32] G Huybrechts, L Meyers and G Verbeke, Trans Faraday Soc., **58**, 1128 (1962)
- [33] G Huybrechts, G Martens, J Olbregts and K. Thomas, L Meyers and G Verberks, Trans Faraday Soc , **61**, 1921, (1965)
- [34] G Huybrechts and L Meyers, Trans. Faraday Soc., **62**, 2191 (1966).
- [35] B G Yasnitskii, Zh. Org. Khim., **3**(5), 798, (1967)
- [36] K L Muller and H J Schaumacher, Z Phys Ch., **B37**, 365, (1937).
- [37] W A Alexander and H. J Schaumacher, Z. Phys. Ch., **B44**, 313, (1939)
- [38] H J Schaumacher and W Thurauf, Z Phys Ch., **A189**, 183, (1941).
- [39] W J Miller and A L Dittman, J Am. Chem., Soc., **78**, 2793 (1956)
- [40] P Dickinson and A Leermakers J Am Chem Soc., **54**, 3852, 4648 (1932)
- [41] L Bertrand, L Exsteen-Meyers, J A Franklin, G Huybrechts, J Olbregts, Int J Chem Kinet , **3**(1), 89 (1971)
- [42] P Goldfinger, G Huybrechts, L Meyers, Final Technical Report, Office of Research and Development Command, U S Dept of Army, Contract DA-91-591-EUC-3559, (1966)

CHAPTER 4.0

CHLORINE ATOM REACTIONS WITH A SERIES OF HALOALKANES

4.1 INTRODUCTION

In 1970, the task of reliably estimating the lifetimes of a wide range of volatile organic compounds including hydrocarbons and halogenated hydrocarbons in polluted atmospheres would have been difficult, if not impossible. The reactive intermediates and mechanisms of their degradation were not known in sufficient detail, and rate constants for many key reactions were unknown or highly uncertain.

Organisations such as the National Atmospheric and Space Administration (NASA) and the IUPAC Task Group on chemical kinetics have been established with the aim of compiling a database of information on the kinetics, mechanisms and reaction products of the chemical species relevant to the atmosphere.

In assessing the impact of any organic species, there is a need to determine

- the atmospheric degradation pathway for the compound,
- its corresponding atmospheric lifetime; and
- the products formed from the parent compound and their fates in the atmosphere

It is now well established that organic chemicals emitted into the troposphere are removed by reaction with a number of reactive intermediates including OH, HO₂ and NO₃ radicals, O₃, by photolysis and by wet and dry deposition [1]. The role of chlorine chemistry in the troposphere has received little attention because, "Cl atoms are sufficiently scarce that they could not compete with OH radicals as a dominant loss

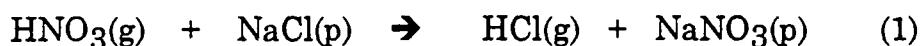
mechanism for hydrocarbons in the troposphere" stated Wofsy and McElroy in 1974 [2]

This scenario is supported by the fact that the reaction of Cl atoms with CH_4 is only 13 times faster than the corresponding OH radical reaction whereas OH radicals are nearly 1000 times more abundant in the lower troposphere. However, by comparison, typical reaction rates of Non Methane Hydrocarbons (NMHCs) with Cl atoms are nearly 100-1000 times faster than the corresponding OH radical rates. As the Cl / OH ratio increases with altitude, and because of the lower activation energies of Cl atom reactions, it has been realised that Cl atoms should play an important role in NMHC oxidation in the lower stratosphere [3-5]. However, Singh et al [6] have determined marine tropospheric levels of Cl atoms of 10^3 cm^{-3} or approximately 1000 times lower than OH radicals. Because of their greater reactivity towards NMHCs, Cl atoms may play an important role in NMHC oxidation at all latitudes. Since Singh et al highlighted the possible importance of Cl atom oxidation of NMHCs in the troposphere, a number of articles have been published reporting Cl atom rate constants, pointing towards the importance of these values not only in stratospheric modelling but also in determining the fate of volatile organic chemicals (VOCs) in the troposphere [7-9]

The gas phase reaction of Cl atoms with alkanes represents an important loss process for Cl atoms and organic compounds in the earth's stratosphere (40 - 90% of NMHC oxidation in the stratosphere is caused by reaction with Cl atoms and between 20 to 40% of NMHC oxidation in the troposphere, Singh et al [6])

The chemical species and sources of gaseous chlorine in the troposphere have been the subject of controversy for many years. Gaseous inorganic chlorine (GIC) is known to be present in the marine boundary layer at concentrations of approximately 1 to 2 ppbv [6]

There is general agreement that the major component of GIC is HCl which is released from sea salt aerosols that have been acidified to very low pH (2 to 3) by the addition of nitric or sulphuric acid produced in the atmosphere [10-12]



The formation of the acids can be explained by looking at the reactions of sulphur and nitrogen oxides in the atmosphere. SO_2 in the atmosphere is steadily oxidised to SO_3 , which being extremely hygroscopic is adsorbed by any particulate matter as H_2SO_4 . This mechanism explains two things, namely, the often observed low pH of precipitation and the presence of chloride in the atmosphere.

This marine source for GIC is supported by gaseous chloride concentration measurements. Highest levels of GIC are found in marine air and these decline as air moves over continental regions [13]. Besides the proposed seasalt source of GIC in the troposphere other minor sources include (combustion of coal and petrochemicals) and from volcanoes. More recently measurements in which HCl is converted to an organic derivative for quantification by GC have been reported [14]. These methods show somewhat lower HCl levels compared to previous determinations but these measurements represented a mix of both marine and continental air.

masses For the determination of NMHC lifetimes with respect to Cl atoms in this report, a concentration of 2×10^3 atoms cm^{-3} was used [6]

The actual concentration of OH radicals in the troposphere and lower stratosphere is obviously of particular importance since reaction with these species is an important loss process for VOCs and their concentration will thus determine the lifetimes of these organics in the troposphere and thus the levels which are transported to the stratosphere

Numerous directly measured and estimated atmospheric OH radical concentrations have been reported in the lower troposphere, measurements using laser induced fluorescence and long path length UV absorption show that OH radical concentrations are generally $< 5 \times 10^6$ molecules cm^{-3} Estimates for the average tropospheric OH radical concentrations have been derived from the ambient tropospheric levels of trichloromethane (CHCl_3), 1,1,1-trichloroethane (CH_3CCl_3) [15] and ^{14}CO These ambient tropospheric measurements yield an average northern hemisphere OH radical concentration of $\text{Ca } 5 \times 10^5$ molecules cm^{-3} More recently, Crutzen [16] has carried out calculations which predict the annually averaged OH radical concentration in the troposphere during a 24 hour period at $\text{Ca } 5 \times 10^5$ and 6×10^5 molecules cm^{-3} for the northern and southern hemispheres respectively

Directly measured [OH] values are typically of the order 1×10^6 radicals cm^{-3} however during smog events, [OH] may be as high as 10^7 radicals cm^{-3} However a value of 7.7×10^5 molecules cm^{-3} was calculated by Prinn et al [15] and represents a globally averaged tropospheric concentration of OH radicals

For the majority of organic chemicals present in the troposphere, reaction with the OH radical during daylight hours is expected to be the dominant removal process [1,17,18] due to the H-atom abstraction power of the hydroxyl radical and its high electrophilicity leading to addition reactions. Hence in order to allow the dominant tropospheric removal processes of these organic compounds to be assessed, and their tropospheric lifetimes with respect to OH radical reaction to be calculated, it is necessary to either experimentally measure, or reliably estimate, the OH radical reaction rate constants.

Great effort has been devoted to devising experimental techniques which allow kinetic data to be obtained under simulated atmospheric conditions i.e. in one atmosphere of air, with reactant and co-pollutant concentrations typical of those found in the troposphere. In many cases duplication of atmospheric conditions is not possible so experiments are carried out under as wide a range of conditions as possible and the results are extrapolated to atmospheric conditions.

Experimental Techniques

The experimental techniques used to study the kinetics of OH radical or Cl atom reactions with organics can be studied using two techniques, namely absolute rate methods and relative rate methods.

Absolute rate methods are measured using techniques which allow the concentration of the OH radical or Cl atom to be determined as a function of time. Since the OH radical / Cl atom are very reactive, short-lived species, these techniques rely on the use of extremely rapid and

sensitive detection systems ie. laser excitation and fluorescence detection [1].

In the case of relative rate studies the most commonly used technique is based on monitoring the relative rates of disappearance of two or more organics in a chemical system containing OH radicals. The UCR (University of California Riverside) Protocol for the determination of OH radical rate constants with volatile organic chemicals details the theory of this technique [19]. Because relative rate techniques do not rely on measurement of absolute concentrations of reactive intermediates, the equipment tends to be simpler and significantly cheaper. As it is the concentration of the VOCs which is monitored in the relative rate technique, the time-scale of reaction is much longer than in the absolute technique, hence the methods of detection are cheaper (GC is commonly used). Relative rate methods also have the advantage that rate constants may be measured with greater precision (but not necessarily greater accuracy) than absolute methods.

As the experimental procedure employed in our laboratory was a relative rate technique, only a quick mention of absolute methods is given here.

(a) Absolute techniques

The main absolute techniques for monitoring both OH radical and Cl atom rate constants include, fast flow discharge systems (FFDS), flash photolysis (FP) [1], and to a lesser extent, molecular modulation (MM) and pulse radiolysis (PR). Pulse radiolysis has found limited use because of the expense and complexity of the equipment [20,21]. The characteristics of the

discharge flow and flash (or laser) photolysis methods are discussed in detail by many workers in several published articles [18,22-24]

In the absolute technique, for the bimolecular reaction,



either the pseudo - first order decay of one species is measured in the presence of a known excess concentration of the other reactant, with

$$-d \ln [A]/dt = K[B] \quad (\text{II})$$

or the concentration of both species are measured and the rate constant K derived from the equation

$$\frac{d[\text{Product}]}{dt} = \frac{-d[A]}{dt} = \frac{-d[B]}{dt} = K[A][B] \quad (\text{III})$$

At lower temperatures, typically $\leq 1000\text{K}$, the discharge flow and flash (or laser) photolysis techniques interfaced to a variety of detection systems have been, and continue to be, widely used. To date, these detection systems for OH radical reactions have included mass spectrometry [25], electron paramagnetic resonance [26], laser magnetic resonance [27], resonance absorption [28-31] (including laser absorption [32]) and resonance fluorescence [33,34] (including laser induced fluorescence [35,36])

(b) Relative rate techniques

Numerous methods have been employed to obtain relative rate constant data for the reaction of OH and Cl atoms with VOCs. The "smog chamber" has been the most widely used approach for relative rate studies. Although the general aims of all chamber studies are similar (i.e. to simulate reactions in ambient air under controlled conditions), the chamber designs and capabilities used to meet this requirement vary widely. In

general, however, components of a smog chamber are similar and usually include

- a reaction chamber
- a series of photolysis lamps
- a detection system

The glass type reactors used in early studies suffered many problems [1] and as a result, larger smog chambers with inert surfaces are generally used today (Conditioned FEP Teflon films have been shown to have relatively low rates of surface destruction. The fact that their volume can easily be varied, they transmit solar radiation in the region 290 - 800 nm as opposed to ≥ 350 nm for pyrex glass and they are inexpensive (An 86dm³ teflon bag was used for our relative rate experiments)

During a normal smog chamber experiment using a teflon bag, as samples are withdrawn, the bag collapses and hence a pressure of 1 atmosphere is maintained throughout the analysis. On the otherhand, pressure and temperature are not easily controlled using collapsible bags. As a result, some evacuable smog chambers have been designed in order to control both temperature and pressure. Ports are included in the chamber for withdrawing samples for analysis. Included in some chambers are ports for in situ spectroscopic measurements using techniques such as FTIR, GC and GC-MS [37,38]

The irradiation sources used in most smog chamber systems to simulate solar radiation are

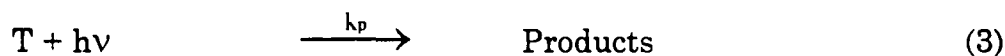
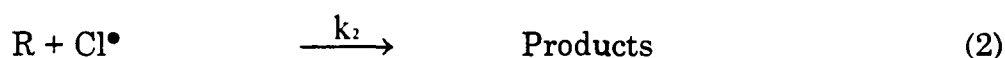
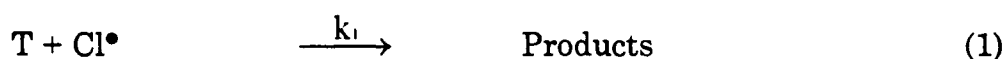
- black fluorescent lamps (output from 320 to 480nm)
- sun lamps (output from 270 to 440nm), and
- xenon lamps (output from 280 - 700nm)

A combination of sunlamps and blacklamps was employed in our experiments depending on the reaction under investigation. For all the work carried out in our laboratory the reactants were monitored by a gas chromatograph fitted with a flame ionisation detector, and the relative rate technique employed in our laboratory has been described in detail by many workers [39,40]

Experimental Protocol

Due to the varying techniques used in smog chamber studies with respect to the production of OH radicals, in the case of OH studies and the presence or absence of scavenger compounds it was decided to establish a well defined protocol as regards laboratory procedures and interpretation for the determination of OH / Cl atom rate constants with volatile organic compounds. This UCR protocol was reviewed by Bufalini and Arnts [39]

The protocol is based upon simultaneously monitoring the disappearance rates of a test compound (T) and a reference compound (R) whose OH radical or chlorine atom rate constant (absolute) is known.



The loss of T is defined by

$$\frac{d(T)}{dt} = k_1(Cl)(T) + k^1(T) \quad (5)$$

and the loss of R is defined by

$$\frac{d(R)}{dt} = k_2(Cl)(R) \quad (6)$$

Where k_1 and k_2 are the relative rate constants for the test compound, T, and reference compound R respectively

The $k^1 = (k_p + k_w)$ term, is the first order photodissociation constant and / or wall loss of the test compound. The integration and combination of equations (5) and (6) result in

$$(1/t_t - t_0) \ln(T_0/T_t) = (k_1/k_2)(1/t_t - t_0) \ln(R_0/R_t) + k^1 \quad (7)$$

Where T_0 and T_t are the concentrations of the test organic at time zero and time t

R_0 and R_t are the concentrations of the reference organic at time zero and time t respectively

A plot of $(t_t - t_0)^{-1} \ln(T_0/T_t)$ vs $(t_t - t_0)^{-1} \ln(R_0/R_t)$ yields a straight line with a slope of (k_1/k_2) and intercept k^1

If $k^1 = 0$ by eliminating the time dependence from equation (7), which then reduces to

$$\ln(T_0/T_t) = (k_1/k_2) \ln(R_0/R_t) \quad (8)$$

A plot of $\ln(T_0/T_t)$ vs $\ln(R_0/R_t)$ yields a slope of k_1/k_2 . As k_2 , the relative rate constant for the reference compound is known the equation can be solved for k_1

The UCR protocol outlines criteria that should be taken into consideration before choosing a reference organic, namely

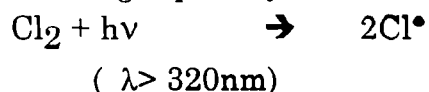
- the reference should have an accurately known room temperature rate constant which is approximately equal to the anticipated rate of the test compound
- the reference rate constant should be accurately measured by an available analytical technique
- the reference should not photolyse, at wavelengths ≥ 290 nm or air oxidise
- the reference should not react with the test compound, ozone, NO_3 , NO_2 or HNO_3

The test organic must also satisfy certain criteria i.e

- an analytical method must be available for making repeated measurements over a two hour period
- the rate of loss by photolysis and wall losses must not be much higher than the loss due to the Cl atom reaction.

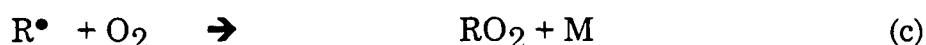
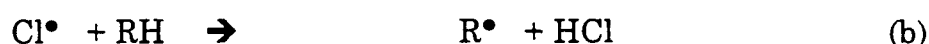
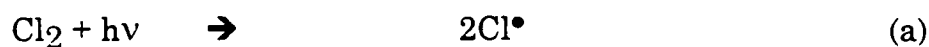
$$(k_{\text{Cl-T}} \times [\text{Cl}]) \gg k_{\text{photolysis}}$$

The chlorine atoms for this relative rate technique were generated in our laboratory by chlorine gas photolysis



This technique has been used extensively in other laboratories [41-43] to determine Cl atom rate constants

Cl atom reactions with organics is also a useful method for generating radical species in the laboratory eg alkyl peroxy radicals



proceeding via a hydrogen abstraction mechanism in a similar manner to OH radical reactions. Both OH radicals and Cl atoms are electrophilic which explains their similar reaction processes. Wallington et al [42] has demonstrated a linear correlation between the reactivities of Cl atoms and OH radicals towards the alkanes

Such a correlation may be used to estimate the reactivities of alkanes towards Cl atoms from the corresponding reactivities towards OH radicals. Greiner in his early studies [44] of OH reactions (which ultimately led to the recognition of the importance of OH in the atmosphere) proposed that the rate data for a series of alkanes could be expressed as the sum of rate constants for primary, secondary and tertiary C-H bonds, respectively

$$K = N_p K_p + N_s K_s + N_t K_t \quad (\text{A})$$

In this expression, K is the overall rate constant for the OH - alkane reaction, K_p , K_s and K_t are the rate constants per primary, secondary and tertiary C - H bond, respectively, and N_p , N_s and N_t are the corresponding numbers of each kind of bond in the molecule. Using equation (A), the room

temperature kinetic data for these simple alkanes were subsequently fit with

$$K_p = 6.5 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

$$K_s = 5.8 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

$$K_t = 2.1 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

The trend to increasing values reflecting the trend in decreasing C-H bond strengths [44]. As expected from a consideration of the detailed thermochemical kinetics [45], in addition to the numbers of each type of C-H bond, the detailed structure of the molecule has an influence on the rate constants [46,47].

The reaction of OH radicals with alkanes has been extensively studied and Atkinson [48] has comprehensively reviewed the current kinetic database. Evaluated sets of rate constants, have been used to establish relationships between structure and reactivity [47]. For example, experiments have shown that even in simple alkanes a secondary C-H bond reacts approximately 40% faster if it is bonded to two other -CH₂- groups rather than a -CH₂- and one -CH₃ group [46,49].

The reaction of Cl atoms with the alkanes although proceeding in a similar mechanism, occurs much faster reflecting the more electronegative character of Cl atoms compared to OH radicals. This relatively high reactivity of the Cl atom has given rise to increased speculation about the importance of Cl atom reactions as a loss mechanism for VOCs in the troposphere [6].

Atkinson et al [50] carried out relative rate constant measurements on reactions of Cl atoms with a series of organics at $296 \pm 2\text{K}$. From the results obtained in these studies, group rate constants for H-atom abstraction from primary, secondary and tertiary C-H bonds were estimated;

$$K_p = 3.4 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ S}^{-1}$$

$$K_s = 5.6 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ S}^{-1}$$

$$K_t = 3.7 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ S}^{-1}$$

where K_p , K_s and K_t are the rate constants for H-atom abstraction by Cl atoms from primary ($\text{CH}_3 -$), secondary ($- \text{CH}_2 -$) and tertiary ($>\text{CH} -$) groups.

The reaction of Cl atoms with haloalkanes has been studied but not to the same degree as alkanes.

Wallington et al [51] carried out reactions of Cl atoms with a series of chloroalkanes at 295K. The studies showed that in all cases chloroalkanes are less reactive than their parent alkanes. The deactivating effect of the chlorine substituent is probably attributable to steric considerations and is most pronounced for the smaller chloroalkanes and for chloroalkanes bearing a chlorine atom at a secondary site. The reactivity increases along the series, 1 - chloropropane, 1 - chlorobutane, 1- chloropentane and corresponds with the increase in reactivity from propane to n-pentane. This indicates that the deactivating effect of the chlorine substituent on the reactivity of the chloroalkanes is restricted to groups α to the carbon carrying the substituent. Attempts to explain the reactivity trends for

chlorine attack on chlorinated and fluorinated haloalkanes has been made by Tschuikow-Roux et al [52,53] and earlier by Wine and Semmes [54]

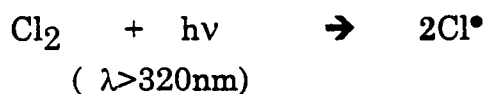
The influences of inductive effects, electronegativity arguments, resonance interactions, steric effects, Van der Waals repulsion, attractive interactions due to dispersion forces, dynamic effects as well as electronic effects have been discussed. It is possible that reaction of Cl atoms with different compounds may be affected by the type of compound and the type, position and number of substituent halogens

The current lack of information with regard to the reaction of Cl atoms with a particular series of chlorinated and brominated alkanes illustrates the importance of the work reported here in increasing the kinetic database with regard to such compounds

4.2 EXPERIMENTAL

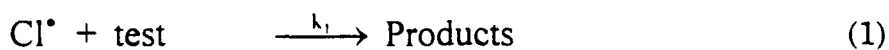
Cl atom rate constants were measured using a relative rate technique similar to that employed by Atkinson et al, described in detail in the literature [1,39,40] and summarised in section 4.1 of this report. Since this is the first report of rate measurements using the present vacuum line-smog chamber system, a series of measurements were also performed on compounds for which reliable data exists in order to validate the experimental procedures. For the Cl atom rate measurements, propane was used for validation.

Chlorine atoms were generated in our laboratory by chlorine gas photolysis



The system also contained the test compound as well as a reference compound for which the Cl atom rate constant was accurately known. Ethane was used as the reference compound.

If the wall loss rates of the test and reference compounds are negligible and if the two compounds do not photolyse, the only significant removal process for the test and reference compounds is reaction with Cl atoms. These reactions may be represented by



As previously described in section 4.1, the rate equations for reaction (1) and (2) can be combined and integrated to yield an expression of the form

$$\ln ([\text{Test}]_0 / [\text{Test}]_t) = (k_1/k_2) \ln ([\text{Ref}]_0 / [\text{Ref}]_t) \quad (3)$$

Where $[\text{Test}]_0$ and $[\text{Ref}]_0$ are the initial concentrations of the test and reference compounds respectively and $[\text{Test}]_t$ and $[\text{Ref}]_t$ are the concentrations at some time t . According to equation (3), a plot of $\ln([\text{Test}]_0 / [\text{Test}]_t)$ versus $\ln ([\text{Ref}]_0 / [\text{Ref}]_t)$ should be linear with a slope equal to (k_1/k_2) and intercept equal to zero. Given an accurate rate value for the rate constant of the reference compound (k_2), the rate constant for the test compound (k_1) can be calculated.

Having calculated the rate constants for the reaction of the test compounds with chlorine atoms, it was then possible to calculate the tropospheric lifetimes (τ) of these compounds using the expression

$$\tau_{\text{Cl}} (\text{seconds}) = 1/k_{\text{Cl}} [\text{Cl}] \text{ where } \cdot$$

k_{Cl} is the rate constant for the reaction of Cl atoms with the test compound. $[\text{Cl}]$ is the tropospheric concentration of the Cl atoms. In this report, a concentration of $2 \times 10^3 \text{ atoms cm}^{-3}$ was used [6]

4.2.1 Materials

Ethane (99.0%) and propane (99.5%) were supplied by Alltech Associates Inc. The Aldrich Chemical Company supplied bromoethane (>99.0%) and 2-Chloropropane (>99.0%). 2-Chloro-2-methylpropane (99.0%) was obtained from Hopkin and Williams. 1-Chloropropane and 1,3-dichloropropane (Riedel-de-Haen) had a stated purity of 98%. The remaining materials, nitric oxide (99.0%), 1-bromopropane (96.0% min), 2-bromopropane (>99.0%), 1-bromobutane (98.0% min), 1-bromopentane (97.0% min) and 1-bromohexane (97.0% min) were all supplied by B D H Chemicals Ltd.

All materials were degassed by a repeated freeze-pump-thaw method and trap-to-trap distilled on the vacuum line prior to use.

Chlorine (99.5%) was supplied by Argo International Ltd. It was degassed several times and stored in a blackened bulb on the line to prevent decomposition.

The gas chromatographic gases, air, hydrogen and nitrogen (oxygen free) were obtained from I I G. The artificial air was zero grade quality (B O C). The nitrogen (O F N grade) used to clean the teflon bag between runs was supplied by Air Products Ltd. The nitrogen was passed through a drying column containing a molecular sieve and self-indicating silica gel (Chromopack) in order to remove all traces of moisture. The air was passed through a drying column and a charcoal column (Chromopack) to remove traces of moisture and organics.

4.2.2 Apparatus

The apparatus, shown in Figure 4.2.1, is the same conventional mercury free, high vacuum line, previously described in section 3.1.2 but with two additional attachments, line 6 and bulb E. The volumes of line 6 (13.5cm^3) and bulb E (306.3cm^3) were measured by sharing known pressures of air into them from bulb D. Chlorine was stored in bulbs A and C, ethane in reservoir G, propane and nitric oxide in reservoir H prior to use. Liquid reactants were stored in fingers attached at positions (a), (b) and (c).

Figure 4.2.2 is a diagrammatic representation of how an 86 litre conditioned teflon bag was connected to the vacuum line and GC using teflon tubing (1.5mm i.d.). Figure 4.2.2 also shows how samples could be taken from the bag for direct injection onto the column using a sampling pump (Edwards, High Vacuum Speedivac 2). The sample loop was manually changed from the fill to inject position. Reactant pressures were measured using an MKS Baratron type 122AA pressure transducer (0-10 torr). A pressure of 1.19 torr in mixing bulb E (306.3cm^3) and line 6 (13.5cm^3) corresponded to a concentration of 10 ppm of reactant when shared into the teflon bag.

To fill the bag, tap (d) was closed and with taps (e), (f) and (g) open, flow regulators were used to measure the required volume of air or nitrogen into the bag. An Edwards, high vacuum speedivac 2 rotary pump was used to empty the bag. Irradiations were carried out in the 86 litre teflon bag (reaction chamber) surrounded by 10 Philips TL 20W/09N sun lamps and 10 Philips TLD 18W/08 black lamps mounted on a metal rectangular frame ($107.0\text{cm} \times 76.0\text{cm} \times 87.5\text{cm}$).

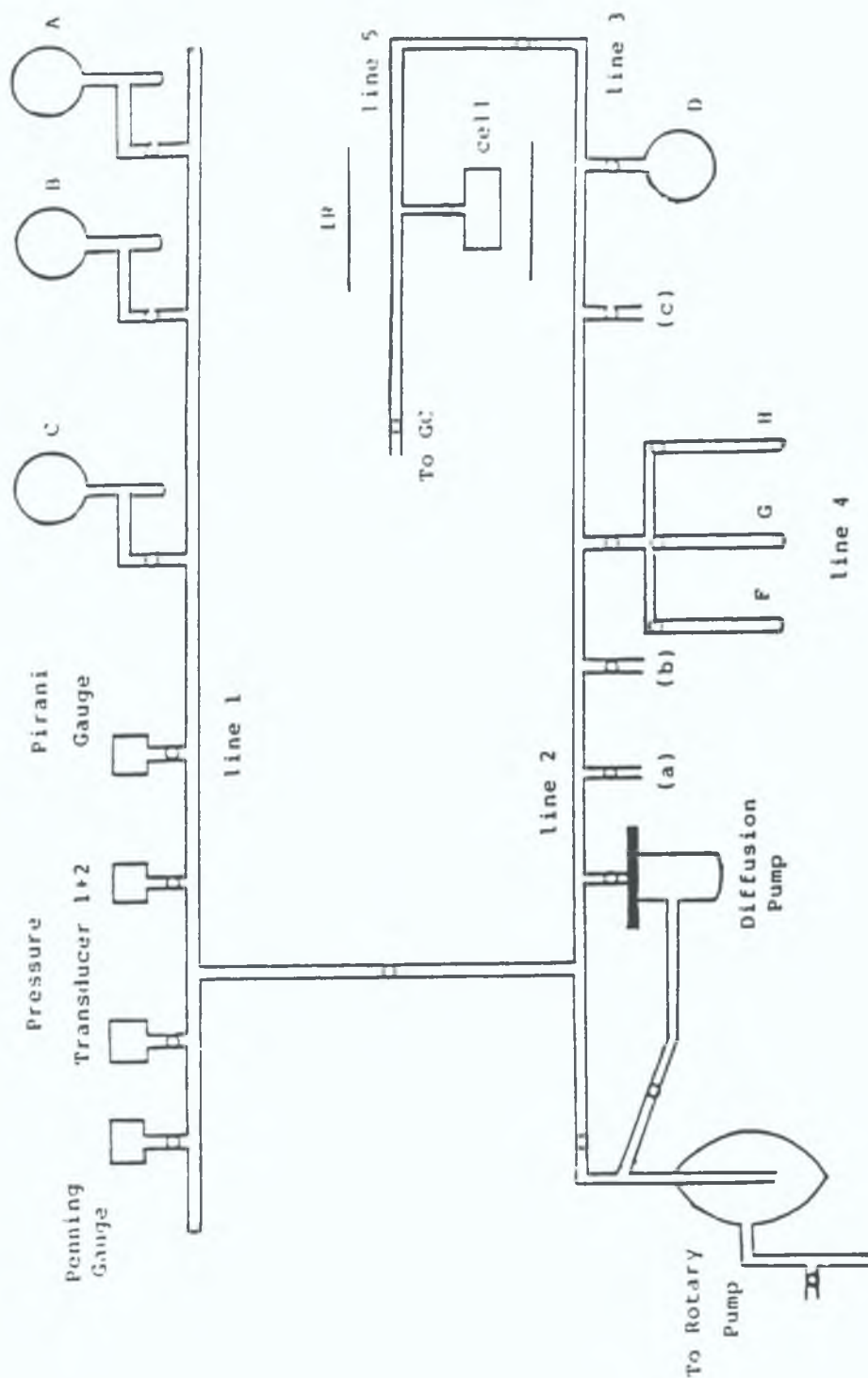


Figure 4.2.1
Diagrammatic representation of the conventional Mercury Free high Vacuum Line used in this work.

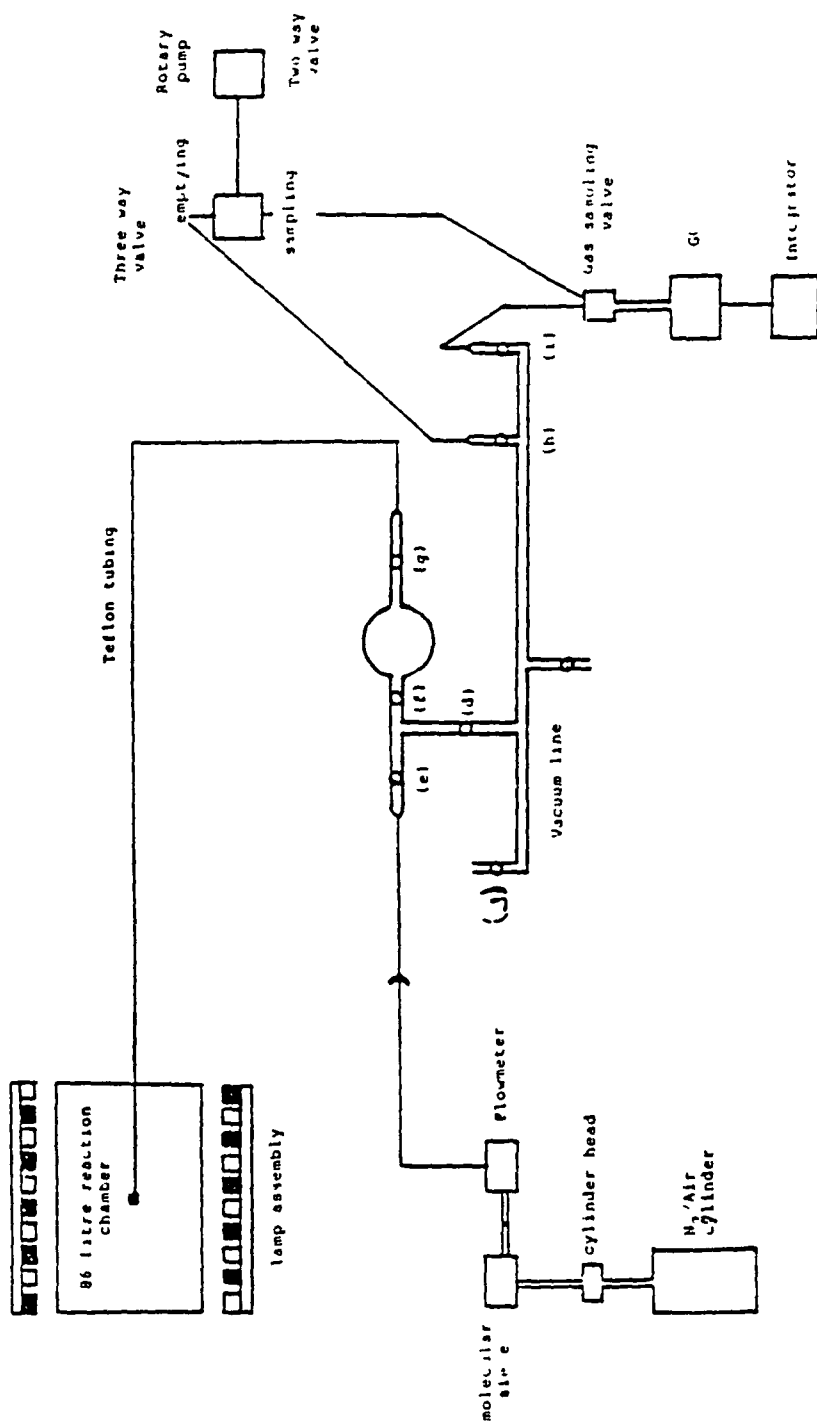


Figure 4.2.2
Schematic representation of smog chamber in relation to vacuum line and GC.

Both emit radiation between 300 and 450nm with a maximum intensity at approximately 352nm. The lamp assembly was arranged on four electrical circuits (two front, two rear) with every second lamp on a different circuit and alternately black and sun lamp. A thermometer was mounted inside the chamber to monitor the temperature during irradiation. The whole chamber was surrounded by black cloth. Prior to irradiation, the reaction chamber was covered with an opaque cover to prevent photolysis of the reactants. In addition, while the lights were on, the opaque cover was used to completely cover the reaction chamber and thus interrupt photolysis as required.

4.2.3 Procedure

Gas chromatography (FID) was used to monitor reactant concentrations following irradiation. Thus an initial requirement before any rate data could be determined was the optimisation of chromatographic conditions to separate the test and reference compounds. Following irradiation of the gas mixtures, the formation of products which might interfere with the gas chromatographic analysis of either the reference or test compound or both had to be considered as a potential complication. Separate experiments (decay profiles) were performed in which mixtures of Cl_2 (for Cl atom reactions) and either the test or reference compound were irradiated and analyses performed to check for the formation of potentially interfering products caused by secondary reactions in our systems. For all the rate constants determined, no such interferences were observed for the irradiation times typical of the present work.

Additionally, to test for any possible photolysis of the reactants used in these studies, mixtures of these reactants in zero grade air in the absence of chlorine were irradiated with the appropriate lamps for up to one hour. No photolysis of any of the reactants was observed. Having optimised the analytical conditions for monitoring the reactant concentrations during irradiation, work could proceed on determining the relative rate constants of the test compounds.

To do this, the apparatus (Figure 4.2.1) was pumped down, with liquid nitrogen around the trap, to give a vacuum of less than 10^{-4} torr pressure by an Edwards Penning Gauge. A reactant was measured into the vacuum line and mixing bulb E. Bulb E was isolated from the remainder of the vacuum line and the reactant was flushed into the bag for a fixed period of time using zero grade air. The reactant remaining in the vacuum line was frozen back into the reservoir by means of a liquid nitrogen trap. The procedure was repeated for each of the reactants and, finally the reaction bag was filled to a capacity of 50 litres with zero grade air. Similar initial concentrations (10ppm) of the test and reference materials were used. For chlorine atom reactions, the initial concentration of chlorine was 84ppm.

The reaction chamber was completely covered at all times except during photolysis. Before analysis, the reaction mixture was left in the dark for approximately 30 minutes to allow for thorough mixing of the reactants. Complete mixing was confirmed by gas chromatographic analysis.

The temperature at which runs were carried out fluctuated in the range $298 \pm 2\text{K}$. For the chlorine atom reactions, five black lamps were used for irradiation of the reaction mixture. The lamps were switched on 10-15 minutes before use. A minimum of two samples were taken from the bag

prior to irradiation. The mixture was irradiated for fixed periods in the range 30-120 seconds, measured by means of a stop-clock. The opaque cover was then replaced and a sample taken from the bag by means of the sampling pump for GC analysis.

Sampling time was two minutes. This process was repeated several times so that the rate of loss of both reference and test reactants could be monitored.

Total irradiation times were approximately 12 minutes. When the final sample was taken, the bag was emptied by opening taps (h), (d), (f) and (g) and closing taps (e), (j) and (i). The reaction chamber was cleaned by filling with nitrogen in between runs. It was filled and emptied at least twice with nitrogen. A sample was taken from the second fill and injected onto the GC to ensure the bag was clean. If this suggested that the bag was not completely free from reactants or products, the bag was emptied and the process repeated until a clear sample was obtained. Peak areas and occasionally peak heights were used to measure changes in the concentration of the test and reference compounds following irradiation, and the relative rate was determined as described in Section 4.1 of this report. The complete procedure as outlined above was repeated under identical conditions, a minimum of three times to ensure experimental reproducibility and to increase the accuracy of our rate data. The rate constant ratios determined from each experiment were then averaged to give the value reported.

4.2.4 Analysis

A Phillips Pye Unicam PU 4550 Gas Chromatograph incorporating a flame ionisation detector was used to monitor the concentration of reactants before and after irradiation. Relative concentrations of reactants during analysis were determined by measuring peak areas and peak heights. Sample injection was carried out with a 2cm³ stainless steel teflon coated loop connected to a Carle six-port sampling valve.

Stationary phases used were 10% SE30 on chromosorb WHP (80-100) support and Porapak Q. The column was operated isothermally at temperatures ranging from 35 to 120°C except for the Cl atom reaction with 1-bromobutane where temperature programming was involved. The flow rate was maintained at 30 ± 0.5 cm³ min⁻¹. Injector and detector temperatures remained constant at 150°C and 200°C respectively.

Chromatograms were recorded on a Spectra - Physics integrator (Model SP 4270/4290).

4.3 RESULTS

Chromatographic conditions were optimised for GC analysis of reaction mixtures containing Cl_2 , test and reference compounds. Table 4.3.1 outlines the optimum operating and analytical conditions found for each of the test compounds. The reference for each test compound was chosen such that it had a similar number of carbon atoms and was expected to have a similar reaction with Cl atoms as the test compound.

Ethane was chosen as the reference compound for Cl atom work and has previously been measured by reliable methods [20,50,55-58]. The analysis of 1-bromobutane was repeated using propane as the reference organic as there was an uncertainty surrounding the experimental values obtained using ethane as the reference organic.

The relative rate technique relies on the assumption that the test and reference organics are removed solely by reaction with Cl atoms. This assumption was verified prior to analysis of each of the test compounds where separate experiments were carried out to establish.

(a) that the test and reference compounds did not react with molecular chlorine in the absence of UV radiation. To test this assumption, mixtures of chlorine with both organic compounds were prepared in the same manner as test runs except in the absence of UV light and found to be stable over timescales typical of experimental runs. Typical dark reaction results are illustrated in Figure 4.3.1.

Table 4.3.1

Operating and analytical conditions established for the reactions of haloalkanes with Cl atoms (298K)

Test	Reference	Column	Operating Parameters
Propane		Porapak Q	Column Temp = 393K Flow = 30 0 cm ³ /min
Ethane		10% SE30 on chromosorb WHP (80-100 µm)	Column Temp = 393K Flow = 30 0 cm ³ /min
1-Chloropropane	Ethane	"	Column Temp = 318K Flow = 30 0 cm ³ /min
2-Chloropropane	Ethane	"	Column Temp = 308K Flow = 30 0 cm ³ /min
1,3 Dichloropropane	Ethane	"	Column Temp = 353K Flow = 30 0 cm ³ /min
2-Chloro 2-methyl- Propane	Ethane	"	Column Temp = 308K Flow = 30 0 cm ³ /min
Bromoethane	Ethane	"	Column Temp = 323K Flow = 30 0 cm ³ /min
1-Bromopropane	Ethane	"	Column Temp = 308K Flow = 30 0 cm ³ /min
2-Bromopropane	Ethane	"	Column Temp = 313K Flow = 30 0 cm ³ /min
1-Bromobutane	Ethane	"	Temperature program ^a Flow = 30 0 cm ³ /min
	Propane	"	Column Temp = 318K Flow = 30 0 cm ³ /min
1-Bromopentane	Ethane	"	Column Temp = 343K Flow = 30 0 cm ³ /min
1-Bromohexane	Ethane	"	Column Temp = 373K Flow = 30 0 cm ³ /min

^aTemperature Programme

Initial Temp = 300K.

Hold - 2 1 mins

Ramp Rate - 283 K/min

Hold - 3 0 mins

Final Temperature = 318K

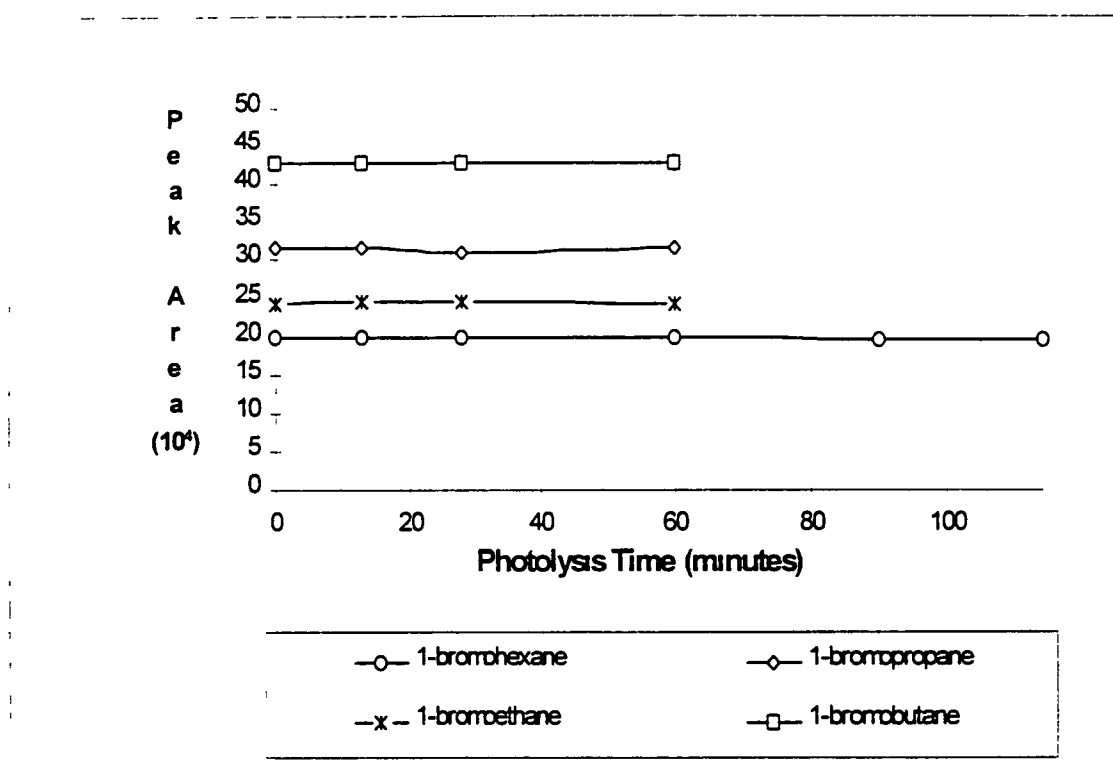


Figure 4.3.1
Cl atom dark reaction observations for a selection of haloalkanes

(b) similarly to verify that the organics did not undergo direct photolysis by the lamps, mixtures of the reactants in synthetic air in the absence of Cl_2 were irradiated. No photodecomposition of either test or reference compounds was observed over the timescales used in the experiments. The stability of a series of test haloalkanes is illustrated from the data plotted in Figure 4.3.2. Hence, we concluded that for our Cl atom work, loss of test and reference was due to reaction with Cl atoms alone.

As stated in the experimental section, the presence of interfering species resulting from the oxidation of either the test or the reference organics were studied. Prior to studying the relative loss of test and reference compounds, reaction of each compound was studied on their own and found not to interfere with the chromatographic analysis of the organic compounds. Typical decay profiles for a selection of haloalkanes is shown in Figure 4.3.3.

The rate constant ratios and their corresponding absolute values measured in our laboratory are listed in Table 4.3.2.

The rate constant ratios k_1/k_2 (or slope) was determined using linear least squares analysis from a plot of $\ln ([\text{Test}]_0/[\text{Test}]_t)$ versus $\ln ([\text{Ref}]_0/[\text{Ref}]_t)$ for each set of data. The concentration of test and reference at time 0 and time t, correspond to the peak areas of each compound prior to irradiation and at some time t, during photolysis. The slopes of the lines thus obtained correspond to $k_{\text{reference}}/k_{\text{test}}$. Knowing $k_{\text{reference}}$ allows us to place our results on an absolute scale.

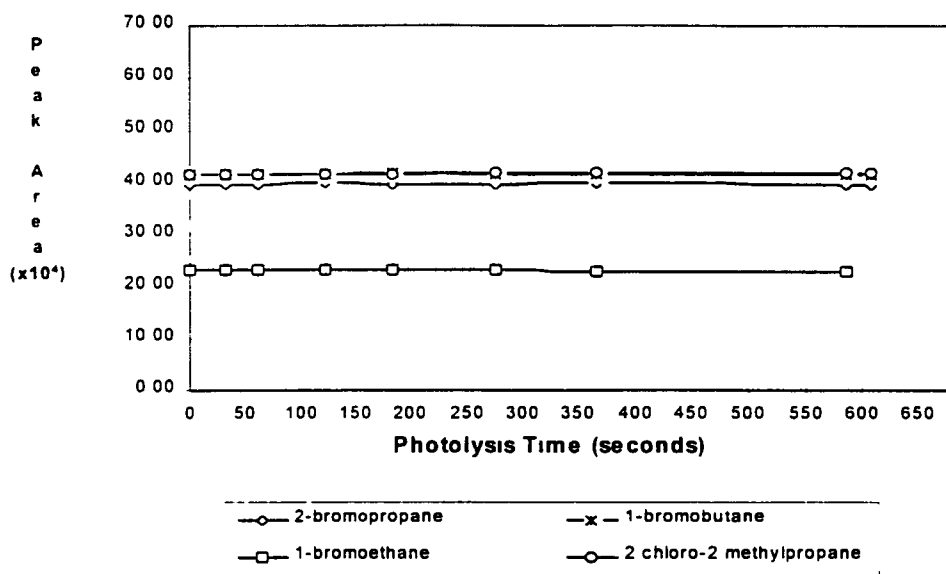


Figure 4.3.2
Photochemical stability of a series of chloroalkanes / bromoalkanes using experimental conditions for Cl atom work.

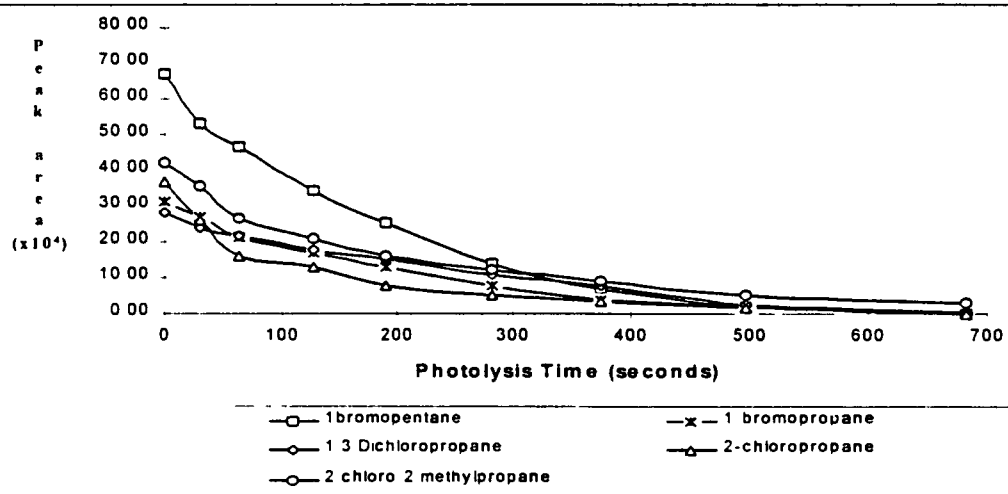


Figure 4.3.3
Decay curves obtained for a selection of haloalkanes studied in this work.

Table 4.3.2

Cl atom rate constant ratios k_1/k_2 and corresponding absolute values k measured in this work for a series of haloalkanes using the relative rate technique.

Test Organic	Cl atom reactions $\times 10^{12}$ ($\text{cm}^3 \text{ molecule}^{-1} \text{s}^{-1}$)		
	$k_1/k_2^{\text{a,b}}$	k^{d}	Lit. Values
Ethane	$0.411 \pm 0.015^{\text{c}}$	62 ± 9	60 ± 6 [55] 59 ± 4 [56] 59 ± 3 [57] 57.0 [22] 63.8 ± 2 [50]
1-Chloropropane	0.854 ± 0.011	49 ± 15	53.50 ± 2 [42]
2-Chloropropane	0.358 ± 0.004	20 ± 6	
1,3 Dichloropropane	0.190 ± 0.004	11 ± 3	
2-Chloro 2-methyl-Propane	0.234 ± 0.003	13 ± 4	
Bromoethane	0.241 ± 0.007	14 ± 4	
1-Bromopropane	1.071 ± 0.021	61 ± 18	
2-Bromopropane	0.480 ± 0.005	27 ± 8	
1-Bromobutane	2.460 ± 0.057	140 ± 42	
	$0.908 \pm 0.005^{\text{c}}$	137 ± 21	
1-Bromopentane	3.756 ± 0.041	214 ± 64	
1-Bromohexane	4.765 ± 0.028	272 ± 81	

a errors quoted as 2δ from the least squares analysis of the data

b reference = C_2H_6

c reference = C_3H_8

d errors quoted include the uncertainties in the reference values, $\pm 30\%$ for C_2H_6 [59] and $\pm 15\%$ for C_3H_8 [58]

Representative plots of data generated for Cl atom work are outlined in Figures 4.3.4 and 4.3.5

The slopes calculated in Table 4.3.2 were obtained from lines having correlation coefficients of >0.996 and having minimal intercepts. The plots are linear with intercepts within 2σ of the origin suggesting that secondary reactions are negligible.

The errors quoted for the rate constant ratios are 2σ from the least squares analysis data, whereas the errors listed for the absolute rates include the uncertainty in the reference value taken as $\pm 30\%$ for $K(\text{Cl}+\text{ethane})$ at 298K [51] and $\pm 15\%$ for $K(\text{Cl}+\text{propane})$ at 298K [58].

For each test compound studied, at least three separate gas mixtures were prepared and irradiated to check the experimental reproducibility. For example a typical Cl atom reaction with 2-bromopropane yields an average slope value of 0.480 ± 0.005 as illustrated in Table 4.3.3. Similar reproducibility was obtained for the rate constant ratios of each of the compounds studied.

Additionally as a check of the apparatus and the technique employed we measured the rate constant for $(\text{Cl} + \text{ethane})$ using propane as the reference organic (Table 4.3.2). Good agreement between our results and the literature values serves to validate our apparatus and experimental technique.

The corresponding tropospheric lifetimes calculated from the rate constants for these compounds are listed in Table 4.3.4. A concentration of 2×10^3 atoms cm^{-3} was used to determine the tropospheric lifetimes of the test compounds with respect to Cl atoms. This value was calculated by Singh et al [6] and represents a concentration up to 2Km in the marine troposphere.

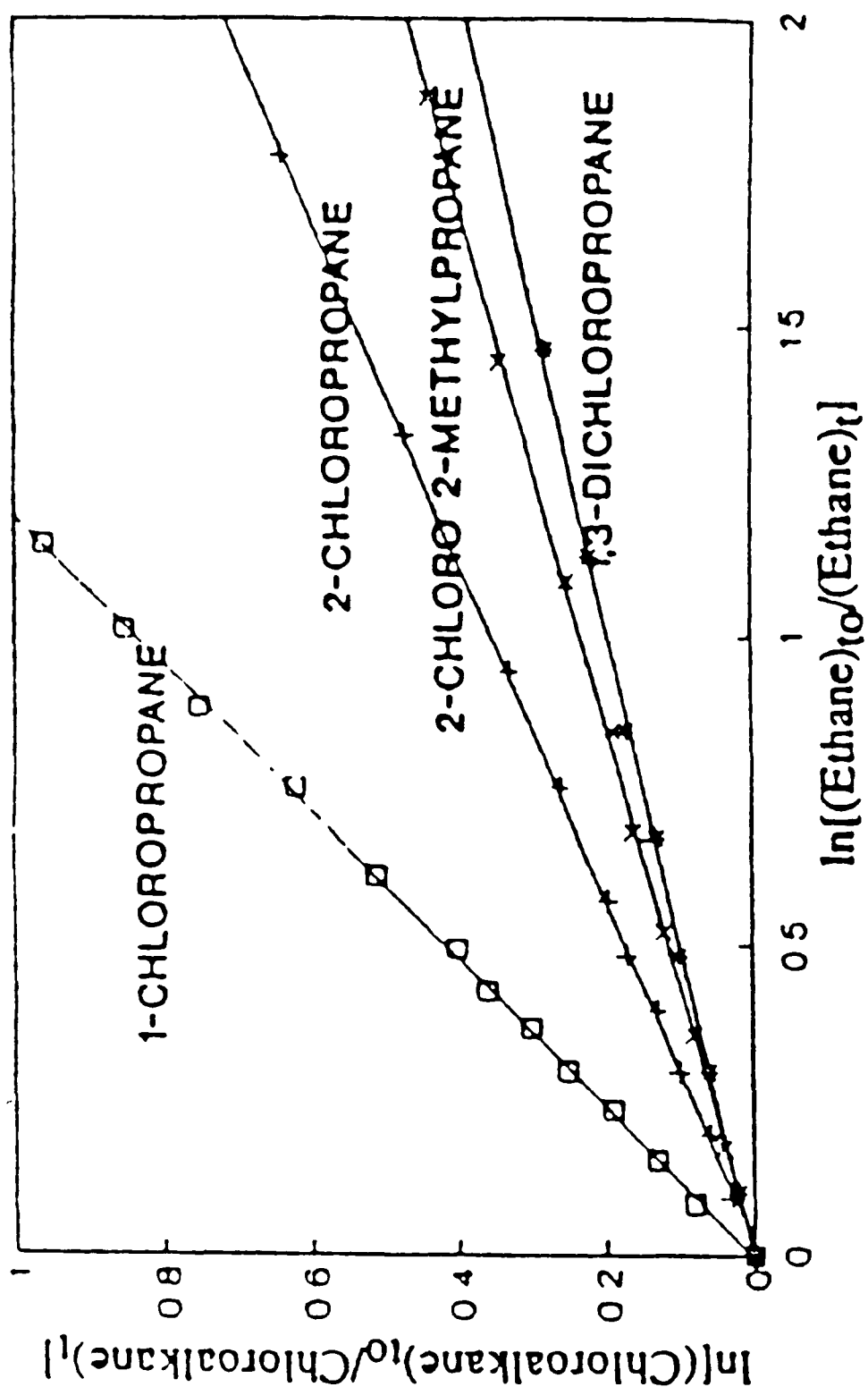


Figure 4.3.4

Typical plots obtained for the determination of Cl atom rate constants for a series of chloroalkanes using a relative rate technique.

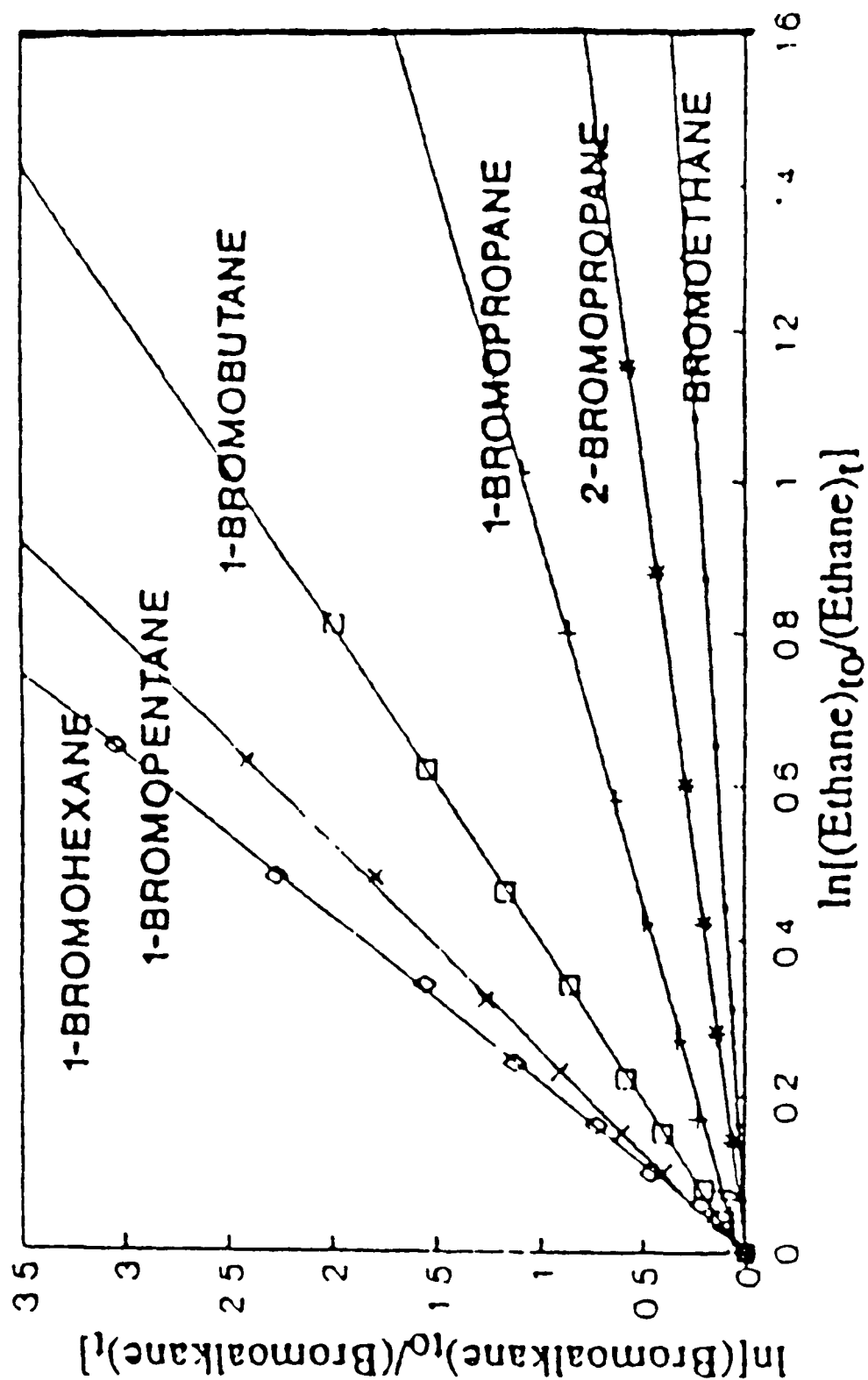


Figure 4.3.5

Typical plots obtained for the determination of Cl atom rate constants for a series of bromoalkanes using a relative rate technique.

Table 4.3.3

Cl atom rate constant data for 2-bromopropane at $298 \pm 2\text{K}$ calculated from three separate determinations

Slope k_1/k_2	Intercept	Correlation Coefficient
0.494 ± 0.002	$9.0 \times 10^{-4} \pm 0.002$	0.9999
0.472 ± 0.004	$2.0 \times 10^{-3} \pm 0.004$	0.9998
0.471 ± 0.006	$2.0 \times 10^{-2} \pm 0.008$	0.9994

Table 4.3.4

Tropospheric lifetimes of the compounds studied in this work. Lifetimes were determined with respect to Cl atoms

Test Organic	τ_{Cl}^a
Ethane	88 days
1-Chloropropane	119 days
2-Chloropropane	284 days
1,3 Dichloropropane	1.5 years
2-Chloro 2-methyl-propane	1.2 years
Bromoethane	1.2 years
1-Bromopropane	95 days
2-Bromopropane	211 days
1-Bromobutane	41 days
	40 days
1-Bromopentane	27 days
1-Bromohexane	21 days

$^a\tau_{\text{Cl}}$ = atmospheric lifetime $\tau = 1/k [\text{Cl}]$, where $[\text{Cl}] = 2 \times 10^3 \text{ atoms cm}^{-3}$

[6]

4.4 DISCUSSION

Irradiations of Cl₂-organic-air mixtures in a smog chamber lead to rapid disappearance of the organics as shown from the decay profiles in Figure 4.3.3. As similar conditions were used for each compound the decay curves demonstrate the relative reactivity of each of the haloalkanes towards Cl atoms i.e. the sharper the decay, the greater the reactivity. The relative rate technique employed in these experiments rely on the assumption that the disappearance of organics is due solely to reaction of the organics with Cl atoms. The validity of this assumption for each of the systems studied here was checked by verifying that the organics were not removed by either dark reactions or photodecomposition over the typical timescales of these experiments, Figures 4.3.1 - 4.3.2. Furthermore, the absence of secondary reactions in these systems was verified experimentally, and no interferences were observed over the timescales of the studies, Figure 4.3.3.

The apparatus and experimental technique used for kinetic measurements have been outlined in Section 4.1. Of particular significance for our system was the fact that the GC used was only equipped with one type of detector, namely a flame ionisation detector (FID) and showed reduced sensitivity with increasing substitution of halogens. Since the kinetic data were derived from chromatographic measurements of the relative concentrations of the organics present at different times the enhanced sensitivity of an electron-capture detector, to halogenated compounds would significantly improve the accuracy and precision of the kinetic results obtained for halogenated species.

However, the apparatus and experimental technique used have allowed for reproducible results for Cl atom rate constant work. An example of the reproducibility of the data is given for the reaction of Cl with 2-bromopropane in Table 4.3.3. The slopes obtained indicate the precision of our results. The large error bars quoted for the rate constants are due to the inclusion of the total uncertainty associated with the reference rate constants used to place our results on an absolute basis. Since the kinetic data reported here [60] represents the first measurements of this type from our laboratory, we remeasured the rate constants for (Cl + ethane) using propane as the reference organic (Table 4.3.2). Good agreement between our results and the literature values [22,50,55-57] serves to validate our apparatus and experimental technique. The validity of the rate constants calculated using the relative rate technique relies heavily on the reference organic used. For Cl atom reactions, the reference value for $K(\text{Cl} + \text{ethane})$ was taken from [59] and $K(\text{Cl} + \text{propane})$ was taken from [58].

Cl atom reactions with alkanes and haloalkanes proceed via H-atom abstraction from C-H bonds with the room temperature rate constants increasing with decreasing bond dissociation energy. The presence of halogen atoms in the alkanes studied would in fact be expected to lower the C-H bond dissociation energy and thus give rise to an increase in the observed Cl atom rate constant values.

It is also of interest to compare the reactivity of OH radicals towards alkanes and haloalkanes with that of Cl atom reactions. Both radical species are electrophilic and are expected to react with the saturated organic compounds studied in this work and that of a colleague via a H-atom abstraction mechanism [60].

Wallington has shown that there is an essentially linear correlation between the reactivities of Cl atoms and OH radicals towards the alkanes [42]

The purpose of our work was to determine whether any trends exist among Cl atom reactions for a series of chloroalkanes and bromoalkanes and to compare for the purposes of this thesis the data, with the corresponding OH radical data for the same compounds carried out by Donaghy et al [60] in the same laboratory Table 4.4.1 lists the combined values for Cl atom and OH radical rate constants for the series of chloropropanes and bromoethanes and their corresponding parent alkanes

For the chloropropane series, the presence of a chlorine substituent significantly lowers the rate constant values especially if the substituent is located on C₂ position as seen for 2-chloropropane or if there is more than one substituent present, (1,3 Dichloropropane) It is interesting to note that the Cl atom rate constants are more affected by the presence and number of Cl atoms relative to the corresponding rates for OH radical reactions

One factor contributing to this reduced Cl atom reactivity to chloropropanes is probably as a result of the electronegativities of both the attacking Cl atom and the chlorine substituent present on the alkane which will have a repelling effect. This is especially reflected in the rates of 1,3-dichloropropane and 2-chloro 2 methyl propane The rate constant for Cl + 2-chloro 2 methyl propane is larger than the rate for Cl + 1,3 dichloropropane, the two chlorine substituents on 1,3-dichloropropane will have a greater deactivating effect on the molecule relative to the presence of one chlorine substituent on 2-chloro 2 methyl propane

Table 4.4.1

Cl atom and OH radical rate constants for a series of chloropropanes and bromoethanes and their corresponding parent alkanes at 298K using the relative rate technique

<i>Alkane</i>	<i>kCl^a</i>	<i>Ref</i>	<i>kOH^a</i>	<i>Ref</i>
Propane	151 ± 23	[58]	1.15 ± 0.34	[48]
1-Chloropropane	49 ± 15	this work	1.12 ± 0.28	[60]
2-Chloropropane	20 ± 6	this work	0.92 ± 0.23	[60]
1,3-Dichloropropane	11 ± 3	this work	0.78 ± 0.19	[60]
2-Chloro 2-methylpropane	13 ± 4	this work	0.41 ± 0.10	[60]
n-Butane	225 ± 61	[58]	2.54 ± 0.51	[48]
i-Butane	144 ± 39	[42,50]	2.34 ± 0.59	[48]
Bromoethane	14 ± 4	this work	0.25 ± 0.05	[60]
1-Bromopropane	61 ± 18	this work	1.18 ± 0.30	[60]
2-Bromopropane	27 ± 8	this work	0.88 ± 0.30	[60]
1-Bromobutane	140 ± 42	this work	2.45 ± 0.61	[60]
	137 ± 21	this work		
1-Bromopentane	214 ± 64	this work	3.96 ± 0.99	[60]
1-Bromohexane	272 ± 81	this work	5.85 ± 1.46	[60]

^a Units of 10⁻¹² cm³ molecule⁻¹ s⁻¹

Also the greater number and availability of abstractable hydrogen atoms on 2-chloro 2 methyl propane relative to 1,3 dichloropropane ensures that the rate constant value will be larger. For the OH radical reactions the situation is reversed reinforcing the theory that the type of C-H bond influences the magnitude of the OH radical rate constants. In 1,3 dichloropropane there are two secondary hydrogen atoms available for abstraction whereas in 2-chloro 2-methylpropane there is only primary hydrogen atoms available, thus despite the presence of two chlorine substituents the magnitude of the rate constant for OH and 1,3-dichloropropane is greater than the magnitude for OH + 2-chloro 2 methyl propane. Comparing the rate data for the homologous bromoalkane series, the deactivating effect of a bromine atom occurs in the same fashion as that for Cl atoms in that the deactivating effect is more pronounced for the smaller bromoalkanes and for bromoalkanes bearing the bromine atoms on a secondary site i.e. the Cl atom rate constant for 1-bromopropane was calculated to be $61 \pm 18 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and the value for 2-bromopropane was measured as $27 \pm 8 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. Similarly the rate constant for OH + 1-bromopropane was $1.18 \pm 0.3 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ relative to 2-bromopropane the value was relatively lower at $0.88 \pm 0.3 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

Figures 4.4.1 and 4.4.2 show the Cl atom and OH radical reactivities for n-alkanes, chloroalkanes and bromoalkanes. For the Cl atom reactions the presence of a halogen atom (chlorine or bromine) significantly lowers the rate constant value. The reactivities for the bromoalkanes are similar to the chloroalkanes which is surprising as bromine atoms are larger and more electronegative than chlorine atoms, so the rate constants would be expected to be smaller in magnitude. The similarity between the rates for OH + bromoalkanes and chloroalkanes has also been noted by Xing et al

[61] in their studies of OH radicals and bromoalkanes. This slight increase in reactivity of the bromo-substituted relative to the chlorine-substituted compound has also been observed by another colleague in our laboratory studying bromine and chlorine substituted ethers [62]. This similarity in reactivity between chlorinated and brominated compounds is consistent with data published by Atkinson [48] for OH reactions with CH₃Br and CH₃Cl.

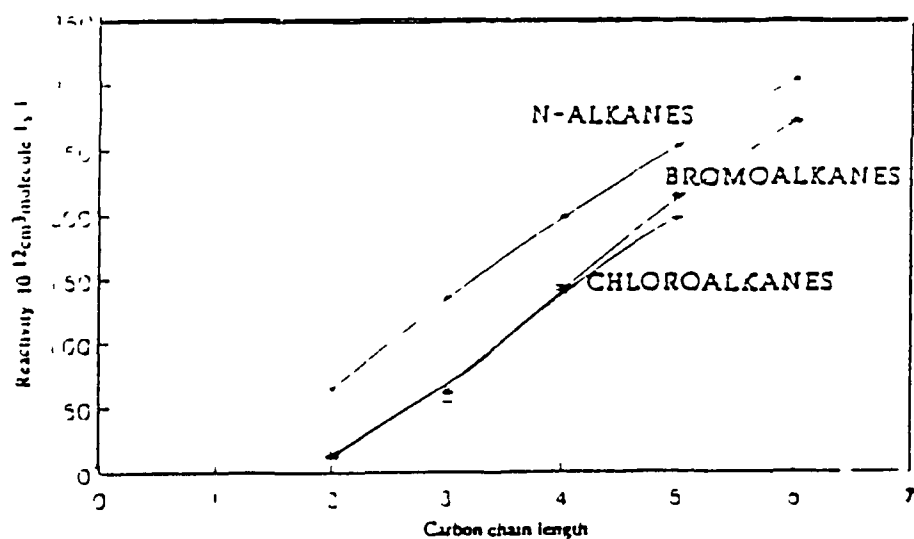


Figure 4.4.1

Reactivities of chlorine atoms towards a series of n-alkanes, chloroalkanes and bromoalkanes. Data for the n-alkanes (n-butane [58]) and the chloroalkanes are taken from [50] and [51] respectively.

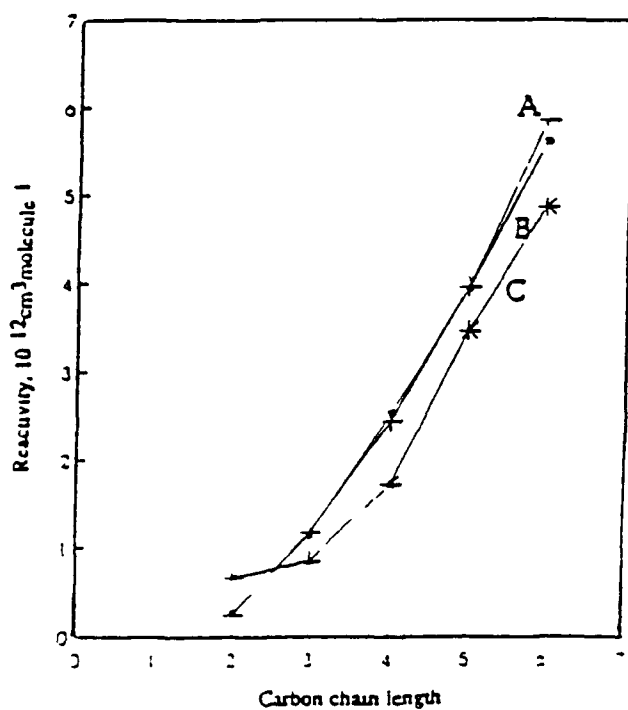


Figure 4.4.2

Reactivities of hydroxyl radicals towards a series of n-alkanes (A) bromoalkanes (B) and chloroalkanes (C). Data for n-alkanes and chloroalkanes taken from [48] and [70] respectively, data for the bromoalkanes taken from [60].

No studies on the chlorination of mixed substituted methanes or bromomethanes appear to have been reported until 1988 by Tschuikow-Roux et al. For comparison Table 4.4.2 lists the available Cl atom rate data obtained from literature for a few halomethanes.

<i>Reaction</i>	<i>K (298K) $\times 10^{13}$ ($\text{cm}^3 \text{ molecule}^{-1} \text{s}^{-1}$)</i>	<i>Reference</i>
Cl + CH ₃ Br	5.53	[63]
	4.38	[64]
Cl + CH ₃ Cl	5.02 $\pm$ 1.5	[53]
	5.01 $\pm$ 1.5	[53]
	4.38 $\pm$ 1.5	[65]
	5.07 $\pm$ 1.4	[56]
	5.28 $\pm$ 1.6	[66]
	4.87 $\pm$ 0.5	[67]
Cl + CH ₃ F	3.72 $\pm$ 1.1	[53]
	3.59 $\pm$ 1.0	[56]

The slight increase in reactivity of the bromine-substituted relative to the chlorine substituted methanes is observed for CH₃Br relative to CH₃Cl, however, the difference in reactivities between the compounds may not be significant.

For the fluoromethanes the computed enthalpies for the hydrogen-abstraction reactions change from exothermic (CH₃F) to endothermic (CHF₃) and display the progressive strengthening of the C-H bond with increasing fluorine substitution. An opposite trend is exhibited by the chloro- and bromomethanes which are exothermic and the exothermicity

increases with halogenation substitution reflecting progressive weakening of the C-H bonds [63].

Atkinson [50] and Wallington [51] have shown that reactions involving Cl atoms and chloroalkanes are slower than the corresponding reactions between Cl atoms and alkanes. The deactivating effect of the chlorine substituents is probably due to steric considerations and is most pronounced for the smaller chloroalkanes and for chloroalkanes bearing the chlorine at a secondary site. The increase in reactivity along the series 1-chloropropane, 1-chlorobutane and 1-chloropentane essentially parallels the corresponding increase in reactivity from propane to n-pentane. Wallington [51] concluded that the deactivating effect of the chlorine substituent on the reactivity of the chloroalkanes is restricted to groups α to the carbon carrying the substituent as seen in our results.

It can be seen that the reactions of the haloalkanes studied with Cl atoms are approximately 40-50 times faster than the corresponding OH reactions [60]. However, OH concentrations are approximately one thousand times more abundant in the troposphere [6] therefore, the dominant pathway for these haloalkanes is via reactions with OH radicals.

Based on the calculated tropospheric lifetimes, τ_{Cl} for 1-3 Dichloropropane is 1.5 yrs and has the longest tropospheric lifetime for the compounds studied in this work, however, for OH reactions the results imply that bromoethane with a tropospheric lifetime of between 51-73 days has the longest τ_{OH} for the same organics studied.

Relative to the tropospheric lifetimes of CFC's for example CFC-11 (76 years) and CFC-12 (140 years), these two figures are insignificant,

however they are large enough to ensure that some amounts if released in substantial concentrations into the atmosphere would reach the stratosphere where bromoethane or 1,3 dichloropropane could contribute to the catalytic destruction of ozone in this region of the atmosphere

The efficiency with which a unit mass of each halogenated alkane will destroy ozone relative to the most important ozone depleting molecules as mentioned earlier CFC-11 and CFC-12 will depend on the following factors the molecular weight of the halogenated alkane, the number and type of halogen atoms per molecule and the compound's atmospheric lifetime [69]. The reactive ozone-depletion potential (ODP) is given by

$$\text{ODP} = \frac{\tau_{\text{RH}}}{\tau_{\text{CFC-11}}} \times \frac{M_{\text{CFC-11}}}{M_{\text{RH}}} \times \frac{n_{\text{Cl}} + \alpha n_{\text{Br}}}{3}$$

Where RH represents the parent haloalkane and $M_{\text{CFC-11}}$ and M_{RH} are the relative molecular masses of CFC-11 and the parent haloalkane species, respectively. The total number of Cl and Br atoms in the molecule are represented by n_{Cl} and n_{Br} and α is the efficiency of Br in destroying stratospheric ozone relative to that of Cl. According to current estimates [69], Br may be between 35 to 80 times more potent as a catalyst than Cl, so that the factor α must be taken into account in deriving ODPs

Finally, to gain mechanistic information on OH radical and Cl atom reactions with haloalkanes, further work is required on compounds containing different halogens at different carbon sites. Product studies should be carried out so that a complete environmental impact assessment can be made regarding the release of such haloalkanes and also to be able to extend the applicability of estimation techniques to cover a wide range of halogenated organics

4.5 CONCLUSION

From the viewpoint of atmospheric chemistry, the present work serves to extend the existing database for the reactions of Cl atoms with organics at temperatures near ambient using the relative rate technique. Since the kinetic data reported here represent the first measurements of this type from our laboratory excepting $K(\text{Cl} + 1\text{-chloropropane})$, the slopes (K_1/K_2) obtained indicate the precision of our results. We can conclude therefore that accurate and precise rate constants were obtained using our system of analysis, and that the major source of error in these results was from the reference rate constant.

Cl atom reaction rates were found to be 40-50 times faster than the corresponding OH reaction rates carried out by a colleague in the same laboratory. However, as OH radicals in the troposphere are approximately 1000 times more abundant than Cl atoms, we can conclude that the major loss process for the halogenated alkanes in the atmosphere, is reaction with OH radicals.

Rate of reaction of the halogenated alkanes with Cl atoms appears to be affected by the type of halogen substitution, the number and position of halogen atoms and influenced by the bond dissociation energies within the molecules. There may also be a steric hindrance contribution and/or an induced polarity effect influencing the rate of reaction of these species.

For the rate constant values the atmospheric lifetimes of the organics with respect to Cl atoms were calculated and found to be relatively short-lived compared to the tropospheric lifetimes of CFC-11 and CFC-12. Consequently the haloalkanes investigated are not detrimental to the destruction of the ozone layer.

4.6 REFERENCES

- [1] B J Finlayson - Pitts and J N Pitts Jr , "Atmospheric Chemistry Fundamentals and Experimental techniques"
Wiley & Sons Publishers, (1986)
- [2] C Wofsy and M B McElroy, Can J Chem., **52**, 1582 (1974).
- [3] H B Singh, Geophys Res lett, **4**,101 (1977)
- [4] J Rudolph and D H Enhalt, J Geophys Res , **86** (C12), 11959 (1981)
- [5] W L Chameides and R J Cicerone, J Geophys, Res , **83** (C2) 947 (1978)
- [6] H B. Singh and J F Kasting, J Atmos chem., **7**,261 (1982)
- [7] T J Wallington, J. M Andino, I M Lorkovic, E W. Kaiser, and G Marston, J. Phys Chem , **94**, 3644 (1990)
- [8] T J Wallington, M. M. Hinman, J M. Andino, W O Siegl, and T.M. Japar, Int J Chem Kinet , **22**, 665 (1990).
- [9] L G Yannis, M Chrysostomos, and P Panos, J Phys Chem., **96**, 1705 (1992)
- [10] R A Duce, J Geophy, Res , **74**, 18, 4597 (1969)
- [11] W C Keene, A Pszenny, D J Jacob, R A Duce, J N Galloway, J J Shultz-Tokos, H Sievering, and J F Boatmann, Global Biochem Cycles, **4**, 4, 407 (1990)
- [12] R J Cicerone, Rev Geophys and Space Phys , **19**, 1, 123 (1981)
- [13] T Okita, T Kanedo, T Yanaka, and R Sugai, Atmos Environ , **8** 927 (1974)

- [14] P Matusca, B Schwatz and K Bachmann, *Atmos Environ.*, **18**, 8, 1667 (1984)
- [15] R. Prinn, D Cunnold, R Rasmussen, P Simmonds, F Alyea, A Crawford, P Fraser, and R Rosen, *Science*, **238**, 945 (1987)
- [16] P J Crutzen, *Atmos Chem Ann Arbor Press* pp 313-328 (1982)
- [17] R Atkinson, W P L Carter, *Chem Rev* , **84**, 437 (1984)
- [18] R Atkinson, *Chem Rev* , **86**, 69 (1986)
- [19] U C R Protocol for the determination of OH rate Constants with volatile organic chemicals
- [20] W A Mulac, A Liu, *J. Phys Chem* , **93**, 4092 (1984).
- [21] W A Mulac, A Liu, C D Jonah, *Int J Chem. Kinet* , **19**, 25, (1987)
- [22] C J Howard, *J Phys. Chem* , **83**, 3 (1979)
- [23] J V Michael and J H Lee, *J. Phys Chem.*, **83**, 10 (1979)
- [24] F Kaufman, *J Phys Chem* , **88**, 4909 (1984).
- [25] E D Morris, Jr , D H Stedman, and H Niki, *J Amer Chem Soc.*, **93**, 3570 (1971).
- [26] A. A Westenberg, *J Chem Phys* , **43**, 1544 (1965)
- [27] C J Howard and K M Evenson, *J Chem Phys* , **61**, 1943 (1974)
- [28] F Kaufman and F P Del Greco, *J Chem Phys* , **35**, 1895 (1961)
- [29] F P Del Greco and F Kaufman. *Disc Faraday Soc* **33**, 128, (1962)
- [30] F Kaufman and F P Del Creco, 9th International Symposium on Combustion (Academic Press, New York) 659 (1963).
- [31] N R Greiner, *J Chem Phys* **45**, 99 (1966)

- [32] A. Wahner and C. Zetzsch, 8th International Symposium on gas Kinetics, Univ. of Nottingham, Nottingham, U. K., July 15-20 (1984).
- [33] J. G. Anderson and F. Kaufman, Chem. Phys. lett., **16**, 375 (1972).
- [34] F. Stuhl and H. Niki J. Chem. Phys., **57**, 3671 (1972).
- [35] J. S. Robertshaw and I. W. M. Smith, J. Phys. Chem., **86**, 785 (1982).
- [36] F. P. Tully, Chem. Phys. Lett., **96**, 148 (1983).
- [37] H. Akimoto, M. Hoshino, G. Inoue, F. Sakamaki, N. Washida and M. Okuda, Environ. Sci. Technol, **13**, 471 (1979).
- [38] A. M. Winer, R. A. Graham, G. J. Doyle, J. P. Bekowies, J. M. McAfee and J. N. Pitts Jr. Adv. Environ. Sci. Technol. **10**, 461, (1980).
- [39] R. R. Arnts and J. J. Bufalini, EPA/600/09, Nov., (1987)
- [40] R. Atkinson, W. P. L. Carter, A. M. Winer and J. N. Pitts Jr., J. Air Pollut. Cont. Assoc., **31**, 10, 1090 (1981).
- [41] R. Atkinson and S. M. Aschmann, Int. J. Chem. Kinet., **19**, 1097 (1987).
- [42] T. J. Wallington, L. M. Skewes, W. O. Siegl, C. H. Wu, and S. M. Japar, Int. J. Chem. Kinet., **20**, 867 (1988)
- [43] T. J. Wallington, L. M. Skewes and W. O. Siegl, J. Photochem. Photobiol., **A45**, 167 (1988).
- [44] N. R. Greiner, J. Chem. Phys., **53**, 1070, (1970).
- [45] S. W. Benson, "Thermochemical Kinetics", 2nd Ed. Wiley, (1976).
- [46] R. Atkinson, S. M. Aschmann and W. P. L. Carter, Int. J. Chem. Kinet., **15**, 37, (1983a).

- [47] G S Jolly, G Paraskevopoulos, and D L Singleton, *Int J Chem Kinet* , 17, 1 (1985)
- [48] R Atkinson, *J Phys Chem Ref Data*, Monograph No 1, (1989)
- [49] R Atkinson, S M Aschmann, W P L Carter, A M Winer and J N Pitts, Jr , *Int J Chem Kinet* , 14, 781 (1982a)
- [50] R Atkinson, and S. M Aschmann, *Int J Chem Kinet.*, 17, 33 (1985)
- [51] T J Wallington, L M Skewes and W O Siegl, *J Phys Chem* , 93 (9), 3649 (1989).
- [52] E Tschuikow-Roux, J Niedzielski, and F. Faraj, *Can J Chem* , 1093, (1985)
- [53] E Tschuikow-Roux, T Yano and J. Niedzielski, *J. Chem Phys* , 82 (1), 65 (1985)
- [54] P. H Wine and D H. Semmes, *J Phys. Chem.*, 87, 3572 (1983).
- [55] D Davis, W Braun, and A. M. Bass, *Int. J Chem Kinet.*, 2, 101 (1970)
- [56] R G. Manning and M. J. Kurylo, *J. Phys Chem.*, 81, 291 (1977)
- [57] G W Ray, L. F Keyser, and R. T Watson, *J Phys Chem.*, 84, 1674 (1980)
- [58] R. S Lewis, S P Sander, S Wagner, and R. T Watson, *J Phys Chem.*, 84, 2009 (1980)
- [59] W B Demore, M J Molina, S P Sander, D M Golden, R F Hampson, M J Kurylo, C J Howard and A R. Ravishankasa, Evaluation No 9 of the NASA Panel for Data Evaluation, *J P L Publications* 87-41, (1987)

- [60] T Donaghy, I Shanahan, M. Hande and S. Fitzpatrick *Int. J Chem. Kinet* , **25**, 273 (1993)
- [61] S B Xing, S H Shi and L X Qui, *Int J Chem Kinet.*, **24**, 1 (1992)
- [62] P McLoughlin, R Kane and I Shanahan, *Int J Chem Kinet.*, **25**, 137 (1993)
- [63] E Tschuikow-Roux, F Faraji, S. Paddison, J. Niedzielski, and K. Miyokawa, *J Phys Chem.*, **92**(6) 1488, (1988).
- [64] T Gierczak, L Goldfarb, D Surper, and A. R Ravishankara, *Int. J Chem Kinet* , **26** 719 (1994)
- [65] G. C Fettis, J H Knox, In "Progress in Reaction Kinetics", Porter, G. Ed., Pergamon, New York, Vol 2, chapter I (1964).
- [66] M A A. Walker, R. F Walker, *J Chem. Soc Faraday Trans 1*, **69**, 1547 (1973)
- [67] R. T. Watson, *J Phys Chem. Ref. Data* **6**, 871 (1977).
- [68] L. F Keyser, *J. Chem Phys.* **69**, 214, (1978)
- [69] J. K. Hamitt, F Camm, P. S. Connell, W E. Mooz, K. A. Wolf, D. J Weubbles, A. Bamezal, *Nature*, **330**, 711 (1987)
- [70] F Markert and O J Neilsen, *Chem. Phys Lett.*, **194**, 1 (1992)