REMOVAL MECHANISMS FOR VOLATILE ORGANIC COMPOUNDS IN THE ATMOSPHERE AND IN WASTE GAS STREAMS

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This work is dedicated to Brian, my parents and to the memory of Jimmy Mc Cotter


HEY, YOUR OZONE IS GETTING PRETTY THIN ON TOP!
I TRIED COMBING IT UP FROM THE EQUATOR, BUT THAT DIDN'T WORK.

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To Maureen and Aodhmar, two of my greatest friends - here's to the Limerick Rap and Bad Bob's in May - may it go on for ever !!! and to all my other close friends (Fiona, Bridget, Barbara, Pauline and Niamh) and those of the philosophy "so many men and not enough time".

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THANKS

Declaration

I hereby certify that this material, which I now submit for assessment on the program of study leading to the award of Ph.D. is entirely my own work and has not been taken from the work of others save and to the extent that such work has been cited and acknowledged within the text of my work.

Signed: Teri Donaghy   Date 16 July 1993

Teri Donaghy

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Removal Mechanisms For Volatile Organic Compounds In The Atmosphere And In Waste Gas Streams

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Abstract

Atmospheric lifetimes were calculated from OH radical and Cl atom rate constants measured using a relative rate - smog chamber technique for a series of haloalkanes and aliphatic and cyclic ketones. The reactivities of these organics with respect to OH radicals and Cl atoms were observed to be affected by the presence and position of halogen atoms and the presence of a carbonyl oxygen atom for haloalkanes and ketones respectively; polarity effects and steric contributions were also observed to influence the magnitude of the rate constant values. The atmospheric lifetimes calculated for the organics under investigation were all sufficiently short to ensure that they would undergo transformation in the troposphere and thus could not be considered a threat to stratospheric ozone.

Of the organic compounds investigated in this work dichloromethane is the most commonly used chemical in the industrial work place, therefore methods of monitoring and removing this compound are important. Biofiltration techniques are currently being considered for this purpose as they are efficient, cheap and clean. In this work a laboratory-scale biofilter unit containing peat fibre as the filter material was used to remove dichloromethane from an artificially generated gas stream. Inlet and outlet gas concentrations were monitored and the percentage removal and the elimination capacity of the biofilter calculated over a time period of 32 weeks. The percentage removal was calculated to be between 40 - 80% and the elimination capacity was found to be a function of the inlet gas concentration.

CHAPTER 1
INTRODUCTION

1.1 THE ATMOSPHERE

The atmospheres of Mars, Venus and Earth all appear to be formed from gases released from within the planets and therefore might be expected to be similar. In reality however, the atmospheres of Venus and Mars consist primarily of CO_2 whereas the Earth's atmosphere is partially oxidised. The differences in composition of these atmospheres are due to photosynthesis which occurs only on the Earth's surface; photosynthesis converts carbon dioxide (CO_2) and water (H_2O) to carbohydrates and oxygen (O_2) which is released into the surrounding atmosphere.

The Earth's atmosphere is an envelope of gases that extends to a height of approximately 2000 km. The major atmospheric gases show a constant composition and are well mixed i.e. N_2-78.1%, O_2-20.9%, Ar-0.93%, CO_2-0.035%; water vapour is a variable component of the atmosphere with a typical concentration of about 1%. Along with these major gases there are dozens of minor trace gases particularly in the lower atmosphere (i.e. less than 20 km) which are of biological or geological origin.

The temperature profile of the Earth's atmosphere is extremely important in interpreting certain aspects of the chemical behaviour and distribution of atmospheric species and is used to divide the atmosphere into distinct layers or regions; Figure 1.1 illustrates the variation of temperature with altitude in the Earth's atmosphere.

The troposphere is the region of the atmosphere from ground level to 15 km. The temperature of this region decreases with increasing altitude from approximately 288K at the surface to around 215K at the tropopause. The troposphere is characterised by strong vertical mixing and allows substances released from the surface to mix with the bulk atmosphere; as a result, individual molecules can traverse the entire troposphere in time periods ranging from minutes to days.

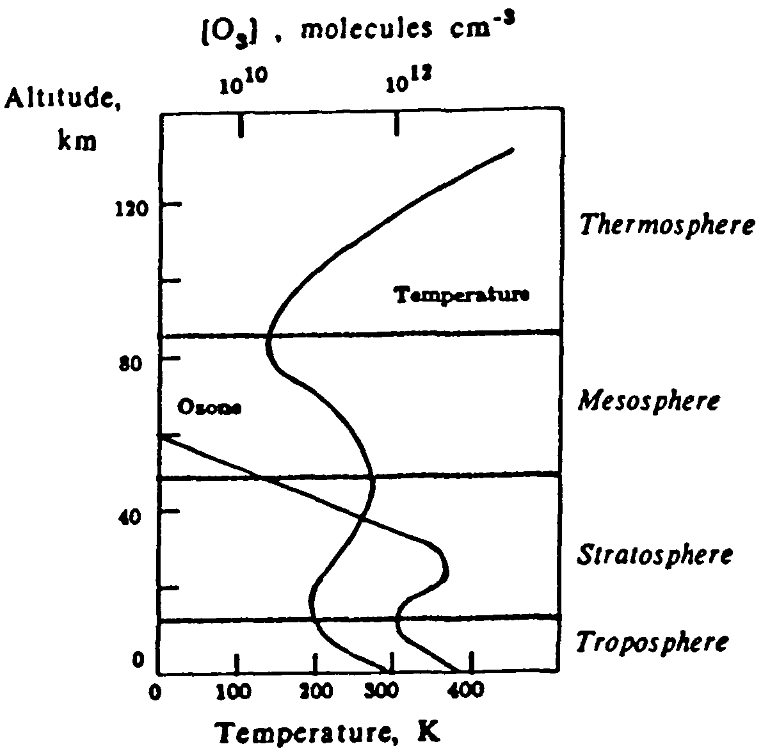

Figure 1.1: The temperature\altitude profile for the Earth's atmosphere (0 - 120 km)

In the troposphere cold air lies on top of warm air resulting in the production of convection currents which are responsible for the weather systems; also all of the water vapour, clouds and precipitation in the Earth's atmosphere are found in this area, therefore removal of water-soluble pollutants by precipation scavenging is an important process.

The stratosphere stretches from 15 km to about 50 km. In the stratosphere the temperature rises with altitude and temperature inversion occurs where warm air lies on top of cold air The atmosphere in this region is very stable and mixing is primarily in the horizontal direction; as a result chemical species can be transported over large distances in a matter of days depending on stratospheric wind speeds from the region where they were released or formed in the atmosphere. Compounds injected into the stratosphere from the troposphere are not rapidly removed physically and can remain available for long periods of time to participate in chemical changes. Before entering the stratosphere a compound must pass through the tropopause which is the boundary between the troposphere and the stratosphere. The tropopause is a low temperature point and acts as a cold trap removing any condensable materials e.g. H_2O vapour. As a result, the stratosphere is very dry and much of the H_2O vapour results from in-situ oxidation of non-condensable precursors e.g. CH_4. Although transport across the tropopause is inhibited, species from the troposphere do reach the stratosphere and vice versa.

The mesosphere is the region within the Earth's atmosphere between 50 - 85 km. Here the temperature falls with altitude and verticle mixing within this region again occurs. At about 85 km (the thermosphere) the temperature rises with altitude due to increased absorption of solar radiation by O_2, N_2 and atomic species.

Chemical changes within the various regions of the atmosphere are driven by the absorption of UV and visible radiation from the sun. Generally, high energy radiation is absorbed in the highest regions of the atmosphere and this region is characterised by high energy reaction processes i.e. ion formation is important above 50 km. At lower altitudes (less than 50 km) however, the photodissociation of molecules to smaller fragments such as atoms and free radicals becomes the dominant photochemical process. These atoms and radicals can initiate secondary thermal reactions and are ultimately responsible for the chemical transformations that occur in the lower atmosphere.

1.2 TROPOSPHERIC CHEMISTRY

Interest in tropospheric chemistry has been stimulated by the problem of depletion of stratospheric ozone by CFCs and other halogen-containing species. About 90% of the total atmospheric mass resides in the troposphere. Chemical changes in this region involve the conversion of fully or partially reduced substances to more oxidised forms. The source of a species in the troposphere can be either by emission from the Earth's surface (biogenic or anthropogenic activities), or in situ by chemical reactions or photochemistry.

If a species is unreactive in the troposphere then it may ultimately undergo transportation to the stratosphere. However, if a species is reactive then a chemical or photochemical transformation can occur. The concentration of tropospheric trace gases (including volatile organic chemicals) is determined by the relative source strength of the gas and the reactivity of the gas relative to tropospheric sink species.

As mentioned previously, the Earth's atmosphere is oxidative in nature; however, molecular oxygen despite its large atmospheric concentration does not contribute to the primary oxidation of atmospheric trace gases due to the large activation energies required to achieve appreciable conversion rates of the trace gases. The oxidising capacity of the troposphere determines the ability of the lower atmosphere to "purify" itself as well as the extent to which tropospheric compounds are transported to the stratosphere.

At concentrations found in the atmosphere, OH radicals are the most efficient oxidising agents in the troposphere [1 - 4] and reactions involving OH radicals is the first rate determining step in the reaction chain leading to oxidation. Those gases that do not react with OH radicals are generally removed by the action of short wave radiation in the stratosphere.

1.2.1 OH Radical Formation in the Troposphere

The concentration of OH radicals in the troposphere is determined by a fast photochemical cycle initiated by O_3 and H_2O vapour and driven by CO and NO. The primary production of OH radicals which accounts for approximately 50% of the total OH radical concentration in relatively unpolluted atmospheres [5] is initiated by the photolysis of O_3:

$$O_3 + h\upsilon\ (\lambda<320nm) \dashrightarrow O(^1D) + O_2 \qquad 1.1$$

Approximately 10% of the excited oxygen atoms $O(^1D)$ react with H_2O vapour to form OH radicals:

$$O(^1D) + H_2O \dashrightarrow OH + OH \qquad 1.2$$

the remaining 90% of $O(^1D)$ atoms are quenched to the ground state ($O(^3P)$) by reactions with N_2 or O_2. Tropospheric O_3 concentrations increase from 15 - 40 ppbv at the Earth's surface to about 100 ppbv in the upper troposphere [4]. Other processes which contribute to the formation of OH radicals in the troposphere include the reactions of HO_2 with NO and O_3 and the photodissociation of H_2O_2; these processes account for roughly 40% and 10% respectively of OH radical production during the day-time. Night-time OH radical concentrations are much lower than in the day-time as the source strengths for OH radical production decrease substantially due to the absence of radiation provided by the sun. OH radical concentrations in the night-time troposphere are as a result of the reaction between O_3 and HO_2 and produces 99% of OH radicals at middle latitudes and 95% at the tropics [5].

The OH radical has two features which combine to make it the most important oxidising species in the troposphere. Despite its high reactivity towards trace gases, it does not react with any of the major components of air e.g O_2, CO_2, H_2O etc., secondly OH radicals are not consumed in reactions with trace gases but are regenerated in various catalytic chain reactions.

OH radicals react mainly with CO (approx. 70%) and CH_4 (approx. 30%):

$$OH + CO \text{ ------->} H + CO_2 \qquad 1.3$$

$$OH + CH_4 \text{ ------->} CH_3 + H_2O \qquad 1.4$$

The product H atom or CH_3 radical adds to oxygen to form HO_2 (hydroperoxyl radical) or CH_3O_2 (peroxymethyl radical). Both these processes require a third body (M) to stabilise the reaction product:

$$H + O_2 + M \text{ ------->} HO_2 \qquad 1.5$$

$$CH_3 + O_2 + M \text{ ------->} CH_3O_2 \qquad 1.6$$

The HO_2 radical acts as buffer for OH radicals, especially at night-time when the reaction between $O(^1D)$ and water vapour does not occur as the formation of $O(^1D)$ requires sunlight. The HO_2 radical produced in reaction (1.5) can react with itself to produce hydrogen peroxide which decomposes to OH when irradiated:

$$HO_2 + HO_2 \text{ ------->} H_2O_2 + O_2 \qquad 1.7$$

$$H_2O_2 + h\upsilon\ (\lambda < 350\ \mathrm{nm}) \text{ ------->} OH + OH \qquad 1.8$$

Similarly, the reaction between CH_4 and OH initiates a complicated sequence of reactions which eventually converts some OH to HO_2 and creates a series of hydrogen-containing compounds e.g. H_2CO, CH_3O_2 etc .

NO (nitrogen oxide) is present in all but the remote areas of the troposphere and has natural sources (forest fires, anaerobic processes, electrical storms) as well as anthropogenic sources. NO reacts rapidly with HO_2 and CH_3O_2 formed in reactions (1.5) and (1.6), with the net result being the regeneration of OH radicals through reactions (1.9), (1.12), (1.13) and (1.14):

$$HO_2 + NO \text{ -------> } OH + NO_2 \qquad 1.9$$

and

$$CH_3O_2 + NO \text{ -------> } CH_3O + NO_2 \qquad 1.10$$

$$CH_3O + O_2 \text{ -------> } HCHO + HO_2 \qquad 1.11$$

$$HCHO + h\upsilon\ (\lambda < 350\text{ nm}) \text{ -------> } H + HCO \qquad 1.12$$

$$H + O_2 \text{ -------> } HO_2 \qquad 1.13$$

$$HCO + O_2 \text{ -------> } CO + HO_2 \qquad 1.14$$

The production of the OH radical is balanced by a net destruction which proceeds mainly by reaction with NO_2:

$$OH + NO_2 + M \text{ -------> } HNO_3 + M \qquad 1.15$$

The ratio of the HO_x (OH and HO_2) conversion to HO_x destruction is 5 i.e. a HO_x radical is cycled five times between OH and HO_2 before it is removed from the atmosphere by reaction with NO_2. Another important removal process for OH radicals is the reaction between members of the HO_x family to form stable non-radical products:

$$OH + HO_2 \text{ -------> } H_2O + O_2 \qquad 1.16$$

$$OH + H_2O_2 \text{ -------> } H_2O + HO_2 \qquad 1.17$$

Thus the steady-state concentration and distribution of OH in the troposphere is influenced by the concentrations of 5 trace gases [5], CH_4, CO, O_3, H_2O vapour and NO; OH radical formation is controlled by the reactions of O_3, water vapour,

HO_2 and NO while the reactions involving CO and CH_4 consumes most OH radicals. As the dominant primary source of OH is the UV photolysis of O_3, there is a large seasonal, diurnal and latitudinal variation in OH production.

The determination of hydroxyl radical concentrations in the atmosphere remains an active area of research due to its extreme importance and complex chemistry. The tropospheric distribution of the OH radical has yet to be unambiguously defined. The measurement of OH radical concentrations in the troposphere has been the subject of intense interest and considerable effort; because of the extremely low levels involved one needs methods that are highly sensitive and selective. To date measurements of OH concentrations in the troposphere have utilised three methods: in situ spectroscopic techniques, chemical tracer methods (^{14}CO, CH_3CCl_3), and chemical modelling studies. Chemical modelling studies can provide global, seasonal and diurnal information on tropospheric OH concentrations, however the reliability of the data depends on the validity of the chemical mechanisms used in the prediction techniques and the accuracy of the individual rate constants required in the model. Spectroscopic techniques such as Laser Induced Fluorescence (LIF), or long path UV absorpion can often be plagued by background fluorescence or absorption far in excess of signal levels which limits the sensitivity of these techniques. Chemical tracer methods allow specific compounds such as ^{14}CO or long-lived hydrocarbon species (CH_3CCl_3) to react with OH radicals for a time period greater than the OH radical atmospheric lifetime. A disadvantage of the tracer method is that it can produce low signals and large background interferences.

As more and more measurements are being carried out on a global scale a clearer picture of the variations in OH radical concentrations are being observed. OH radical concentrations vary depending on whether the sample site is located in a rural or an industrial area. Global OH radical concentration values are typically of the magnitude of 1 x 10^6 molecules cm^{-3}; however, local effects may alter this value e.g. smog episodes can result in OH concentrations reaching values of 10^7 molecules cm^3. Therefore there may be a discrepancy between "global" atmospheric lifetimes and "local" atmospheric lifetimes [6]. It is necessary therefore when citing atmospheric lifetimes to list the OH radical concentration used in the calculations. Some of the more reliable OH radical concentrations (measured using various techniques) [5] are listed in Table 1.1.

The value of the OH radical concentrations used in this work was taken from the work of Prinn et al [7], who used an optimal estimation inversion scheme combined with the knowledge of industrial emissions of CH_3CCl_3 to calculate a globally averaged OH concentration. The measurements were made over a seven year period (July 1978 to June 1985) at three sampling stations in the northern hemisphere (Ireland, Oregon, Barbados) and two stations in the southern hemisphere (Samoa and Tasmania).

1.2.2 Cl atoms in the troposphere

To date the role of Cl atoms in the troposphere has received little attention because Cl atoms are sufficiently scarce so that they could not possibly compete with the oxidising capacity of OH radicals. At room temperature, the reaction of CH_4 with Cl atoms is only 13 times faster than the corresponding reaction with OH radicals, whereas OH radicals in the troposphere are nearly 1000 times more abundant [8]. As a result Cl atom chemistry in the troposphere seemed irrelevant. However, as the preexponential A factor in the rate equation for Cl atom reactions is greater than that for OH radical reactions [9] and the fact that the Cl/OH ratio increases with altitude, it has been realised that Cl atom reactions are important processes in the troposphere. It has been estimated that between 20 - 40% of non-methane hydrocarbons (NMHC) oxidation in the troposphere and 40 - 90% of NMHC oxidation in the lower stratosphere is caused by reaction with Cl atoms [8].

[OH] (molec. cm^{-3})			METHOD
NH[a]	SH[b]	G[c]	
4.9	6.3	5.5	CM[d]
		5.2±1.7	
		5±2	CT[e]
		8±6	CT
7.5±1.4	7.9±1.5	7.7±1.4	CT
		7.5±2.5	CM
		8.2	CM

Table 1.1: Global OH radical concentrations calculated using various techniques [5].[a-southern hemisphere, b-northern hemisphere, c-global, d-computer modelling, e-chemical tracer.]

The most important source of atmospheric chlorine is the ocean surface which injects sea salt particles into the surrounding atmosphere. Much of this particulate matter is redeposited in the ocean by sedimentation, diffusion and impaction; however important amounts of chloride ions (3 - 20%) [10] find their way into precipitation over both continents and oceans. Gaseous inorganic chlorine (GIC) is known to be present in the marine boundary layer at concentrations of 1 - 2 ppbv (parts per billion by volume) [8]. The major component of GIC is HCl which is released from sea salt aerosols that have been acidified to very low pH's (2 - 3) by the addition of nitric or sulphuric acid produced within the atmosphere [10 - 14].

$$2NaCl + H_2SO_4 \text{ -------> } Na_2SO_4 + 2HCl \quad 1.18$$

$$NaCl + HNO_3 \text{ -------> } NaNO_3 + HCl \quad 1.19$$

If ppbv concentrations of HCl are generated, then the reaction with OH radicals can produce sufficient Cl atoms to photooxidise a significant fraction of non-methane hydrocarbons (NMHC) in the troposphere [8]·

$$HCl + OH \longrightarrow H_2O + Cl \qquad 1.20$$

However, measurements of the HCl concentrations off the east coast of the U.S. found that the surface concentrations were < 1 ppbv and decreased with altitude and distance from the coast line indicating that Cl atoms reactions may not be as significant as previously thought [15, 16].

Aside from the sea-salt source of GIC in the troposphere other natural sources include rain forests and volcanic eruptions [17]. Man-made sources include combustion of coal and fossil fuels. For the determination of atmospheric lifetimes with respect to Cl atoms, for the volatile organic compounds (VOCs) studied in this work the concentration of Cl atoms in the marine troposphere was taken to be 1 x 10^3 molecules cm^{-3} [8].

1.2 3 Reactions of OH radicals and Cl atoms in the troposphere

The scavenging process in the troposphere is divided into physical removal processes (absorption at the Earth's surface or precipitation) or chemical removal processes which involves reactions in the atmosphere, primarily with OH radicals and to a lesser extent with Cl atoms.

Chemical removal of organics by reaction with OH radicals has been shown to be an important tropospheric removal mechanism [3, 18] when the organics contain hydrogen atoms or carbon-carbon double bonds. Similarly Cl atom reactions with organic compounds is also an important removal process in the marine troposphere (0 - 3 km) [8]. The sink process is represented by the equation·

$$\mathrm{OH\backslash Cl + ORGANIC} \xrightarrow{k} \mathrm{SINK} \qquad 1.21$$

where k is a temperature-dependent rate constant for either OH radical or Cl atom reactions and OH\Cl is a globally averaged concentration of OH radicals or Cl atoms.

The measurement of the length of time a species resides in the troposphere is the atmospheric lifetime which can be simply represented by the equation [17]:

$$\tau = 1/k[\mathrm{OH}]\backslash([\mathrm{Cl}]) \qquad 1.22$$

where τ is the atmospheric lifetime, k is the rate constant for the reaction of the organic with either OH radicals or Cl atoms and [OH]\([Cl]) is the globally averaged concentration of either OH radicals or Cl atoms.

The atmospheric lifetime of an organic compound is an important value as it gives an estimation of the time period a compound will spend in the atmosphere and whether the compound will ultimately end up in the stratosphere. Equation (1.22) gives a somewhat simplified representation of the atmospheric lifetime of an organic as the more reactive organics and the sink species are not distributed uniformly throughout the troposphere.

1.3 STRATOSPHERIC CHEMISTRY

In the stratosphere a series of photochemical reactions involving ozone (O_3) and molecular oxygen (O_2) occur. The presence of oxygen (O_2) in the stratosphere is of vital importance to life on Earth as it prevents short wave radiation ($\lambda < 200$ nm) reaching the Earth's surface; another important function of O_2 in the Earth's stratosphere is the formation of ozone (O_3). O_3 is also a very important atmospheric species as it absorbs radiation lethal to unicellular organisms and to the surface cells of higher plants and animals (i e between 240 and 290 nm) O_3 is also responsible for the temperature profile of the stratosphere as it absorbs UV, visible and thermal IR radiation, and also provides significant energy for driving the circulation of the mesosphere

The essential steps for the photochemical formation of ozone in the stratosphere were described by Chapman [19] in 1930, and involves the photolysis of molecular oxygen to atomic oxygen followed by the addition of atomic oxygen to molecular oxygen to form ozone as outlined in reactions (1 23) to (1 26).

$$O_2 + h\nu\ (\lambda < 242\ \text{nm}) \longrightarrow O + O \qquad 1.23$$

$$O + O_2 + M \longrightarrow O_3 + M \qquad 1\ 24$$

$$O_3 + h\nu\ (\lambda < 320\ \text{nm}) \longrightarrow O + O_2 \qquad 1.25$$

$$O + O_3 \longrightarrow O_2 + O_2 \qquad 1\ 26$$

Reactions (1.23) and (1 26) determine the balance between production (1.24) and loss (1.26) of ozone in the stratosphere Figure 1.1 shows the change in ozone concentrations with altitude, where ozone concentrations reach a maximum between the altitudes of 15 - 30 km as a result of a compromise between solar ultra-violet flux and molecular oxygen density. This area is commonly referred to as the "ozone layer"

Based on the Chapman cycle for ozone formation the ozone layer should contain higher concentrations of ozone than is actually found. This is the result of the occurrence of natural reaction processes that destroy ozone in addition to reaction (1.26). These processes are catalytic chain reactions that are propagated by atoms and radicals derived from trace constituents of the atmosphere i.e :

$$X + O_3 \text{ -------> } XO + O_2 \qquad 1.27$$

$$O + XO \text{ -------> } O_2 + X \qquad 1.28$$

$$\text{NET } O + O_3 \text{ -------> } O_2 + O_2 \qquad 1.29$$

Three main catalytic families have been identified, in which X = OH (the hydroxyl radical), NO (nitric oxide), or Cl (the chlorine atom), with NO_x reactions dominating in the lower stratosphere and HO_x reactions becoming relatively more important at higher altitudes [20]. All three cycles, especially the reactions involving OH radicals and NO occur in the natural atmosphere, dominating the loss of ozone and as a result controlling its concentration in the stratosphere [21].

Although the importance of atmospheric ozone has been recognised over the past five decades, research into stratospheric ozone has intensified dramatically over the last fifteen years since the hypothesis that the decrease in springtime Antarctic ozone was coincidental with increases in tropospheric organochlorine concentrations [22].

Antarctic ozone concentrations have been monitored since 1957 [23] and have shown a downward trend in ozone concentrations during the months of September/October since the late 1970's. A "hole" in the ozone layer located over Antarctica was discovered in the early 1980's [24]. This discovery quickly prompted theoretical studies aimed at understanding its origin. The leading scientific theories put forward to explain this phenomenon included purely dynamical effects i.e. no chemistry, nitrogen chemistry associated with the solar cycle and halogen chemistry resulting from anthropogenic emissions of volatile organic chemicals (VOCs) from the Earth's surface. This theory is the one most clearly supported by field observations [24, 25] where the Antarctic Airbourne Ozone Expedition in 1987 established that the Spring time depletion of ozone in Antarctica was most probably due to photochemical destruction brought about by the increasing concentrations of halogen atoms (Cl and Br) [16]. Figure 1.2

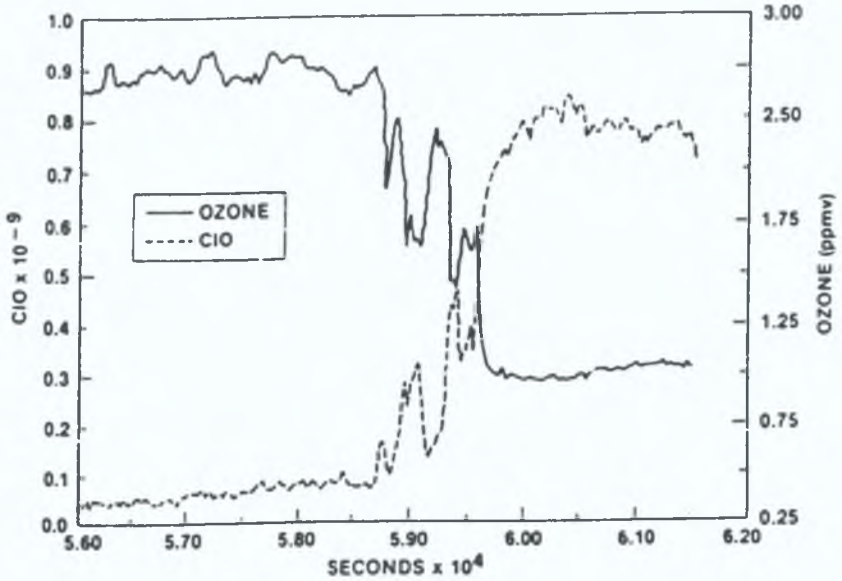

Figure 1.2: Measurements of ozone and ClO concentrations carried out by the Antarctic Airbourne Ozone Expedition in 1987.

illustrates some of the the findings of the expedition where increased concentrations of ClO corresponded with decreased O_3 concentrations [26]. The observed increase in the reactive ClO and the concurrent decrease in O_3 concentrations over Antarctica shown in Figure 1.2 gave a strong indication that the proposed chlorine chemistry was involved in the ozone loss.

The main contribution to background concentrations of halogen atoms in the Earth's atmosphere originates from the World's oceans, which are capable of producing significant quantities of CH_3Cl and CH_3Br [16]; however, the major sources of halogen atoms in the stratosphere are from VOCs of anthropogenic origin which are a result of the technological advances made by man in this century.

For a VOC to pose a threat to the stratospheric ozone layer firstly it must contain halogen atoms that can catalytically interact with the natural ozone formation and destruction cycles (reactions (1.27) - (1.29)); secondly if it has a sufficiently long tropospheric lifetime i.e. it reacts slowly or is unreactive with the tropospheric sink species, and thirdly if the compound is insoluble in water i.e. it is not removed by precipitation. VOCs containing halogen atoms (Cl or Br) can be emitted into the atmosphere from either natural (biogenic) sources or as a result of man's activities on Earth (anthropogenic sources).

Biogenic Sources of Cl and Br containing VOCs

The largest source of atmospheric chlorine is the ocean surface where the action of wind, waves and bubbles produces sea-salt aerosols [25], as a result significant amounts of chloride ions find their way into precipation over both continents and oceans. Methyl chloride (CH_3Cl) is produced by the oceans and is the most abundant natural chlorine containing molecule in the atmosphere [25].

Bromine species are relatively minor components of the stratosphere compared to chlorine species, the major biogenic sources of bromine from the naturally occurring organobromine species include CH_3Br, CH_2Br_2 and $CHBr_3$ which are produced by the oceans and algae [17].

Anthropogenic Sources of Cl and Br containing VOCs

The largest group of anthropogenic VOCs capable of injecting chlorine atoms into the stratosphere are the chlorofluorocarbons (CFCs). CFCs are compounds containing chlorine, fluorine, carbon and sometimes hydrogen. CFCs have been used extensively since their development in the 1930s, primarily as refrigerants, aerosol propellants and blowing agents. CFCs are ideally suited for such uses as they are generally non-toxic, non-flammable and chemically inert. The dominant CFCs released from anthropogenic activities are: CCl_3F-(CFC-11), CCl_2F_2-(CFC-12), and $CHClF_2$-(CFC-22). The numbers refer to the number of halogen and hydrogen atoms present [1]. The first number denotes the number of hydrogen atoms plus one and the second number gives the number of fluorine atoms. For CFCs containing two or more carbon atoms a three-digit numbering system is used. The first digit gives the number of carbon atoms minus one, the second digit gives the number of hydrogens plus one and the third digit gives the number of fluorine atoms; the balance of atoms is made up of chlorine atoms, e.g. CCl_2FCClF_2 is CFC-113.

CFCs are inert in the troposphere, they are not removed by either physical means (as they are insoluble in water so they cannot be removed by rainout), or by chemical means - they are not photolysed in the troposphere as they do not absorb light of wavelengths > 290nm, nor do they react with the major sink species (OH radicals, Cl atoms, NO_3 radicals or O_3) due to the predominant absence of abstractable hydrogen atoms or C=C bonds. As a result CFCs have very long tropospheric lifetimes and are ultimately transported to the stratosphere.

CFCs are photolysed in the stratosphere by the absorption of radiation in the spectral window between the strong absorptions of O_2 and O_3 ($\lambda = 185 - 210$ nm), as a result the C-Cl bond breaks releasing a chlorine atom into the surrounding area which produces a stratospheric burden of reactive chlorine species i.e. Cl and ClO. To a lesser extent, reactions between CFCs and $O(^1D)$ occurs, which also results in the production of chlorine atoms, however this removal process occurs mainly in the 30 - 50 km altitude range.

In addition to the CFCs there are a number of other VOCs emitted into the atmosphere due to man's activities on Earth. Methyl chloroform (CH_3CCl_3), carbon tetrachloride (CCl_4), dichloromethane (CH_2Cl_2) and the bromine-containing species: bromodifluoromethane ($CBrClF_2$· halon 1211) bromotrifluoromethane ($CBrF_3$ halon 1301) and ethylenedibromide (CH_2BrCH_2Br). The chlorinated organics are primarily used as solvents and degreasing agents while the brominated organics are used as fire fighting agents (halon 1211 and 1301), ethylenedibromide is used as a gasoline additive.

According to recent analysis [27] the relative contribution of various chlorine containing source gases to the total atmospheric chlorine in 1985 is given in Table 1.2:

Substance	CFC	%
$CFCl_3$	CFC-11	20
CF_2Cl_2	CFC-12	25
$C_2F_3Cl_3$	CFC-113	0 3
C_2F_4Cl	CFC-114	<1
C_2F_5Cl	CFC-115	<1
$CHClF_2$	HCFC-22	3
CCl_4		13
CH_3CCl_3		13
CH_3Cl		20

Table 1.2: Major organics that contribute to the total atmospheric chlorine concentration [27].

Of these compounds only CH_3Cl is of natural origin. As a consequence the present stratospheric chlorine loading by anthropogenic compounds exceeds the natural level by a factor of 5 [27].

Bromine compounds are present in the stratosphere at lower concentrations relative to chlorine concentrations i.e. approximately 0.02 ppb [28, 29]. It has been recognised however, that Br atoms have a greater potential to destroy O_3 than Cl atoms [16] particularly in the lower stratosphere where O_3 concentrations are the highest, as approximately 50% of the available Br is present in the active form (i.e. Br and BrO) whereas only a few percent of the Cl atoms are available in the reactive form i.e. ClO. Moreover, BrO primarily reacts synergistically with ClO in a fast catalytic cycle to destroy O_3 even in the absence of oxygen atoms. Thus as the abundances of Cl atoms increase throughout the stratosphere, O_3 destruction by Br atom catalysis will increase proportionally to the increase in the abundances of both stratospheric Cl and Br concentrations.

Figure 1.3 shows a schematic representation of the fate of a chlorine containing organic species released in to the atmosphere. Once the compound reaches the stratosphere it releases its chlorine atom into the surrounding atmosphere as a direct result of photolysis. The Cl atom can either form reservoir species such as HCl, $ClONO_2$, HOCl or ClO outlined in reaction (1.27) which results in the catalytic destruction of ozone.

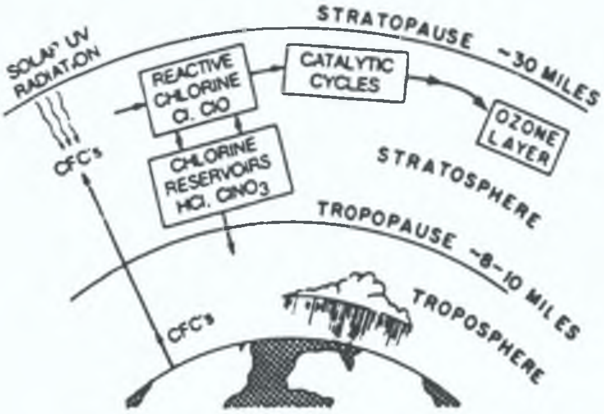

Figure 1.3: A schematic representation of the fate of halogen-containing organics in the Earth's atmosphere.

The time scale over which ClO is formed and remains available to react with O_3 depends critically on the abundances of the NO_x speciespresent in the atmosphere as NO_x controls the rate of formation of the reservoir species HCl and $ClONO_2$:

$$\mathrm{ClO + NO_2 + M \longrightarrow ClONO_2 + M} \qquad 1\ 28$$

and

$$\mathrm{ClO + NO \longrightarrow Cl + NO_2} \qquad 1\ 29$$

$$\mathrm{Cl + CH_4 \longrightarrow HCl + CH_3} \qquad 1.30$$

Heterogeneous reactions on the surface of Polar Stratospheric Clouds (PSCs) are thought to play a central role in the chemistry of the stratosphere [25, 26] by providing surfaces on which the heterogeneous chemical processes can take place NO_x species are removed from the gas phase by converting the short lived nitrogen compounds to more stable species (N_2O_5) listed in reactions (1.33) and (1.34) which is then converted into nitric acid and trapped in the cloud particles leaving a gaseous air mass in which nitrogen oxides are essentially absent. The chlorine reservoir compounds (ClONO, HCl) react with each other or H_2O to form reactive Cl_2 or HOCl which escapes into the gas phase while HNO_3 remains in the clouds.

$$\mathrm{N_2O_5 + H_2O \longrightarrow 2HNO_3(s)} \qquad 1\ 33$$

$$\mathrm{N_2O_5 + HCl \longrightarrow ClNO_2(g) + HNO_3(s)} \qquad 1\ 34$$

$$\mathrm{HCl + ClONO_2 \xrightarrow{ICE} Cl_2 + HNO_3} \qquad 1.35$$

$$\mathrm{H_2O + ClONO_2 \longrightarrow HOCl + HNO_3} \qquad 1\ 36$$

In the cases where the NO_2 concentrations are very low, $ClONO_2$ cannot form; as a result ClO concentrations increase to a point where chlorine oxide dimers (ClOOCl) form [26, 30]

$$\mathrm{2ClO + M \longrightarrow ClOOCl + M} \qquad 1.37$$

Photolysis of this dimer occurs in Antarctica with the appearance of the sun in the Spring time releasing the Cl atoms into the surrounding atmosphere. Thus the formation of PCSs causes a supression of the NO_x species and the liberation of reactive chlorine atoms.

Global ozone concentrations are monitored using a combination of ground-based Dobson UV spectrometers and instruments aboard the Nimbus 7 satellite i.e. the Total Ozone Mapping Spectrometer (TOMS) and the Solar Band Ultraviolet (SBUV) spectrometer. To date the ozone hole has appeared each September and reaches a maximum depth in early October before breaking up around mid-November. In 1988 the ozone loss over Antarctica (amounting to about 50% of the ozone column in the Spring) coincided with a significant decline (approx. 10%) over mid-latitudes during Spring and Summer [31]; also in northern-mid latitudes more modest ozone decreases in late Winter and early Spring were also observed [32]. In 1991 it was observed that the ozone hole was slightly more severe than in previous years [33]. Apart from the normal springtime ozone depletion occurring between 12 - 20 km there were additional O_3 losses in the upper and lower stratosphere. The upper stratosphere ozone loss occurred in the 25 - 30 km region and seems to be associated with the transport of ozone poor air from lower regions. The ozone loss in the lower stratosphere (11 - 13 km) is believed to be a new development peculiar to the 1991 polar vortex and its relationship to volcanic activity in previous years has been examined.

The largest ozone depletions in the future are expected to coincide with peak chlorine loading of the atmosphere. The depletion predicted in the upper stratosphere with an increase in chlorine concentrations from 3 - 5 ppb is modest: 1-2% in the tropics and 4-6% at high latitudes [25], however in the lower stratosphere, ozone depletions through chlorine and bromine catalysed reactions is magnified by the presence of PSCs and would be expected to be much more enhanced.

It has been reported however, [34] that in 1992 the destruction of ozone in Antarctica has begun earlier, extends to lower altitudes and was spread over a wider geographical area than ever before. The unprecedented intensity of the ozone hole more than likely results from chlorine catalysis that followed heterogeneous reactions on the surfaces of sulphate aerosols produced from the eruptions of Mount Hudson [Chile] and Mount Pinatubo [Philippines] [16].

Recovery of the Antarctic ozone hole will not occur unless chlorine levels fall below 2 ppb, although recovery might also depend on changes in the Antarctic climate and concentrations of other gases such as methane.

To date the appearance of an ozone hole in the Arctic region has not occurred, however perturbations in ozone concentrations have been monitored by the second Airborne Arctic Stratospheric Expedition (AASE-II) [35]. Studies have shown that due to the presence of PSCs virtually all the chlorine in this region was present in the active forms; scientists have also recorded record-high concentrations of ClO over Canada and New England. By tracking air masses over Iceland, calculated ozone destruction was observed to be 1-2% per day during the (short) sunlight hours with a total ozone decrease of 10%. Recent NASA satellite measurements show the worst ozone depletion on record for the first three months of 1993 [36] with recorded ozone levels being 14% lower in the Northern Hemisphere than measured in previous years.

PSCs are sensitive to the temperature of the polar night which is controlled by infra red cooling and the upward propagation of meterological disturbances from the troposphere; as the Northern Hemisphere is warmer [21] and is dynamically more active than the Southern Hemisphere cloud formation is not as prevalent [37]. The liklihood of increasing PSC formation occurring in the Arctic region will increase over the next 50 years or so due to increasing CO_2 emissions and a cooling of the stratosphere due to long term decreases in ozone concentrations. This effect coupled with large halogen concentrations will increase the potential for ozone hole formation in this region [37, 38].

Since the discovery of the ozone hole and subsequent research efforts to monitor ozone concentrations in the atmosphere, it has been recognised that decreasing ozone concentrations in the stratosphere will have potentially detrimental effects on living organisms on the Earth's surface. As the ozone layer thins, more high energy radiation (UV(B)) will reach the Earth's surface. The effects of UV(B) radiation on both human health and biotic resources are cumulative reflecting integrated exposures over extended temporal scales ranging from single to several growing seasons for agricultural resources and to decades for human health.

There are two primary issues underlying the effects of enhanced UV(B) radiation on human health - skin cancer and photoimmunology. Skin cancer can be divided into non-melanoma and melanoma type cancers. Scientific evidence [39] suggests that projected increases in UV(B) concentrations due to stratospheric ozone depletion would accelerate the incidence of non-melanoma tumors. It is estimated that an atmospheric amplification factor of 2 (i.e. 1% O_3 depletion produces a 2% increase in ground level UV(B) radiation) would result in a 2 - 5% increase in basal-cell carcinoma and a 4 - 10% squamous-cell carcinoma increase. These cancer rates may increase significantly among UV(B)-sensitive populations i.e. mid to upper latitudes (people of Celtic descent). Melanoma is a much more serious concern; melanoma cancer appears most often on the under-exposed areas of the body as opposed to the UV(B) saturated areas (nose , forearms etc.). Melanoma kills three times more people per annum relative to other types of skin cancer, however, there is an inverse correlation of latitude and deaths from melanoma which suggests a possible effect of UV(B) radiation on growth or metastasis of melanoma or a lulling of the immune response to melanoma.

Based on studies that link UV(B) exposure and a change in the body's autoimmune response [39] it is hypothesised that UV(B)-induced DNA lesions in the skin will elevate the concentration of antinuclear antibodies which in-turn will ellict autoimmune-like reactions. It is also hypothesised that UV(B) exposure will lead to a supression of the body's intrinsic capacity to immunologically reject tumor growth and development.

Many species of agricultural crops, forest trees, native herbaceous species and aquatic phytoplankton are classified as UV(B)-sensitive. High levels of ozone can cause a decrease in yields of important crops such as cereals, sugar beet and potatoes which are particularly sensitive [36]. Upon excessive exposure these species would experience a reduction in growth due to the effects of UV(B) on carbon metabolism.

With increasing awareness of the causes and environmental effects of ozone depletion, international comittees have been set up to introduce legislation banning the manufacture and use of chemicals that threaten the ozone layer. As early as 1974, after the findings of Rowland and Molina [22] attempts were made to legislate a ban on the use of CFCs as aerosol propellants in the U.S.. It wasn't until 1985 however, corresponding with the publication of the results announcing substantial losses of stratospheric ozone over Antarctica [24] that a convention was held (The Vienna Convention), to discuss the status of the ozone layer. The Montreal Protocol arose from the second resolution adopted by the Vienna convention on the protection of the ozone layer in 1987. This protocol is an international treaty designed to regulate the introduction of man-made chlorine sources (CFCs) and bromine-containing substances (Halons) into the atmosphere. The total number of compounds covered by the Protocol is eight and they are divided into two groups:

Group 1		Group 2	
Substance	CFC	Substance	HALON
CCl_3F	11	$CBrClF_2$	1211
CCl_2F_2	12	$CBrF_3$	1301
$C_2Cl_3F_3$	113	$C_2Br_2F_4$	2402
$C_2Cl_2F_4$	114		
C_2F_5Cl	115		

Table 1.3: Halogenated organics covered by the Montreal Protocol.

Under the Montreal Protocol, begining July 1 1989 (six months after the Protocol entered into force), annual production and consumption of Group 1 compounds was to be curtailed to 1986 levels; by July 1993, production and consumption was to decrease to 80% of 1986 levels and finally, by July 1998 production and consumption must be reduced to 50% of 1986 levels. Group 2 compounds were treated slightly differently as it was considered that halons were essential fire fighting agents. As a result their production was subjected only to a freeze as opposed to a mandatory decrease, therefore their production was frozen at 1986 levels 3 years after the agreement entered into force. No further constraints were placed on Group 2 compounds. The Montreal Protocol was strengthened by meetings held in 1990 and 1991 in London and Nairobi and again in November 1992 in Copenhagen. At the last meeting the deadlines for phasing out CFCs, halons, carbon tetrachloride and methylchloroform were advanced from the year 2000 to 1996, however essential use exemptions were included in the amendment for these compounds which allows continued production after the phase out date. The latest ammendments also place a cap on HCFC production in 1996 with a gradual phase out by the year 2030.

Many of the CFC-producing countries are independently committed to an even faster phaseout of CFCs. Nevertheless, the amounts of CFCs emitted into the atmosphere in the period 1985 - 1989 exceeded the emissions in any preceeding five year period [40]. Measurements of CFCs in the atmosphere do not yet show any slackening in the rate of increase in their atmospheric concentrations. Model calculations predicting the concentration change of CFCs with time show that adherence to the Montreal Protocol will alleviate the problem of increasing atmospheric CFC concentrations; however, a reduction of 85% of the current CFC production levels would be required to stabilise CFC concentrations at 1989 values [21].

Because CFCs have such slow emission rates, tropospheric concentrations of the CFCs will not reach a maximum level until 10 years after the completion of the phaseout process. The maximum stratospheric effect on ozone probably will not occur for an additional 5 - 10 years due to the time lapse between emission at the Earth's surface and reaching the upper stratosphere. As a result the effects of ozone loss will be felt on a global scale into the 21st century and it will be well into the 22nd century before atmospheric halogen concentrations return to the levels they were at in 1960 [21].

Concern over the global environmental consequences of fully halogenated CFCs has sparked the development of replacement compounds some of which have now been covered by the amendments to the Montreal Protocol. The two major environmental considerations for these chemicals are possible changes in stratospheric ozone and the effects on global climate. These compounds include HFCs - hydrofluorocarbons (contain no chlorine atoms) and HCFCs-hydrochlorofluorocarbons. As both of these compounds contain hydrogen atoms they are potentially far more reactive towards tropospheric OH radicals than CFCs. The OH radical destruction mechanism results in significantly shorter atmospheric lifetimes of these species relative to CFCs which is a primary factor in considering the potential effect these replacement organics may have on stratospheric ozone and global warming. Some of the most common replacement organics are listed in Table 1.4.

Substance	Name	Replaces
$CHClF_2$	CFC-22	CFC-12
CF_3CCl_2H	CFC-123	CFC-11
C_2HF_4Cl	CFC124	CFC-114
CH_3CCl_2F	CFC-141b	CFC-11
$C_2H_3ClF_2$	CFC-142b	CFC-12
$C_2H_2F_4$	CFC-134a	CFC-12
$C_2H_4F_2$	CFC-152a	CFC-12

Table 1.4: Replacement compounds for commonly manufactured CFCs.

It is necessary that these replacement organics undergo rigorous testing to ensure that they meet the physical, dynamic and chemical requirements as substitute compounds. When assessing the environmental impact of these replacements several criteria are evaluated:

- the ozone depleting potential (ODP)
- the halocarbon global warming potential (HGWP)

and

- the ozone forming potential (OFP).

The ODP of a compound estimates the relative potential of trace gases in being able to reduce stratospheric ozone. It is defined as the ratio of calculated ozone column change for each mass unit of gas emitted into the atmosphere relative to the calculated depletion for the reference gas CFC-11.

The HGWP calculation is based on a concept similar to the ODP and is used to describe the relative potential of each halocarbon as a green-house gas. It is defined as the ratio of calculated warming for each mass unit of a gas emitted into the atmosphere relative to the calculated warming for a mass unit of reference gas CFC-11. Examples of ODPs and HGWP for two of the alternative halocarbons are given in Table 1.5:

Species	**Ratio to CFC-1**	**ODP**
CFC-11	1.00	1.0
HCFC-22	0.047	0.042
HCFC-123	0.0147	0.013
Species	**Ratio to CFC-1**	**HGWP**
CFC-11	1.0	1.0
HCFC-22	0.30	0.29
HCFC-123	0.016	0.015

Table 1.5: ODPs and HGWPs for two alternative halocarbons.

To calculate the OFP of a compound it is necessary to have information on the emission-strength of the organic under investigation and the resulting ambient concentration for a particular source region as the major technological uses of HFCs and HCFCs implies that almost all their release will occur in urban surroundings.

Other possible alternatives for CFCs include a variety of fluorinated propanes, butanes and ethers [41]. All of these compounds have boiling points and critical temperatures that are similar to those for fully halogenated CFCs.

Aside from calculating the ODP, HGWP and the OFP for VOCs and alternative CFCs, to quantitatively asses the impact of a VOC on stratospheric ozone it is necessary to have a thourough understanding of OH radical and Cl atom reactions in the troposphere; this information can be obtained by compiling information on [17]:

(a) the rate coefficient of the organic with OH radicals\Cl atoms and

(b) its variation with temperature and pressure throughout the troposphere,

(c) the tropospheric distribution of OH radical\Cl atom concentrations;

(d) the transport mechanisms of the organics within the troposphere;

(e) the organic source strength and its spatial distribution;

(f) the nature and behaviour of any long-lived products;

(g) the transport mechanisms of halocarbons to the stratosphere.

Ideally, the only solution to the ozone problem is to prevent halogen atoms from reaching the stratosphere by halting production of halogen-containing organics, however this is not an attainable goal in the immediate future as much of today's technology relies heavily on these compounds The replacement of CFCs with alternative halocarbons is only a means to an end rather than a complete solution. Many of these organics have brief atmospheric lifetimes due to the presence of abstractable hydrogen atoms so that it is possible that the atmosphere could recover quickly from large emissions of HCFCs. However the short term damage may be significant (taking near-term ODPs as opposed to steady-state ODP values [42]) and it is in the short term i e the next few decades that the danger to the ozone layer is most acute.

One of the objectives of this work as detailed in Chapter 2 was to contribute to the assessment of some VOCs of atmospheric importance by measuring the rate coefficients for OH radical and Cl atom reactions. These measurements were carried out at room temperature and atmospheric pressure using the relative rate technique. The relative rate constants for OH radical and Cl atom reactions with a series of chlorinated and brominated alkanes was measured and the effects of halogen substitution on rate coefficients was observed and using equation (1 22), atmospheric lifetimes for these compounds were calculated and predictions made as to whether the haloalkanes were sufficiently unreactive in the troposphere so as to be transported to the stratosphere where they could contribute to perturbations in the chemistry of this region. Relative rate constants for a series of aliphatic and cyclic ketones were also measured as carbonyl compounds are important atmospheric species in that they can be formed in the atmosphere as a result of the photooxidation of alkanes. Little kinetic information is presently available on atmospheric reactions of ketones and the results obtained in this work serve to increase the data base of information on these compounds and also gives a further insight into the fate of VOCs in the atmosphere.

Chapter 3 is a feasibility study of the performance of a peat biofilter on the removal of dichloromethane (DCM) from an artificial gas stream. Biofiltration is a relatively new elimination technique and is based on the degradation of waste substrates to mineral end products by the action of microorganisms contained within the biofilter. DCM is a volatile organic chemical which is used extensively in many industrial processes e.g. paint manufacturing and as a solvent in many pharmaceutical industries. Large amounts of this chemical can be emitted into the atmosphere as a result of evaporation; because this compound contains chlorine it is a potential threat to stratospheric ozone; also it is a dangerous and toxic chemical which is a health hazard to those who are in contact with it either in a liquid or gaseous form, therefore removal processes for this chemical are an important consideration in the work place.

The aim of this work was to monitor the performance of a peat fibre biofilter in removing DCM from an artificially generated waste gas stream with the ultimate objective of using the system for industrial applications.

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CHAPTER 2
OH RADICAL AND Cl ATOM REACTIONS WITH HALOALKANES AND A SERIES OF KETONES

2.1. INTRODUCTION

To determine the atmospheric importance of an organic compound in relation to stratospheric ozone depletion, it is necessary to have a thorough knowledge of the reactions it may undergo once it has entered the atmosphere. Since the predictions of Rowland and Molina two decades ago [1] a vast amount of experimental work involving laboratory, environmental chamber and ambient atmospheric studies has been completed to investigate the physical and chemical processes in the atmosphere which pollutants undergo.

Since the early 1980's attention has been focused on the atmospheric reactions of halogen-containing organics e.g. chlorofluorocarbons (CFCs), halons and other chlorine-containing species as it is thought [2, 3] that halogen chemistry is responsible for perturbations in the stratospheric ozone layer. It has also been recognised however, that kinetic studies of atmospheric reaction intermediates and products of the haloorganics in the atmosphere must be carried out as they may be potentially more hazardous than the original chemical.

Organisations such as the IUPAC Task Group on Chemical Kinetics and AFEAS (Alternative Fluorocarbons Environmental Acceptability Study) have been established with the aim of compiling information on the kinetics, mechanisms and reaction products of the relevant atmospheric reactions with the result that great effort has been devoted to upgrading existing experimental techniques and also devising new techniques which allow kinetic data to be obtained under simulated atmospheric conditions. In many cases it is difficult to precisely reproduce atmospheric conditions, therefore a wide range of experiments are required to enable the atmospheric fate of the organics to be predicted.

It is generally accepted that the dominant loss mechanisms for most non-methane hydrocarbons (NMHC) in the troposphere is by reaction with OH radicals, other atmospheric oxidants capable of removing hydrocarbons include

O_3, NO_3 radicals and Cl atoms. For saturated hydrocarbons the major reaction pathways in the troposphere are reactions with OH radicals and to a lesser extent with Cl atoms. In order to determine the fate of an organic compound in the atmosphere, reactions involving OH radicals and Cl atoms are investigated.

The experimental techniques used to study the kinetics of OH radical and Cl atom reactions can be divided into two categories: absolute and relative rate techniques. Estimation methods are also used; these methods were developed from existing kinetic data.

2.1.1 DETERMINATION OF OH RADICAL RATE CONSTANTS

2.1.1 1 Absolute Techniques

Atmospheric reactions involving OH radicals (A) and the volatile organic chemicals (B) can be envisaged as simple bimolecular reactions where:

$$A + B \xrightarrow{k} \text{PRODUCTS} \qquad 2.1$$

and the rate law is expressed in the form:

$$-d[A]/dt = k[A][B] \qquad 2.2$$

If a small concentration of OH radicals is generated in the presence of excess organic, then the organic concentration remains essentially unchanged so:

$$\ln[A]_t/[A]_o = -(k[B_o]) \qquad 2.3$$

which is the rate equation for a pseudo-first order reaction. The absolute rate constant is calculated from the slope of a plot of the decay rates (calculated from the plots of ln[A] vs time for a given value of $[B]_o$) vs the value of $[B]_o$.

Essentially all absolute methods for determining rate constants for OH radical reactions involve monitoring the decay of the OH radical (A) in the presence of excess concentrations of the reactant (B). Absolute techniques used in studying OH radical reactions include among others Fast Flow Discharge Systems, Flash Photolysis and Molecular Modulation Spectroscopy [4 - 6].

Fast Flow Discharge Systems (FFDS)

FFDS consist of a flow tube typically 2-5 cm in length in which reactants A and B are mixed in the presence of an inert gas e.g. Ar or He. The decay of A as it reacts with B is monitored along the length of the tube and using equation (2.3) the rate constant for the reaction is calculated.

Two different approaches to the FFDS technique can be used. The first is where reactant A enters the tube at the upstream end and it is mixed with reactant B. The decay of A is monitored by a detector which moves along the length of the flow tube. The second method involves adding one of the reactants into the tube through a moveable inlet while the other reactant is added at the upstream end of the tube. In this case the detector is fixed at the downstream end of the apparatus and the reaction time is varied by moving the moveable inlet relative to the fixed detector.

The most common method for generating OH radicals for the FFDS technique is by generating H atoms from the microwave discharge of H_2 gas in Ar or He (hence the name "discharge technique") which subsequently reacts with NO_2 to produce OH radicals:

$$H + NO_2 \text{ ------->} OH + NO \qquad 2.4$$

This method is free from interfering species i.e. vibrationally excited species originating from the parent molecules.

A number of detector systems can be used for monitoring the loss of the OH radicals as it reacts with the test species. Spectroscopic techniques include resonance-absorption (RA), resonance-fluoresence (RF) and laser-induced-fluorescence (LIF); electron paramagnetic resonance (EPR) and laser magnetic resonance (LMR) detectors are based on shifts in molecular energy levels induced by the presence of a magnetic field. Mass spectroscopy is also used where ionisation or fragmentation of the sample is caused by electron impaction. The limitations of the FFDS technique include pressure gradients, axial and radial concentration gradients and flow parameters which results in an overall accuracy of ± 10 - 15%.

Flash Photolysis Systems

This system relies on the Flash Photolysis (FP) of a precursor species to produce reactant A. OH radicals are typically produced from the pulsed photodissociation of H_2O or HNO_3, or the photolysis of N_2O-H_2 or NO_2-H_2 mixtures where OH radicals are formed via the reaction of $O(^1D)$ and H_2O. The pulsed UV vacuum photolysis radiation is produced by a flash lamp or a pulsed rare gas laser (ArF, KrF). The reaction process is carried out in a cell fitted with spectral windows which allows the "flash" radiation to penetrate e.g. LiF, MgF_2, CaF_2, sapphire or Supracil [6]. RA or RF detector systems are used with FP systems giving good sensitivity of detection of OH radicals, also complications from secondary reactions or photofragment formation does not occur.

Molecular Modulation Spectroscopy

Molecular modulation spectroscopy has been primarily applied to the determination of the kinetics of the ground state oxygen atom reactions $O(^3P)$. $O(^3P)$ is produced by the mercury photosensitised decomposition of NO_2 with resonance radiation ($\lambda < 253.7$ nm) being used to excite the ground state $Hg(6^1S_o)$ to the metastable (6^3P_1) state i.e. Hg*.

$$Hg\ (6^1S_0) + h\upsilon \text{ ------->} \quad Hg(6^3P_1)\ (Hg^*) \qquad 2.5$$

$$Hg^* + N_2O \quad \text{------->} \quad Hg + N_2 + O(^3P) \qquad 2.6$$

$$O(^3P) + B \quad \text{------->} \quad \text{Products} \qquad 2.7$$

If B is a hydrocarbon e.g propane then $O(^3P)$ can abstract a hydrogen atom to produce OH radicals. The OH radicals formed then react with B and the rate constant for this reaction can be determined by following the concentration of OH radicals (e.g. by absorption spectrometry). The production of $O(^3P)$ is monitored by modulating the photolysing light which results from the formation of $O(^3P)$.

Pulse Radiolysis

OH radicals are produced by the pulsed radiolysis of H_2O vapour and its reaction kinetics are studied using optical absorption to follow its decay in the presence of an excess of reactant. This technique is particularly convenient for high temperature experiments and for application to atmospheric chemistry since it can be used at total pressures of one atmosphere or more. The disadvantage is that it is expensive and the equipment is quite complex.

Absolute methods for determining rate constants, aside from their technical advantages and disadvantages, can be very costly, especially in the case of the FP apparatus which requires a multichannel analyser to carry out the time resolved signal averaging. Very fast reactions can be followed (10^{-18} $cm^3molecule^{-1}s^{-1}$) using absolute techniques; however the reactants used must be of a very high purity as impurities can often be more reactive than the compound under investigation. FFDS are low pressure techniques (0.5-100 torr) and for this reason it is more limited relative to the FP system which can be used at high pressures i.e. 5 to greater than 1 atm., with the main limitation being the detection of the reactants under investigation.

The magnitude of the rate constants that each of the systems are capable of measuring is predetermined by the ability of the apparatus to withstand extreme pressures. Thus the FP system can measure rate constants as low as 10^{-18} cm ^{3}molecule^{-1}s^{-1}, while the FFDS method can measure rate constants as low as 10^{-16} cm ^{3}molecule^{-1}s^{-1}. Both techniques can be used over large temperature ranges i.e. 200 - 1000K and 100 > 1000K for FFDS and FP respectively. The upper temperature is established by the onset of problems with the thermal stability of reactants and the selection of materials for fabricating the apparatus. At very low temperatures FFDS are more restricted relative to FP because of heterogeneous reactions. It has also been observed that the rate of destruction of radicals such as Cl, OH and HO_2 on the reactor surface increases significantly at temperatures greater than 250^{o}C [7]. An additional advantage of FP over FFDS is the cell dimensions, ensuring that wall reactions are negligible whereas in the case of FFDS the major uncertainty in the method arises from the removal of radical species at the walls of the flow tube. A major advantage of the FFDS technique however, is the large number of detectors that can be employed; this advantage over the FP system is a result of the steady-state nature of the FFDS system in which the progress of the reaction is frozen at any fixed observation point along the tube. Since the concentration of the reactants are constant at that point there are no constraints on the detector speed. FP experiments are studied in real time and require a detector with a time resolution that is at least one tenth of the period of the experiment i.e. in the millisecond range [7]. FFDS also allow the investigation of reaction mechanisms by the identification of reaction intermediates and products whereas in FP systems little mechanistic data is avaliable unless the products and intermediates can be followed by induced fluorescence (IF) or absorption techniques. The type of reactants that can be studied by FP is limited to those species that can be generated by flash photolysis as opposed to FFDS which utilises a variety of methods from microwave discharge to multi-photon induced decomposition.

2.1.1.2 The Relative Rate Technique

Using the relative rate technique, the rate constants for the gas-phase reactions of atmospheric interest are determined as a ratio of rate constants as opposed to an absolute value. Thus if one of the rate constants has been determined independently by a reliable absolute method, then the second rate constant can be calculated from the experimentally determined ratio. The relative rate technique has the advantage that relative measurements can be made with greater precision as only relative concentrations of the reactants need be measured, however increased precision does not imply greater accuracy. The accuracy of the results depends on the knowledge of the mechanistic details of the reaction system to ensure that the kinetic analysis is valid. Also obtaining an accurate rate constant value from the rate constant ratio requires an accurate knowledge of the reference rate constant. Usually reference rate constants are measured using absolute techniques.

The apparatus for measuring relative rate constants is much simpler (and therefore cheaper) compared to the systems used for absolute determinations. The key components of the apparatus are:

(a) a reaction chamber (smog chamber);
(b) a light bank;
(c) a detection/monitoring system.

Smog chambers were first used to simulate air pollution conditions observed in the Los Angeles atmosphere [4]. Since then they have been used to generate kinetic and mechanistic data on individual reactions of atmospheric importance. Smog chambers can be constructed of borosilicate glass or Teflon. Glass chambers were traditionally small resulting in a high surface to volume (S\V) ratio, which resulted in increased occurrence of surface reaction; also the glass material prevents radiation less than 350 nm from reaching inside the chamber [7]. Teflon chambers are much more versatile in that the size can be varied thus reducing the S\V ratio, also Teflon also transmits radiation in the region 290 -

800 nm. As the bags do not have a rigid structure they are operated at atmospheric pressure and dilution due to sampling is avoided as the bag collapses when samples are removed for analysis. Controlling the temperature inside the chamber can often be a problem and this problem and was repeatedly encountered in this work; fans can be used to over come this by circulating air around the chamber.

The smog chamber contains ports through which it can be filled and from which samples may be withdrawn. Sample removal can be carried out either manually using a gas-tight syringe or by means of a pump system attached to a gas sampling valve. Several types of detection systems can be used including GC, GC\MS or FTIR; in our case a pump/valve system was used for sample removal and the samples were analysed using GC incorporating a Flame Ionisation Detector (FID).

The main disadvantages of the smog chamber is chamber contamination through the absorption of compounds onto the chamber walls and wall reactions which alter the kinetics of the reactions under investigation [4]; another potential problem with Teflon bags is the release of low molecular weight compounds from the bag material itself [8].

Three types of light source may be used to provide the radiation necessary for the photolysis reactions in side the smog chamber. Black lamps and sun lamps are low pressure mercury lamps coated with a phosphor which determines the spectral output. Black lamps provide radiation in the 290 - 340 nm region, however the output is poor as most of the spectral intensity is concentrated in sharp mercury lines. Sun lamps transmit radiation between 270 - 400 nm. Xenon lamps provide radiation similar to the solar energy distribution at the Earth's surface i.e. 290 - 700nm and have substantial intensity in the critical region around 300 nm. However, xenon lamps are very expensive and a combination of sun and black lamps is most frequently used.

The relative rate technique has been described in detail [9, 10] and is essentially based upon simultaneously monitoring the disappearance rates of a test compound (T) and a reference compound (R) whose absolute rate constant is known:

$T + OH$ ---k_1---> PRODUCTS 2.8
$R + OH$ ---k_2---> PRODUCTS 2.9
$T + h\upsilon$ ---k_p----> PRODUCTS 2.10
T + Walls ---k_w----> Loss to walls 2.11

The loss of T is defined by:

$$d[T]/dt = k_1[OH][T] + k'[T] \qquad 2.12$$

and the loss of R is defined by:

$$d[R]/dt = k_2[OH][R] \qquad 2.13$$

where k_1 and k_2 are the relative rate constants for the test compound T and the reference compound R respectively. The $k' = (k_p + k_w)$ term is the first order photodissociation constant and\or wall loss of the test compound. The integration of equations (2.12) and (2.13) result in:

$$\frac{\ln(T_o/T_t)}{(t-t_o)} = \frac{\ln(R_o/R_t)}{(t-t_o)} \times (k_1/k_2) + k' \qquad 2.14$$

Therefore, a plot of $(t-t_o)^{-1}\ln(T_o/T_t)$ vs $(t-t_o)^{-1}\ln(R_o/R_t)$ yields a straight line with a slope k_1/k_2 and an intercept k'.

In cases where k' = 0, Atkinson [6] recommended evaluating k_1 by eliminating the time dependence from equation (2.14) which reduces to:

$$\ln(T_o/T_t) = (k_1/k_2)\ln(R_o/R_t) \qquad 2.15$$

and again solving for k_1 by calculating the product slope (k_1/k_2) and k_2.

Atkinson [6] noted that the use of regression analysis with equation (2.14) to solve for (k_1/k_2) and intercept (k') places most weight on those data points collected in the earliest part of the irradiation where the least amount of the test compound has reacted. Equation (2.15) requires that the loss or test of reference compounds be measured in the presence of OH as a function of time.

It has been recommended by Arnts and Bufalini [9] that the reference compound (R) should be chosen using the following criteria;

(i) the reference organic (k_2) should have an accurately known room temperature rate constant which approximates that anticipated for the test organic;

(ii) the reference organic should not photolyse (at $\lambda > 290$ nm) or oxidise in air;

(iii) the reference organic should be sufficiently volatile to remain in the gas phase and not be absorbed on the walls of the reaction chamber;

(iv) the reference organic should be accurately measurable by an available analytical technique;

(v) the reference compound should not react with the test compound or O_3, NO_3, NO_2 or HNO_2;

Similarly, the test organic must satisfy certain criteria in order to be a candidate for the above protocol [9, 10]:

(i) an accurate analytical method must be available for making repeat measurements of the test compound over a two hour period and

(ii) the rate of loss by photolysis and by wall losses must not be greater than the loss due to reaction with OH radicals i.e.:

$$(k_{OH\text{-}T} \times OH) >> k_{\text{photolysis}}$$

OH radicals used in the relative rate technique can be generated by the photolysis of: (a) NO_x-hydrocarbon-air mixtures, (b) HONO-NO-air mixtures or (c) CH_3ONO-NO-air mixtures. Method (a) can only be used for organics that have OH radical rate constants > 1x $10^{-12}cm^3$ molecule$^{-1}s^{-1}$ [11] Rate constants greater than this value can be calculated using method (b) as a higher concentration of OH radicals are generated in the photolysis of HONO-NO-air mixtures; however HONO is not readily prepared, handled or analysed in the laboratory [12]. The use of CH_3ONO as a source of OH radicals avoids the disadvantages of the other methods and is relatively easily generated in the laboratory [10]; C_2H_5ONO can also be used to generate OH radicals in cases where CH_3ONO interferes chromatographically with the reactant peaks [13]. Non photolytic sources of OH radicals include the reactions of H_2O_2/NO_2 and N_2H_4/O_3 mixtures [14 -17].

In our work OH radicals were generated in the laboratory by the photolysis of methyl nitrite in the presence of excess nitric oxide:

$$CH_3ONO + h\upsilon\ (\lambda > 290\ nm) \text{ -------> } CH_3O + NO \qquad 2.16$$

$$CH_3O + O_2 \text{ -------> } HCHO + HO_2 \qquad 2.17$$

$$HO_2 + NO \text{ -------> } NO_2 + OH \qquad 2.18$$

Nitric oxide is added to the reaction mixture to drive reaction (2 18) to completion and also to prevent the formation of O_3 since the NO_2 produced in reaction (2.18) will also photodissociate to form ozone:

$$NO_2 + h\upsilon\ (\lambda < 430\ nm) \text{ -------> } NO + O \qquad 2.19$$

$$O + O_2 \text{ -------> } O_3 \qquad 2.20$$

$$O_3 + NO \text{ -------> } NO_2 + O_2 \qquad 2\ 21$$

Using the methyl nitrite technique described above, rate constants > 3 x 10^{-13} $cm^3 molecule^{-1} s^{-1}$ can be determined [10]. Systematic errors using this technique can be as low as < 5%, however the total error in the rate constant value depends on the error associated with the reference compound rate constant (k_2) used.

2.1.1.3 Estimation Technique:

With the increase in volume of the kinetic data base on the reactions of OH radicals with organics, estimation techniques have been developed to predict the rate constants for OH radical reactions. These estimation techniques have permitted a cost effective estimation of OH radical rate constants for organic compounds whose volatility or chemical complexity makes experimental investigation difficult.

Estimation techniques can be classified into two general categories:
(a) those which utilise a physical or chemical property such as ionisation potential or bond dissociation energy;
(b) those which rely on the structure of the organic;
Category (a) includes (i) the Transition State Theory (TST) developed by Cohen and Benson [18] which utilises the variational transitional state theory to provide a conceptual frame work for the theoretical calculation of reaction rate constants for bimolecular reactions and (ii) the Bond Energy Bond Order (BEBO) method developed by Johnston [19], which is an empirical method for calculating E_a and A parameters of the Arrhenius equation.

Category (b) is the simplest of the estimation methods and will be dealt with more thoroughly. The first development of the relationship between structure and reactivity was carried out by Greiner [20] . As more experimental data became available this method was updated periodically [6, 11, 21 - 26]. Atkinson [26] has further updated the structure/reactivity (SAR) technique to take account of neighbouring groups, a greater range of compounds and a wider temperature range. In the case of alkanes and carbonyl compounds (with which we are primarily concerned) the calculation of the hydrogen-atom abstraction rate constant (k_{OH}) is based on the estimation of rate constants for the reaction of -CH_3, -CH_2-, >CH- groups which is influenced by the identity of substituents around the groups. Thus:

$$k\,(CH_3 - X) = k^o_{prim}\,F(X)$$

$$k\,(X - CH_2 - Y) = k^o_{sec}\,F(X)F(Y)$$

and

$$k\,(X - CH <^{X}_{Y}) = k^o_{tert}\,F(X)F(Y)F(Z)$$

where k^o_{prim}, k^o_{sec} and k^o_{tert} are the OH radical rate constants per CH_3, - CH_2 - and - CH < group respectively and F(X), F(Y) and F(Z) are the substituent factors for X, Y and Z substituent groups. The most recent values calculated for the group rate coefficients [27] are: $k^o_{prim} = 1.51 \times 10^{-13} cm^3 molecule^{-1} s^{-1}$, $k^o_{sec} = 8.37 \times 10^{-13} cm^3 molecule^{-1} s^{-1}$, $k^o_{tert} = 1.88 \times 10^{-12} cm^3 molecule^{-1} s^{-1}$. The SAR technique predicts to within a factor of two the rate constants for approximately 300 organic compounds.

The reliability of estimating OH radical rate constants depends on the accuracy of the group rate constants, the group substituent factors and on the applicability of the underlying assumptions. However, as more data becomes available, more reliable predictions will be possible.

2.1.2 DETERMINATION OF Cl ATOM RATE CONSTANTS

2.1.2.1 Absolute Techniques

Absolute methods for determining Cl atom rate constants with hydrocarbons also follow pseudo-first order reaction kinetics as outlined in section 2.1.1.1. Flash photolysis systems are commonly used in conjunction with resonance fluorescence detectors [28 - 34] as are fast flow discharge systems incorporating

Mass Spectrometer detectors [35 -42] or Resonance Fluorescence detectors [43 - 45].

The kinetic methods described above have employed the pseudo-first order approximation by measuring either the time resolved relative fluorescent decay of Cl atom emission or the mass spectrometry signal of the Cl atom. The use of the pseudo-first order approximation is only valid when the substrate concentration (B) is unchanged throughout the course of the reaction and no secondary reactions occur. This is generally not the case when very fast bimolecular Cl-radical processes (e.g. $Cl + C_2H_6$ or higher hydrocarbons) and fast radical-radical reactions occur. Such anomalies can be found in FP systems [34], flow cells [36] and DF techniques [46].

Another absolute technique that was used by Benson in 1978 [47] and has become more fashionable in recent years [48 - 50] is the Very Low Pressure Reactor (VLPR). The VLPR is a constant flow cell reactor system, but it does not have a velocity profile as it is a well stirred reactor which eliminates basic problems such as viscous flow, diffusion and other inhomogeneities characteristic of flow tubes and non-steady-state reactors. Wall reactions can be minimised by coating the reactor vessel with Teflon or CFC wax. Using the VLPR technique it is possible to study and measure very fast atom-molecule reactions over an extended temperature range (193K - 473K). In the VLPR system, the bimolecular reaction occurs in a cell at steady state pressures less than 5 mTorr. Both the reactants are introduced into the reactor through separate capillary inlets and are allowed to react for a short period of time. Consequently both reactants and products are discharged through a small aperture in the reactor to the first stage of a differential pumped system, maintaining a continuous molecular beam which is sampled from by a quadrupole Mass Spectrometer which is mounted in the second stage vacuum chamber. Cl atoms are generated by microwave discharge and Cl atom concentrations are calculated by measuring the actual intensities of the peak at I_{Cl} (m/e = 35).

The VLPR technique avoids the problems encountered with other absolute techniques listed above in that it abandons the pseudo-first order approximation and uses a second order system by varying the initial concentrations of both components. The obvious disadvantage here is that absolute concentrations of the reactants must be known [49]. Dobis et al found a favourable comparison between the rate constants for the reaction of Cl atoms with C_2H_6 calculated using the VLPR method and other absolute techniques [50].

2.1 2 2 The Relative Rate Technique

Smog Chamber Apparatus

As with OH radical rate constants, Cl atom rate constants are also measured using the relative rate technique and the apparatus described in section 2.1.1.2. Equation 2.15 is used to calculate the rate constant ratio k_1/k_2 from which k_1 is calculated. For Cl atom reactions in a smog chamber, the Cl atoms were generated by the photolysis of Cl_2.

$$Cl_2 + h\nu\ (\lambda > 320\ nm) \ \text{------->}\ 2Cl \qquad 2.22$$

As attention has only recently been focused on Cl atom reactions, protocols outlining the criteria for choosing suitable reference organics when using the relative rate technique have not yet been published. In this work we have followed the recommendations for OH radical reactions listed by Arnts and Bufalini [9] in section 2.1 1.2.

Competitive Chlorination Method

Competitive chlorination reactions were initially carried out to calculate Activation energies and A factors for Cl atom reactions; however they have since been used to calculate Cl atom rate constants by a relative rate method [51 - 53]. Competitive chlorination reactions involve the chlorination of a reference and a test organic. The basic mechanism for the photochlorination of a hydrocarbon is [32]:

$$Cl_2 + h\upsilon\ (\lambda > 320\ nm) \text{-------}> Cl + Cl \qquad 2.23$$

$$Cl + RH \text{-------}> R + HCl \qquad 2.24$$

$$R + Cl_2 \text{-------}> RCl + Cl \qquad 2.25$$

CHAIN TERMINATION REACTION

Since the experimental conditions are such that the termination step for R is slow compared to the chain propagation reactions of Cl_2, the chains are very long and the amount of RCl formed is a measure of the rate at which Cl reacts with RH compared to competing paths [32]. In the case of a mixture of two hydrocarbons e.g. CH_4 and C_2H_6, the relative rate constant expression is:

$$\frac{kC_2H_6}{kCH_4} = \frac{[C_2H_5Cl]\,[CH_4]}{[CH_3Cl]\,[C_2H_6]} \qquad 2.26$$

where $[CH_3Cl]$ and $[C_2H_5Cl]$ are the net product yields and $[CH_4]$ and $[C_2H_6]$ are the initial concentrations of the species used. The initial $[CH_4]/[C_2H_6]$ ratio and the product ratio can be measured with great accuracy using standard techniques (e.g. GC, FTIR). Once the reaction rate is known for one of the organics then the other value can be calculated.

Several factors must be considered when using the competitive chlorination method:

(a) product loss by further reaction of RCl;

(b) depletion of reactants;

(c) impurities in the reaction mixture;

(d) back reaction: R + HCl -------> RH + Cl.

Lin et al [34] obtained good agreement for the reaction of Cl + CH_4 using both the competitive chlorination method and DF/MS

2.1.2.3 Estimation Techniques

The SAR estimation technique is the most commonly used method (described in Section 2 1.1.3) for Cl atom reactions with hydrocarbons. Atkinson [54] calculated group rate constants for Cl atom reactions with alkanes:

$$k^{o}_{prim} = 3.4 \times 10^{-11} cm^{3} molecule^{-1} s^{-1} \qquad 2.27$$

$$k^{o}_{sec} = 5.6 \times 10^{-11} cm^{3} molecule^{-1} s^{-1} \qquad 2.28$$

$$k^{o}_{tert} = 3.7 \times 10^{-11} cm^{3} molecule^{-1} s^{-1} \qquad 2.29$$

The SAR technique for Cl atom reactions has not received as much attention as that for OH radical reactions; as a result it has not been developed to its full potential as an estimation technique.

2.1.3 OH RADICALS AND Cl ATOM REACTIONS WITH ALKANES AND HALOALKANES

One of the principal objectives of atmospheric chemical research is the elucidation of the fates of chemical species emitted into the atmosphere both naturally and as a result of man's activity on Earth i.e. anthropogenic sources. OH radical reactions [3, 55] and to a lesser extent Cl atom reactions [56] are recognised as the major loss process for many organic species present in the atmosphere. Thus the calculation of atmospheric lifetimes for such species from accurate OH radical and Cl atom rate data has resulted in a significant effort to accurately define the kinetics and mechanisms of OH and Cl reactions with a wide variety of organic compounds.

Alkanes are emitted into the troposphere from both biogenic and anthropogenic sources. Biogenic emissions include ethane, propane and butane released from sources such as seepage and bacterial fermentation while methane is the largest naturally produced hydrocarbon in the world. Anthropogenic sources include emission from combustion of fossil fuels. In order to determine the impact of alkanes on the atmosphere it is necessary to measure the reaction rates of alkanes with both OH radicals and Cl atoms, since this will give some indication of the lifetime of these species in the atmosphere together with their most likely impact on atmospheric processes.

(a) OH radical reactions with alkanes

The reaction of OH radicals with alkanes proceeds via a hydrogen-atom abstraction reaction to form an alkyl radical and water:

$$RH + OH \text{ -------> } R + H_2O \qquad 2.30$$

The alkyl radical reacts with O_2 to from alkylperoxy radicals:

$$R + O_2 \text{ ------->} RO_2 \quad 2.31$$

which can react with either HO_2 or NO which is present in all but remote atmospheres:

$$RO_2 + HO_2 \text{ ------->} ROOH \quad 2.32$$

$$RO_2 + NO \text{ ------->} RO + NO_2 \quad 2.33$$

Carbonyl compounds can be formed by the reaction of RO with O_2 or by unimolecular decomposition or isomerisation via a hydrogen-atom shift [57]:

$$RO + O_2 \text{ ------->} R'R''CO + HO_2 \quad 2.34$$

$$RO \text{ ------->} R' + R''CHO \quad 2.35$$

The reaction of OH radicals with alkanes has been extensively studied using both absolute and relative rate techniques. Atkinson [58] has published a comprehensive review on these reactions and where possible has derived rate expressions including the temperature dependence of these rate constants.

The magnitude of the rate constants for the reactions of OH radicals with alkanes is typically in the range of $10^{-12}cm^3molecule^{-1}s^{-1}$. The reactions are all exothermic with low E_a values and for alkanes containing tertiary C - H bonds, the temperature dependencies are small [5]. The major influences on the rates of hydrogen-atom abstraction from alkanes by OH radicals is the type of C - H bond involved; This is reasonable as the bond strength follows the order primary > secondary > tertiary (i.e. 410 > 393 > 385 kJ mol^{-1} respectively) and the ease of hydrogen-atom abstraction will follow the order tertiary > secondary > primary. In addition to the number of bond-types in a molecule, the detailed structure of the molecule has an influence on the rate of hydrogen-atom abstraction also i e. secondary C - H bonds react 40% faster if bonded to two $-CH_2-$ groups as opposed to a $-CH_2-$ group and one $-CH_3$ group [4, 59]

OH radical reactions with cycloalkanes have also been reviewed by Atkinson [58]. These reactions also proceed via a hydrogen-atom abstraction reaction. It is interesting to compare the reaction rates of cycloalkanes and n-alkanes as listed in Table 2.1. The reactivities of $c\text{-}C_3H_6$ and $c\text{-}C_4H_8$ are well below the corresponding reactivities for the alkanes, whereas the reactivities of $c\text{-}C_5H_{10}$, $c\text{-}C_6H_{12}$ and $c\text{-}C_7H_{14}$ are correspondingly larger. It is thought that the presence of ring strain alters the reactivity of the lower cycloalkanes as the ring strain influences the bond dissociation energy [60, 61]. The reactivities for the > C_5 cycloalkanes are larger than the values for the corresponding alkanes as the ring strain decreases with increasing carbon number and there are more secondary hydrogen-atoms available for abstraction.

(b) OH radical reactions with haloalkanes

Reactions of OH radicals and haloalkanes also proceed via a hydrogen-atom abstraction mechanism with the magnitude of the rate constant values being determined by the position and number of halogen substituents present. Primarily the reaction of halomethanes and ethanes with OH radicals have been studied; however few measurements for > C_3 alkanes have been reported [62 - 65]. Atkinson [58] has reviewed the reactions of OH radicals with haloalkanes; however since that publication much work has been accomplished on measuring the OH radical rate constants for HCFCs and HFCs which are replacement

CARBON NUMBER	$k_{alkane} \times 10^{12}$ ($cm^3 molec.^{-1} s^{-1}$)	$k_{cycloalkane} \times 10^{12}$ ($cm^3 molec.^{-1} s^{-1}$)	RING STRAIN[a]
C_3	1.15	0.08	115.5
C_4	2.54	1.2	110
C_5	3.94	5.16	26.4
C_6	5.61	7.49	0
C_7	7.15	13.1	26.8

a - taken from [61], units in kJ mol^{-1}.

Table 2.1: Room temperature rate constants for the reactions of OH radicals `with a series of n-alkanes and c-alkanes. Data taken from [61].

compounds for CFCs and are also haloalkanes [65 - 67].

Focus has been placed on chlorine and to a lesser extent bromine-containing alkanes as it is these halogen atoms that are thought to be responsible for ozone depletion in the stratosphere whereas fluorine atoms form much stronger bonds with carbon atoms and as a result they do not photolyse in the stratosphere (the bond dissociation energy for the C-Cl bond is 318 kJ mol^{-1} whereas the bond dissociation energy for the C-F bond is 460 kJ mol^{-1}[4]). By calculating the OH radical rate constants, an insight into the molecular parameters that influence the reactivity of haloalkanes is gained. A comparison of the OH radical reactivity of bromoalkanes and chloro/fluoro alkanes shows that the reactivity of the bromoalkanes lies between the reactivities for chloroalkanes and fluoroalkanes [68] and that the rate constant values of bromoethanes were roughly equivalent to the corresponding chloroethanes. The presence of a chlorine atom lowers the reactivity of alkanes towards OH radical attack. In the case of chlorinated methanes, the presence of a chlorine substituent serves to lower the C - H bond dissociation energy, this is counter balanced by polar forces which result in the reactivities of the chloromethanes being less reactive relative to methane [6, 66]. Several studies have been carried out on reactions of chlorinated ethanes and OH radicals [68 - 73]; where the presence of the chlorine substituent was found to lower the reactivity of ethane, especially with increasing chlorine substitution on the β carbon. This reduction in reactivity was attributed to an inductive effect occurring in the transition state involving polar repulsion between the electrophilic OH radical and the abstracted hydrogen atom [62, 69 - 72, 74 - 76].

For alkanes containing more than three carbon atoms the influence of the chlorine substituent was found to decrease with increasing carbon number [62, 63] and the $-CH_2-$ group rate constants begin to dominate the reactivity of these organics.

(c) Cl atom reactions with alkanes

The reactions of atomic chlorine with hydrocarbons have been extensively studied for various chemical and theoretical purposes for many years. Early investigations were confined mainly to competitive chlorination techniques and provided reliable kinetic data [34, 77]. In recent years however, interest in Cl atom reactions with hydrogen-atom containing molecules has been a result of the stratospheric Cl atom - ozone problem and the fact that Cl atoms are being considered as major sink species for hydrocarbons in the marine troposphere [56].

As with OH radical reactions, the reaction of Cl atoms and alkanes proceeds via a hydrogen-atom abstraction mechanism in a similar manner to OH radical reactions i e.:

$$Cl + RH \longrightarrow R + HCl \qquad 2.36$$

and for the case of the reaction between Cl atoms and C_2H_6 the following reaction process occurs [78]:

$$Cl + C_2H_6 \text{ -------> } C_2H_5 + HCl \quad 2.37$$

$$C_2H_5 + O_2 + M \text{ -------> } C_2H_5O_2 + M \quad 2.38$$

$$C_2H_5O_2 + C_2H_5O_2 \text{ -------> } 2C_2H_5O + O_2 \quad 2.39$$

$$C_2H_5O_2 + C_2H_5O_2 \text{ -------> } CH_3CHO + C_2H_5OH + O_2 \quad 2.40$$

$$C_2H_5O_2 + C_2H_5O_2 \text{ -------> } C_2H_5O_2C_2H_5 + O_2 \quad 2.41$$

Cl atom reactions with alkanes have been studied using both absolute and relative rate techniques. A list of rate constant values for a series of n-alkanes and some c-alkanes has been published by Atkinson [54]. From this data which includes the work of Knox and Nelson [51] and Lewis et al [40], it has been observed that as with OH radical reactions the reactivity of the C-H bonds toward Cl atom attack follows the order: tertiary > secondary > primary. The activation energies were also seen to decrease as the hydrocarbons become more complex and the rate constants were observed to exhibit negligible temperature dependences over significant temperature ranges.

In a similar fashion to OH radical reactions with cycloalkanes, the E_a values for Cl atom reactions with cyclopropane and cyclobutane were observed to be larger than the values for the Cl + propane and n-butane. Again this was attributed to the effects of ring strain associated with the c-alkanes [40].

The reaction of Cl atoms with alkanes proceed much faster compared to OH radical reactions with alkanes reflecting the more electronegative character of Cl atoms relative to OH radicals. Wallington [78] demonstrated a linear correlation between the reactivities of Cl atoms and OH radicals towards alkanes which can be used to estimate the reactivities of alkanes towards Cl atoms from OH radical rate constants and vice versa.

(d) Cl atom reactions with haloalkanes

Reactions of Cl atoms and halogenated alkanes are expected to give rise to the formation of haloalkylperoxy radicals and halogenated alkyl radicals with the alkoxy radicals undergoing decomposition and/or reaction with O_2 to form carbonyl compounds, halogenated alkyl radicals, Cl atoms and HO_2 radicals [3].

To date the study of Cl atom reactions has been confined primarily to reactions with halogenated methanes and ethanes with the aim of determining the effect of halogen substitution on the reactivities of the molecules with respect to Cl atom reactions. Tschuikow-Roux [79] found that the E_a values for all monosubstituted methanes were smaller and the A values larger relative to the values for unsubstituted methane. In the case of fluorine substitution the enthalpies for hydrogen-atom abstraction changed from exothermic to endothermic with increasing substitution, thus displaying a strengthening of the C-H bonds while conversely with increasing substitution of chlorine and bromine atoms all hydrogen-atom abstraction reactions were exothermic reflecting the progressive weakening of the C-H bonds.

A comparison of the data for ethane and chlorinated ethanes [30, 52, 53, 80 - 83] showed that Cl substitution decreases the reactivity of ethane with respect to attack by Cl atoms i.e. in going from ethane to 1,1,1 trichloroethane the rate constant per available hydrogen-atom is reduced by three orders of magnitude [80]. The E_a values were observed to increase with increasing substitution, with the largest increase occurring with the first Cl atom substitution, while smaller increases were observed for highly chlorinated derivatives [83]. The decrease in reactivity of the chlorinated ethanes was explained in terms of a combined effect of repulsion (between the bound Cl atom and the incoming Cl atom) and electron withdrawal by the bound Cl atom in the molecule, the latter process is the most predominant and ultimately decreases the reactivity of the molecule. The effect of electron withdrawal arises as a result of the electronegative nature of the Cl substituent which draws electrons towards it thus weakening the C - H bonds on the α carbon and simultaneously strengthens the C - H bonds on the β carbon. This effect was also observed by Wallington [84] who found that the reactivity of a homologous series of chloroalkanes was lower than the parent alkanes and that the deactivating effect of the Cl substituent was thought to be due to steric considerations and was observed to be more pronounced for smaller chloroalkanes and for chloroalkanes bearing a Cl substituent at a secondary site. This indicated that the effect of the Cl substituent is restricted to groups α to the carbon carrying the substituent. As the α C - H bonds are weakened due to the presence of Cl atoms it would therefore be expected that the reactivities of the compounds would increase, however it has been hypothesised that the Cl substituent also has a repelling effect on the incoming Cl atom, thus reducing the reactivity of chlorinated alkanes with respect to Cl atom attack.

Tuazon [85] compared the rates of the Cl atom reactions with the corresponding OH radical rates for a series of HCFCs and HFCs and found an extreme range of reactivities for the organics towards Cl atom reactions (a factor of 1400) compared to the OH radical rate values (a factor of 23) despite the fact that the geometric mean of both sets of rate constants are of a similar magnitude i.e. $10^{-14}\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$. These reactivity trends were linked to polarity effects in the reaction transition stage.

2.1.4 REACTIONS OF OH RADICALS AND Cl ATOMS WITH OXYGENATES

Oxygenated species in the atmosphere can be classified as either primary or secondary pollutants. Alcohols and ethers are widely used as industrial solvents and are also applied as additives in hydrocarbon fuels. The use of oxygenated additives in fuels is being proposed as a means of reducing carbon monoxide, reactive evaporative and exhaust emissions which lead to the formation of ozone in urban atmospheres Halogenated ethers are used world wide as inhalation anaesthetics, so large amounts of these compounds would be expected to be released into the atmosphere annually

Atmospheric concentrations of aldehydes and ketones are mostly due to product formation resulting from tropospheric photooxidation reactions of alkanes and alkenes [57] producing low molecular weight organics. Therefore, to assess the tropospheric impact of oxygenated organics it is necessary both to understand the reaction mechanisms and to have a knowledge of the rate constants for the reactions of oxygenated organics with OH radicals and Cl atoms.

2.1.4.1 OH Radical and Cl Atom Reactions with Alcohols and Ethers

(a) OH radical reactions with alcohols, ethers and haloethers

Reactions of OH radicals with alcohols and ethers proceed via a hydrogen-atom abstraction mechanism. Hydrogen-atom abstraction from alcohols can occur from either the hydroxyl or the alkyl group although the latter process is more thermodynamically favoured i.e $D(CH_2OH\text{-}H) = 393.4 \pm 8.4$ kJ mol^{-1} and $D(CH_3O\text{-}H) = 435.3 \pm 4.2$ kJ mol^{-1} [86].

Reactivities of OH radicals with aliphatic alcohols and ethers increase linearly with the increasing number of CH_2 groups mirroring the increase in reactivity of n-alkanes with respect to OH radical attack. The hydroxyl and ether functional groups serve to activate the surrounding C - H bonds by decreasing the bond dissociation energies i.e. $D(CH_3CH_2\text{-}H) = 410.2 \pm 4.2$ kJ mol^{-1}, $D(CH_2OH\text{-}H) = 393.4 \pm 8.4$ kJ mol^{-1}, $D(CH_3OCH_2\text{-}H) = 389.3 \pm 4.2$ kJ mol^{-1} [87], resulting in the reactivity of the CH_2 groups being a factor of 2 and 4 higher (for alcohols and ethers respectively) relative to the CH_2 groups in alkanes [86]. The increase in reactivity for ethers is significantly higher than for alcohols, which may be attributed to the slightly weaker bonds in ethers, however this has not been confirmed by bond dissociation data.

The long range effects resulting from the hydroxyl and -O- functional groups in alcohols and ethers have been found to extend up to the fourth carbon atom [88]; however, this effect cannot be explained in terms of bond energy or inductive effects and thus indicates an alternative reaction pathway to the direct hydrogen-atom abstraction pathway.

From rate constant measurements of OH radicals with alcohols and ethers, [88 - 91] Wallington has developed a group reactivity scale for rate constant predictions for oxygenated organics which has been extended to difunctional oxygenates [92] and polyethers [93]. The SAR approach was found to be unsuccessful as it only includes next-neighbour interactions in the derivation of the group values.

Recent studies involving OH radical reactions with ethers have focused on methyl-t-butyl ether and ethyl-t-butyl ether [94 - 97] and on halogenated ethers. To date little work has been carried out on haloethers although it has been recognised since 1989 that the commonly used inhalation anaesthetics (enflurane and isoflurane) which are haloethers were a potential threat to the ozone layer as almost all administered doses will end up in the atmosphere. [98]. Recent work by McLoughlin et al [99] on haloethers (including the anaesthetics) showed that a halogen substituent (chlorine or bromine) caused a decrease in the reactivity of the molecules towards OH radical attack and was attributed to polarity changes in the transition state. This is also the case for fluorinated ethers [100] where a fluorine substituent results in reducing the activating effect of the ether functional group and is felt by the α C - H bonds on both sides of the ether linkage. This effect also occurs when the fluorine atom is located on the β carbon position. In the case of cyclic ethers the activation of the ether link is completely supressed by the presence of a fluorine substituent.

(b) Cl atom reactions with alcohols, ethers and haloethers

Hydrogen-atom abstraction by Cl atoms from the alkyl group in alcohols occurs exclusively as abstraction from the hydroxyl group is endothermic [101]. A straight forward hydrogen-atom abstraction reaction occurs for the reaction of Cl atoms and ethers. As opposed to the reactions of OH radicals with alcohols and ether organics, the presence of a functional group does not appear to activate the C - H bonds other than at carbon atoms directly bonded to the functional group [86]. It is possible that Cl atom reactions are sufficiently facile that any long range effect on reactivity may be small and not easily identified.

Wallington [78] observed that there was no apparent correlation between the reactivites of Cl atoms and OH radicals towards alcohols or ethers indicating that the reaction of either OH radicals or Cl atoms (or both) with these species does not proceed via a simple direct hydrogen-atom abstraction mechanism.

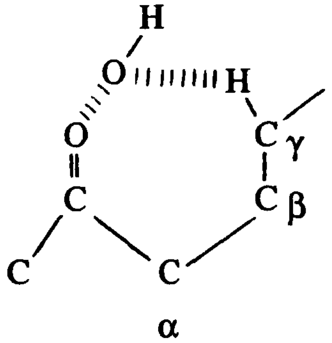
Research involving Cl atom reactions with haloethers has been confined to the work of McLoughlin et al from this laboratory [99], who found that the the rate constant values were more adversly effected by the presence of a halogen atom which was attributed to steric effects.

2.1.4.2 OH Radical and Cl Atom Reactions with Aldehydes and Ketones

(a) OH radical reactions with aldehydes and ketones

Reactions between OH radicals and aldehydes proceed by hydrogen-atom abstraction from the formyl group. Methyl substition in the β position to the CO group moderately enhances the hydrogen-atom abstraction rate while halogen-atom substitution (Cl, F) at any position decreases the OH radical reactivity of the compound [102 - 104]. In the case of chlorinated aldehydes [103] the drop in OH radical reactivity is more pronounced upon substitution by the first Cl atom than by the second and third Cl atom. A more pronounced decrease in OH radical reactivity was observed with F atom substitution. The decrease in reactivity due to chlorine\fluorine-atom substitution was attributed either to changes in bond strength of the formyl C - H bond [103] or by inductive effects in the transition state as the halogen atom opposes the electron delocalisation on the carbonyl group [69, 102 - 104]; the reduction in reactivity for F substituted compounds is more pronounced relative to Cl atom substitution [104] as F atoms increases the degree of charge seperation in the transition stage as a result of its larger electronegativity.

It is generally accepted that ketones react with OH radicals via a hydrogen-atom abstraction mechanism For aliphatic ketones it has been shown that the reactivity of the C - H bonds α to the carbonyl group is lower than in alkanes [105, 106] while it is higher in the β and γ positions; this is a result of the reactivity enhancement in the β and γ positions due to the formation of a six membered ring adduct prior to hydrogen-atom abstraction [106] i.e.



In addition, it has been demonstrated that the reactivities of the aliphatic chains on either side of the carbonyl group are independent and additive [106]. The kinetic study of carbonyl compounds has been extended to the kinetic study of OH radicals with diones and cyclic ketones [107]. The presence of an additional carbonyl group in the diones serves to activate the alkyl groups at the β and γ positions. The kinetic study of OH radical reactions with cyclic ketones further supports the ring adduct mechanism showing no enhancement of reactivity for C - H bonds in the β position [107] A method has been developed [106, 107] allowing the prediction of OH radical rate constants for aliphatic saturated ketones at 298 K.

To date reactions of OH radicals and halogenated ketones have not yet been reported, however these reactions would be considered to be of environmental importance as it is possible that such halogenated ketones are produced in the troposphere by reactions of OH radicals and Cl atoms with HCFCs and HFCs.

(b) Cl atom reactions with aldehydes and ketones

Some work has been carried out on reactions of halogenated aldehydes with Cl atoms [104] as it is thought that these species may be the resulting oxidation products of halogenated ethane compounds. As with the OH reactions the presence of the halogen atom(s) (Cl, F) decreases the reaction rate constant, this effect was attributed to polar effects in the transition state which was induced by the halomethyl substituents

Very little work has been published on the reactions of Cl atoms with ketones; as a result our work is of interest from a mechanistic point of view and serves to increase the data base on Cl atom reactions with carbonyl compounds.

The aim of the present study is to measure the relative rate constants for the reactions of haloalkanes, aliphatic and cyclic ketones with OH radicals and Cl atoms. From the conclusions reached in the literature and from our own results the effects of molecular structure on the rate values can be examined

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2.2

EXPERIMENTAL DETAILS FOR OH RADICAL AND Cl ATOM REACTIONS

2.2.1 INTRODUCTION

This work reports the first measurements of OH radical and Cl atom rate constants for haloalkanes, aliphatic and cyclic ketones using a smog chamber in conjunction with the relative rate technique. The relative rate technique has been described in detail in the literature [1 - 3] and was outlined in Sections 2.1.1.2 and 2.1.2.2 of this report. OH radicals were generated by the photolysis of methyl nitrite in air and excess NO (Section 2.1.1.2), while Cl atoms were produced by the photolysis of Cl_2 in air (Section 2.1.2.2(a)). The systems also contained the reference organic under investigation and the appropriate test organic; the organic concentrations were monitored using gas chromatography. The rate constant ratios were calculated using equation 2.15 from which the rate constants for the test organics were evaluated.

2.2.2 MATERIALS

Methyl nitrite was prepared by the dropwise addition of 50% v/v sulphuric acid (Analar grade) to a saturated solution of sodium nitrite (stated purity - 96%, BDH Chemical Co.) in methanol (Analar grade) [4]. The CH_3ONO that evolved passed from the reaction bulb through a saturated solution of sodium hydroxide (to remove any sulphuric acid) and was dried by passing through calcium carbonate. The CH_3ONO was collected in a flask surrounded by liquid nitrogen (Coopers Cyro Service) and transferred onto the vacuum line by flask to trap distillation. The CH_3ONO was purified and degassed using an acetone slush bath (temp. = 173K). The purity of the CH_3ONO was checked prior to use by IR spectroscopy and it was stored in the dark on the vacuum line.

The nitric oxide used in the OH radical system (BDH) had a stated purity of 99%; the chlorine gas used in the Cl atom work (Argo International Ltd.) had a stated purity of 99.5%. Both gases were degassed and stored on the vacuum line; with the Cl_2 stored in a blackened bulb to prevent photodecomposition. The dilution gases used in these experiments were zero grade air (Air Products) for the OH radical reactions and zero grade air and nitrogen (Air Products) for the Cl atom reactions. Both zero grade air and nitrogen were used to clean the bag after each run.

All traces of moisture in the nitrogen were removed by passing the gas through a drying column (Phase - Sep) filled with molecular sieve and self-indicating silica gel. Organic traces were removed from the zero grade air by passing through a drying column (Phase - Sep) and a charcoal column (Phase - Sep).

All test and reference organics used in this work were used without further purification and were thoroughly degassed using the freeze-pump-thaw method. A list of the stated purities and the suppliers is given in Sections 2.3 and 2.4 for the haloalkanes and the aliphatic and cyclic ketones respectively.

2.2.3 APPARATUS

The vacuum apparatus shown in Figure 2.1 was the apparatus used in this work to accurately measure gas pressures. It consists of a conventional mercury-free high-vacuum line made of Pyrex glass. The different regions within the vacuum line are described in Table 2.2. The volumes of these regions were calculated using Boyle's Law and a detailed description is given in section 2.2.4.

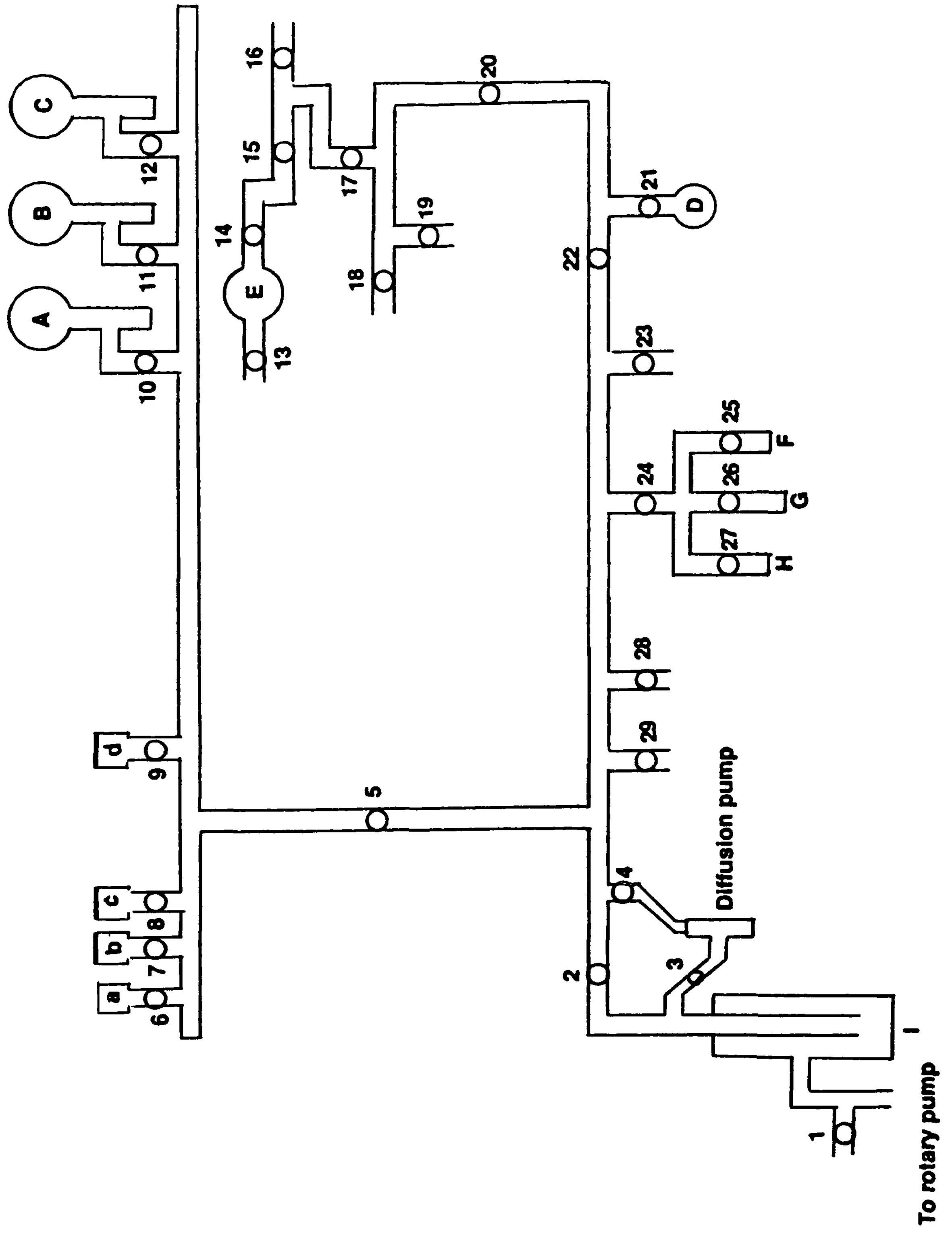


Figure2.1: Mercury free high vacuum line used for the relative rate studies.

VACUUM LINE SECTION	SECTION DESCRIPTION
Line 1	Tap 5 to taps 6, 7, 8, 9, 10, 11 and 12 (includes volume to transducer c)
Line 2	Taps 5 to taps 2, 4, 21 - 26,
Line 3	Taps 20 - 22
Line 4	Taps 17 - 20
"T" - piece	Taps 14, 16 and 17
Bulb E	Flushing reactants into the smog chamber
A, B and C	Storage bulbs
D	Mixing bulb
F,G and H	Storage lines
a	Penning gauge
b	Pressure transducer (0 - 10 τ)
c	Pressure transducer (0 - 1000 mbar)
d	Pirani gauge

Table 2.2: Various regions and positions of pressure transducers and gauges within the vacuum line.

An Edwards high vacuum double stage rotary pump (Model E2M2) combined with a Edwards silicone oil diffusion pump (Model E040\55) was used to maintain a vacuum within the system. Reactant pressures were measured using a pressure transducer (Edwards EPS 10).

Pressure measurements within the vacuum lines were made using an Edwards Pirani gauge (Model PEE 10K) for pressures down to 10^{-3} mbar and an

Edwards Penning gauge (Model CP25-K) to measure pressures in the range 10^{-2} to 10^{-4} mbar. Greaseless taps using Teflon o-rings (J.Young Ltd.) were used in all of the valve positions on the vacuum line.

CH_3ONO was stored on the vacuum line in bulb B, Cl_2 in bulb C and NO in line F. Samples of the reference organics were stored in glass fingers attached to the vacuum line at taps 23, 25 and 26 and the test organics (ethane, n-butane, i-butane and propane) were stored in lines G and H.

Figure 2.3 is a schematic diagram illustrating the relative positions of the 86 litre conditioned Teflon bag, the vacuum line and the gas sampling valve which were connected using 1.5 mm Teflon tubing. The diagram demonstrates how samples were withdrawn from the bag using an Edwards Speedivac 2 single stage pump and directly injected onto the the G.C column (a PU 4450 Gas Chromatograph was used) via a gas sampling valve (Carle). The average time for sample removal via the pump-valve mechanism was sixty seconds.

To fill the smog chamber tap 17 was closed and taps 13, 14, 15 and 16 were opened, flow regulators were used to flush the required volume of air or nitrogen into the bag.

The irradiation chamber consisted of the Teflon bag which was surrounded by two light banks supported by a rectangular metal frame (106.5 cm x 94 cm x 77 cm). Each light bank consisted of five black lamps (Philips TLD 18W / 08) and five sun lamps (Philips TL 20W / 09N). The entire chamber was covered with black plastic with two thermometers placed at opposite sides of the chamber to measure the chamber temperature during irradiation. An opaque plastic sheet was used to completely cover the Teflon bag to prevent irradiation occurring as the lamps warmed up (a warm up period of 30 minutes was used) and also to interrupt photolysis as required.

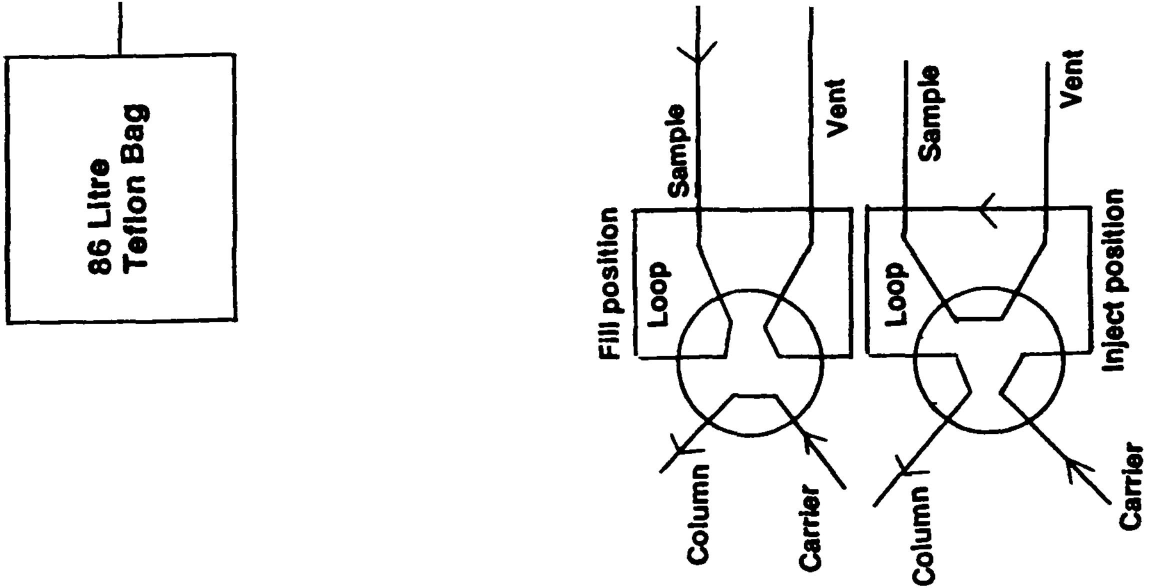
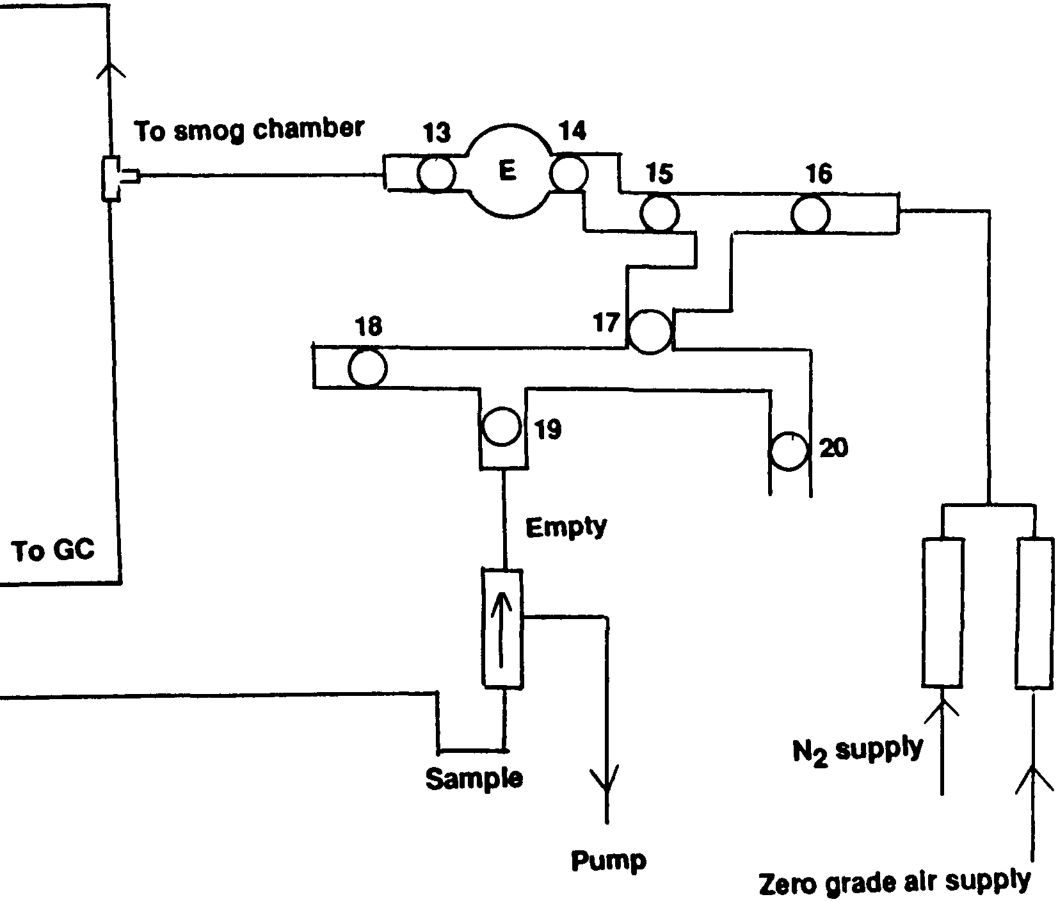


Figure 2.2: Schematic diagram illustrating the layout of the bag, vacuum line and the GC


To smog chamber
13
E
14
15
16
17
18
19
20
Empty
To GC
Sample
Pump
N_2 supply
Zero grade air supply

2.2.4 PROCEDURE

In order to determine the correct pressure of reactants to release into the vacuum line and subsequently into the smog chamber the volumes of the various sections of the vacuum line were calculated. Bulb A in Figure 2.2 was the primary volume from which each volume within the vacuum line was calculated using the Boyle's law expression:

$$\text{VOLUME} \quad \alpha \quad 1 / \text{Pressure} \qquad 2.42$$

and

$$P_1 V_1 = P_2 V_2 \qquad 2.43$$

The volume of bulb A was determined prior to its attachment to the vacuum line using a weight difference technique.The volumes of the various sections of the vacuum line are given in Table 2.4

VAC. LINE SECTION	VOLUMES (cm^3)
A	1143
B	1174
C	1178
Line 1	620
Line 2	606
Line 3	19
Line 4	79
"T" piece	10
Bulb E	288

Table 2.4: Volumes within the vacuum line

A Perkin Elmer (Model 4450) Gas Chromatograph fitted with a flame ionisation detector (FID) was used to monitor reactant concentrations during each analysis. An initial requirement prior to the determination of rate data was the optimisation of the chromatographic conditions for separation of the test and reference organic and in the case of OH radical reactions the separation of CH_3ONO and the reference organic. Product formation as a result of irradiation of either the test or reference organic also had to be considered as a source of potential interference in the chromatographic analysis of the reactants. Decay profiles were carried out to test for interferences caused by secondary reactions in our system where mixtures of the test or reference organic and CH_3ONO/NO (or Cl_2 for Cl atom reactions) were irradiated and analysis performed to determine whether any products were detected. In all cases secondary product formation was not a problem for the irradiation times typical in this work.

Additional reactions were carried out to determine whether (a) photodecomposition of the reactants occurred in the absence of OH radicals or Cl atoms i.e. light reaction or (b) whether the reactants reacted with the photolytic precursors (CH_3ONO/NO or Cl_2) in the absence of radiation i.e. dark reaction. In both cases no decrease in reactant concentration was observed over the time periods typical of our experiments. Once the analytical conditions were optimised and the decay curves, dark reactions and the light reactions were performed then work could proceed on measuring the relative rate constant ratios (k_1/k_2).

The apparatus shown in Figure 2.1 was evacuated using liquid nitrogen around trap I to a vacuum of approximately 10^{-2} - 10^{-4} mbar. Boyle's law ($P_1 V_1 = P_2V_2$) was used to calculate the pressure of the reactant required in bulb E such that when the contents of the bulb were swept into the bag using zero grade air (or nitrogen in the case of some of the Cl atom experiments), the required concentration of this reactant would result in the bag once a final volume of 50 dm^3 was reached. The required reactant pressure was measured into lines 1 - 4, the "T" piece and bulb E using pressure transducer b to monitor the concentration of reactants released. Tap 17 was then closed and taps 13 - 16 opened and the reactants were flushed into the bag at a flow rate of 1.2 dm^3 min^{-1}. Having added each of the reactants to the bag to a final volume of 50 dm^3 the diluent gas was switched off and taps 13 - 16 were then closed. The vacuum line was then evacuated to a pressure of 10^{-2} - 10^{-4} mbar.

Initial concentrations of 10 ppm were typically used for the test and reference organics. For the OH radical reactions 50 ppm and 25 ppm of CH_3ONO and NO were used respectively and for the Cl atom reactions initial concentrations of 50 ppm were used. Some of the ketones however had low vapour pressures and reactant concentrations of 5 ppm were used, with concentrations of 25 ppm and 12 ppm of CH_3ONO and NO and 25 ppm of Cl used.

The reaction chamber was completely covered at all times except during photolysis. The chamber temperature fluctuated between 296K and 308K for individual runs for the OH radical reactions and remained at a constant temperature (298 K) for the Cl atom reactions. It was very difficult to control the chamber temperature as the apparatus was located beside a window. Several stepe were taken to control the chamber temperature including using a circulating fan inside the chamber and also covering the window; however the temperature still continued to vary. As a result the lamps were allowed to warm up until a steady chamber temperature was reached (usually 30 minutes). For the OH radical reactions all 20 lamps were used for photolysis ($\lambda > 260$ nm), while for the Cl atom reactions 5 black lamps were used ($\lambda > 310$ nm). A minimum of three samples were taken before irradiation of the bag contents i.e. at $t = 0$ minutes. The opaque sheet was then removed from the bag and the reaction mixture irradiated for fixed periods (in the range 0 - 30 minutes for OH radical reactions and 0 - 15 minutes for Cl atom reactions). The irradiation times were measured by means of a stop clock. The covering was replaced after each photolysis period to stop the reaction. Samples were removed from the bag by switching the two-way valve (illustrated in Figure 2.2) to the "sample" position which pulled a small volume of the reactant mixture from the bag through the gas sampling valve. The valve was switched from the "fill" to the "inject" position after 60 seconds. This procedure was repeated after each irradiation of the bag. The bag was emptied by switching the two-way valve to the "empty position" and taps 13, 14, 15, 17 and 19 opened and taps 16, 18 and 20 closed.

After each analysis the bag was filled and emptied several times with zero grade air or nitrogen to prevent carry over between experiments. Samples were taken from each fill and injected onto the GC to determine whether the bag was clean. From the very beginning of this work we had problems with obtaining a so-called "clean" sample from the bag as a chromatographic peak (retention time of < 1 minute) was always obtained. Several strategies were implemented to determine the cause of this peak including using a different bag (which was "chromatographically" clean using another GC and gas sampling valve), analysing the contents of the bag using a different GC with a gas sampling valve, in this case no peaks were detected and also changing the Carle gas sampling valve for a Valco gas sampling valve. Colleagues working in the same area were also consulted; however, eventually this condition was accepted as the results obtained using this system were always very reproducible.

Peak areas and sometimes peak height were used to measure changes in reactant concentration following irradiation. To ensure experimental reproducibility and to increase the accuracy of our data, the experimental procedure outlined above was repeated a minimun of three times. The rate constant ratios determined from each experiment were then averaged to give the value reported.

2.2.5 ANALYSIS

A Pye Unicam (Model 4450) gas chromatograph fitted with a flame ionisation detector (FID) was used to monitor the concentrations of the reactants before and after irradiation. The fuel gases were air (Irish Industrial Gases) and hydrogen (Irish Industrial Gases). Each of the gases were prefiltered through moisture traps (Phase - Sep) and charcoal filters (Phase - Sep) prior to entering the GC. All gas cylinders used needle valve controls. Two meter glass columns (3mm i.d) were used with typical stationary phases of 10% SE-30, PEG and OV-17 The columns were usually operated under isothermal conditions; however some temperature programming was used Flow rates of the nitrogen carrier gas (Irish Industrial Gases) were varied from 30 - 45 cm^3 min^{-1}. Specific conditions employed for the analysis of the various test compounds are given in sections 2 3 and 2.4. Chromatograms were recorded on a Hewlett Packard 3390A and a Spectra Physics 4290 integrating recorders. A Perkin Elmer infrared spectrometer (Model 983G) was used to determine the purity of the CH_3ONO and was scanned over the spectral region of 4000 to 600 cm^{-1}

2.2.6 REFERENCES.

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2.3

THE REACTION OF OH RADICALS AND Cl ATOMS WITH HALOALKANES

2.3.1 INTRODUCTION

Halogenated hydrocarbons are produced in large quantities world wide and have many uses such as solvents, cleaning agents, gasoline additives and agricultural fumigants not to mention refrigerants and blowing agents. In most applications large amounts of halogen-containing organics are eventually released in the vapour phase to the troposphere and possibly to the stratosphere where the halogen atoms enter into catalytic cycles which destroy ozone. Since the predictions of Rowland and Molina in 1974 [1] and the discovery of the ozone hole in 1985 [2] attention has been focused on the tropospheric reactions and fates of halogenated organics.

An important class of halogenated hydrocarbons are the haloalkanes of which CFCs and their replacement organics (HFCs and HCFCs) are members. CFCs are chemically stable compounds; as a result they can persist in the troposphere for several years until they are ultimately transported to the stratosphere where they release their halogen atoms which precipitate ozone depletion [3]. In order to understand the impact of halogenated species on the ozone layer we need a better understanding of the tropospheric loss process that haloalkanes can undergo such as photolysis and photooxidation reactions which are dominated by OH radical reactions [4 - 6] and to a lesser extent with Cl atoms [7].

Atkinson has listed the OH radical reaction rates for haloalkanes in his most recent review [8]; however these organics are primarily halogenated methane and ethane compounds, with only two halogenated propanes being listed. More recently with the development of HCFCs and HFCs the kinetic information on OH radical and Cl atom reactions has been restricted to methane and ethane compounds containing fewer halogen substituents [9, 10]. However, preliminary studies have been carried out on some halogenated propane compounds which are used as replacements for CFCs [9, 11].

Our work is concerned with measuring the relative rate constants for OH radical and Cl atom reactions with a series of chlorinated propanes and a homologous series of brominated alkanes. Although the compounds we have chosen to study are not replacements for CFCs the kinetic data obtained will give a further insight into the mechanistic effects of halogen substitution on the rate constant values and will serve to increase the kinetic data base of information on haloalkanes.

2.3.2 EXPERIMENTAL

As the experimental procedures employed to determine the OH radical and Cl atom rate constants for haloalkanes have been described in detail in Section 2.2 only specific details related to the analysis of the haloalkane reactions will be outlined here. Table 2.5 lists the various compounds studied along with their purities and suppliers. All compounds were used without further purification and were thoroughly degassed using the freeze-pump-thaw method prior to use. Sample mixtures were subsequently prepared in the smog chamber as outlined in Section 2.2.

The test and reference organics used along with the optimum analytical conditions established to determine the OH radical and Cl atom rate constants for the haloalkanes are given in Tables 2.6 and 2.7 respectively.

ORGANICS	PURITY (%)	SUPPLIER
Methane	99	Natural Gas
Ethane	99	Alltech Associates
Propane	99.5	Alltech Associates
n-Butane	99	Alltech Associates
i-Butane	99	Air Products
Cyclohexane	99+	Aldrich Chemicals
Dichloromethane	99.8	Riedal-de Haen
1-Chloropropane	98	Riedal-de Haen
2-Chloropropane	99	Aldrich Chemicals
1,3-Dichloropropane	98	Riedal-de Haen
2-Chloro 2-methylpropane	99	Hopkins and Williams
Bromoethane	99+	Aldrich Chemicals
1-Bromopropane	97	Aldrich Chemicals
2-Bromopropane	98	Aldrich Chemicals
1-Bromobutane	98	B.D.H
1-Bromopentane	97	B.D.H
1-Bromohexane	97	B.D.H

Table 2.5: Organic compounds used in the relative rate studies of OH radical and Cl atom reactions with haloalkanes together with their associated purities and suppliers.

ORGANIC	REF. ORGANIC	RXN. TEMP. (K)	COL. TEMP. (K)	N_2 flow $cm^3 \, min^{-1}$	COLUMN TYPE
n-Pentane	i-Butane	302	301	33	A
1-Chloropropane	c-Hexane	303	338	34	B
	i-Butane	305	T.P[a]	32	A
	n-Pentane	308	303	30	B
2-Chloropropane	c-Hexane	303	T.P[b]	34	B
1,3-Dichloropropane	c-Hexane	305	346	30	B
2-Chloro 2-methylpropane	c-Hexane	298	338	32	B
Bromoethane	Ethane	300	308	30	B
1-Bromopropane	c-Hexane	300	313	32	B
2-Bromopropane	c-Hexane	298	333	30	B
1-Bromobutane	c-Hexane	299	333	30	B
1-Bronopentane	c-Hexane	304	358	30	B
1Bromohexane	c-Hexane	306	368	30	B

a T.P = temperature programming: initial temp. = 301K, final temp. = 311K.

b T.P = temperature programming: initial temp. = 323K, final temp. = 338K.

A column type: 11% OV 17 on Chrom. W AW (60-80μm).

B column type: 10% SE 30 on Chrom. W AW (60-80μm).

Table 2.6: Analytical conditions for the reactions of OH radicals with haloalkanes. [injector temp. = 473K, detector temp. = 523K].

ORGANIC	REF. ORGANIC	COL TEMP. (K)
Ethane	Ethane	393
1-Chloropropane	Ethane	318
2-Chloropropane	Ethane	308
1,3-Dichloropropane	Ethane	353
2-Chloro 2-methylpropane	Ethane	308
Bromoethane	Ethane	323
1-Bromopropane	Ethane	308
2-Brompropane	Ethane	313
1-Bromobutane	Ethane	T.P[a]
	Propane	318
1-Brompentane	Ethane	343
1-Bromohexane	Ethane	373

a T.P initial temp. = 300K, final temp. = 318K.

Table 2.7: Analytical conditions for Cl atom reactions with haloalkanes at 298 ± 2K. [N_2 flow = 30 cm^3 min^{-1}, injector temp = 423K, detector temp. = 473K. Column type = 10% SE 30 on Chrom. W HP (80-100μm).]

2.3.3 RESULTS

Before measuring the relative rate constants for the haloalkanes studied in this work we first had to ensure that our system was capable of measuring rate constants with an acceptable degree of precision and accuracy. We chose to remeasure the rate constant ratios for OH + n-pentane and Cl + ethane. The relative rate constants and their corresponding absolute values are listed in Tables 2.8 and 2.9 along with relevant literature data. The values quoted for the rate constant ratios represent the average value calculated from at least three repeat determinations. The errors quoted are ± 2σ from the least squares analysis of the data, except in the cases of the Cl atom reactions with 1-chloropropane, 2-chloropropane and 1-bromohexane where the errors were calculated from the chromatographic reproducibility of the sample injections. The errors quoted for the absolute values includes the errors in the reference organic rate constants.

The relative rate technique relies on the assumption that the test and reference organic are removed solely by reaction with either OH radicals or Cl atoms. This assumption was verified prior to the analysis of each of the haloalkanes whereby seperate experiments were carried out to establish that: (a) the test and reference organics did not react with the radical precursors (Cl_2 and CH_3ONO) in the absence of uv radiation; typical dark reactions are illustrated in Figures 2.3 to 2.6 and (b) that the organics did not undergo direct photolysis by the lamps (i e. light reaction), this stability is observed in Figures 2 7 to 2.10 and (c) that the presence of secondary species resulting from the oxidation of either the test or the reference organic did not interfere with the chromatographic analysis of the organics. This was accomplished by irradiating mixtures containing either the test or the reference compound and CH_3ONO/NO or Cl_2. These decay curves are illustrated in Figures 2.11 to 2.14.

ORGANIC	$k_1/k_2{}^{a,b}$	CHAMBER TEMP. (K)	k^e	Literature Values
n-pentane	1.79±0.02	302	4.25±0.85	5.3[12] 4.08±0.08[12] 4.1, 4.6[13] 4.12[14] 4.05±0.19[15] 4.22±0.37[15] 4.09±1.08[16]
1-chloropropane	0.148±0.012	303	1.12±0.21	0.82±0.04[17]
	0.464±0.012^c	305	1.11±0.28	
	0.212±0.006^d	308	0.90±0.23	
2-chloropropane	0.121±0.006	303	0.92±0.23	0.43±0.04[17]
1,3-dichloropropane	0.120±0.004	305	0.78±0.19	
2-chloro 2-methylpropane	0.055±0.006	298	0.41±0.1	
bromoethane	0.885±0.038	300	0.25±0.05	0.33±0.07[18] 0.32±0.07[19]
1-bromopropane	0.156±0.008	300	1.18±0.3	
2-bromopropane	0.117±0.015	298	0.88±0.3	
1-bromobutane	0.327±0.01	299	2.45±0.61	
1-bromopentane	0.52±0.018	304	3.96±0.99	
1-bromohexane	0.763±0.027	306	5.85±1.46	

a errors quoted are ± 2σ from the least squares analysis of the data.

b reference - cyclohexane

c reference - i-butane

d reference - n-pentane

e units = $10^{-12}cm^3molecule^{-1}s^{-1}$.

Table 2.8: Relative rate constant ratios, absolute values and relevant literature values for the reactions of OH radicals with haloalkanes.

ORGANIC	k_1/k_2[a,b]	k[f]	Literature Values
Ethane	0.411±0.015[c]	62±9	60±6[20] 59±4[21] 59.5±3[22] 54.8±1[23] 63.8±2[24] 57.0[25]
Dichloromethane	3 49±0.11[d]	0.4±.01	
1-Chloropropane	0 854±0.011[e]	49±15	53.5±2[26]
2-Chloropropane	0 358±0.004[e]	20±6	
1,3-Dichloropropane	0 19±0.004	11±3	
2-Chloro 2-methylpropane	0.234±0.003	13±4	
Bromoethane	0.241±0.007	14±4	
1-Bromopropane	1.071±0.021	61±18	
2-Brompropane	0.48±0.005	27±8	
1-Bromobutane	2.46±0.057	140±42	
	0.908±0 005[c]	137±21	
1-Brompentane	3.756±0.041	241±64	
1-Bromohexane	4.765±0.028[e]	272±81	

a errors quoted are ± 2σ from the least squares analysis of the data.

b reference - ethane.

c reference - propane

d reference - methane

e errors calculated from the chromatographic reproducibility of the data.

f units = $10^{-12}cm^3molecule^{-1}s^{-1}$

Table 2.9: Rate constant ratios and their corresponding absolute values for the reactions of Cl atoms and haloalkanes measured at 298 ± 2K.

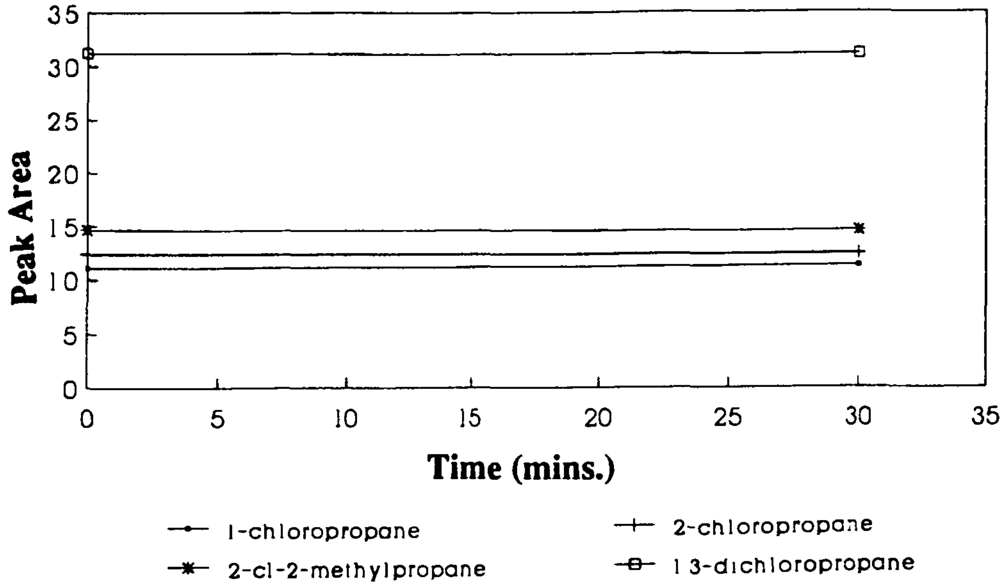


Figure 2.3: Dark reaction for OH radicals with chloroalkanes.

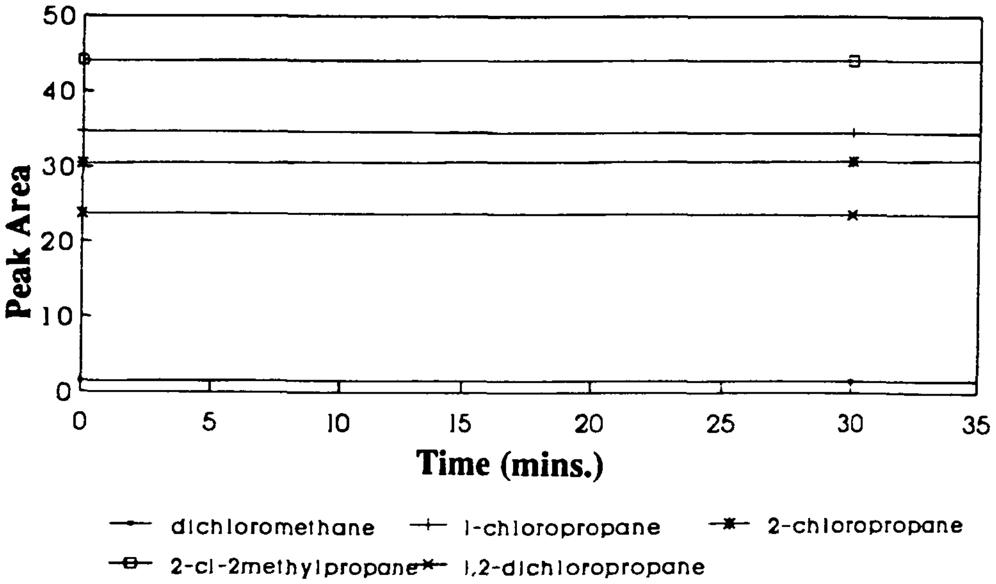


Figure 2.4: Dark reactions for Cl atom with chloroalkanes

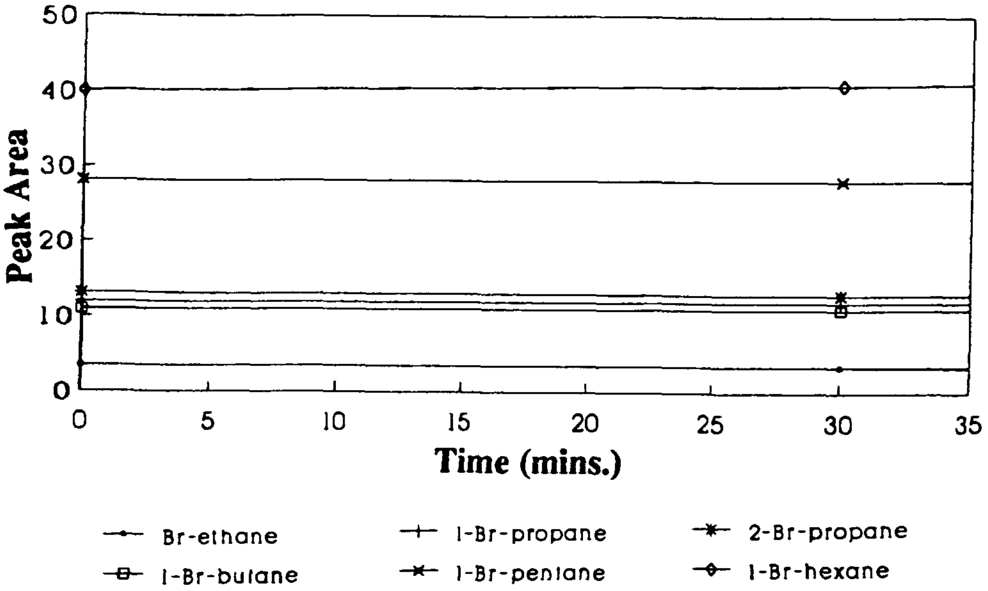


Figure 2.5: Dark reaction for OH and bromoalkanes.

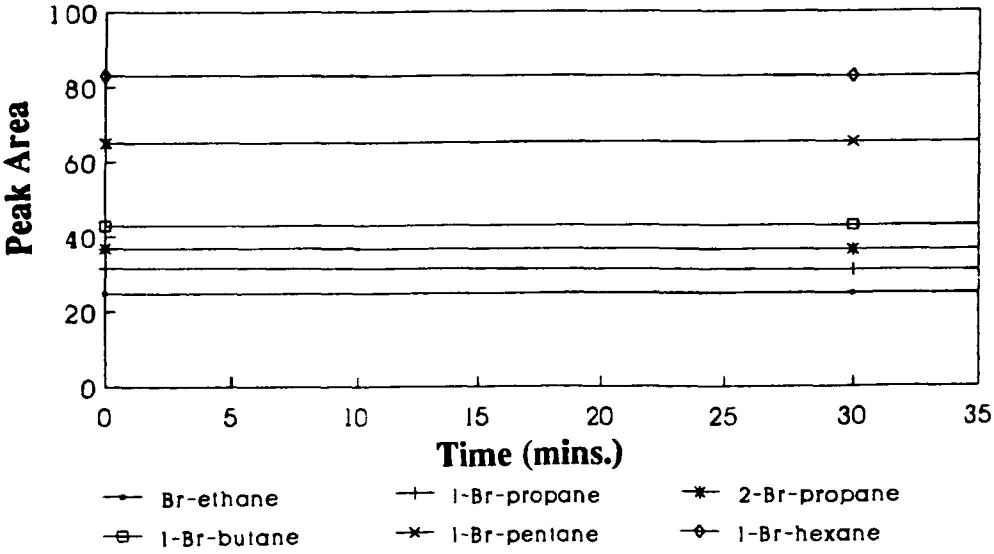


Figure 2.6: Dark reaction for Cl and bromoalkanes.

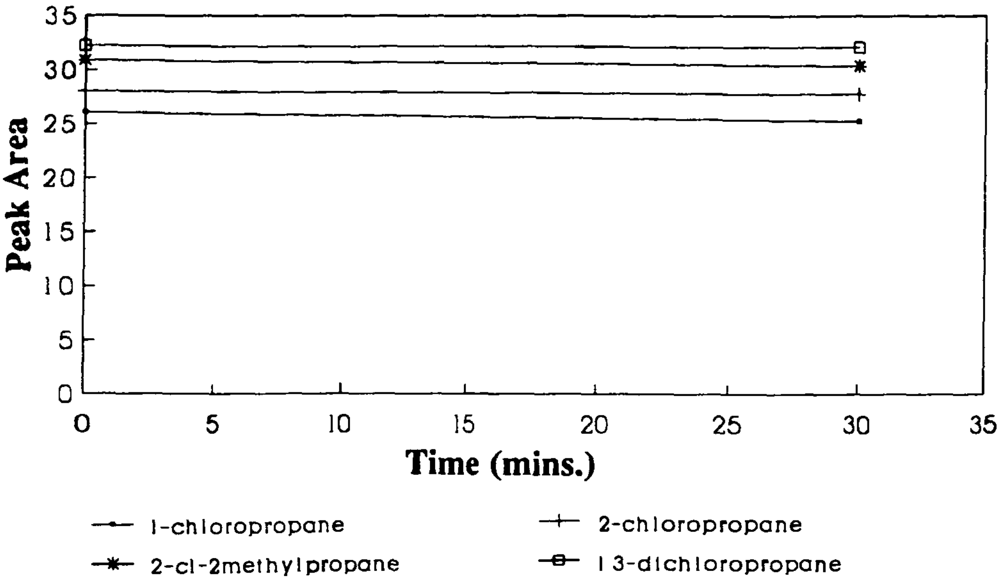


Figure 2.7: Light reaction for OH and chloroalkanes.

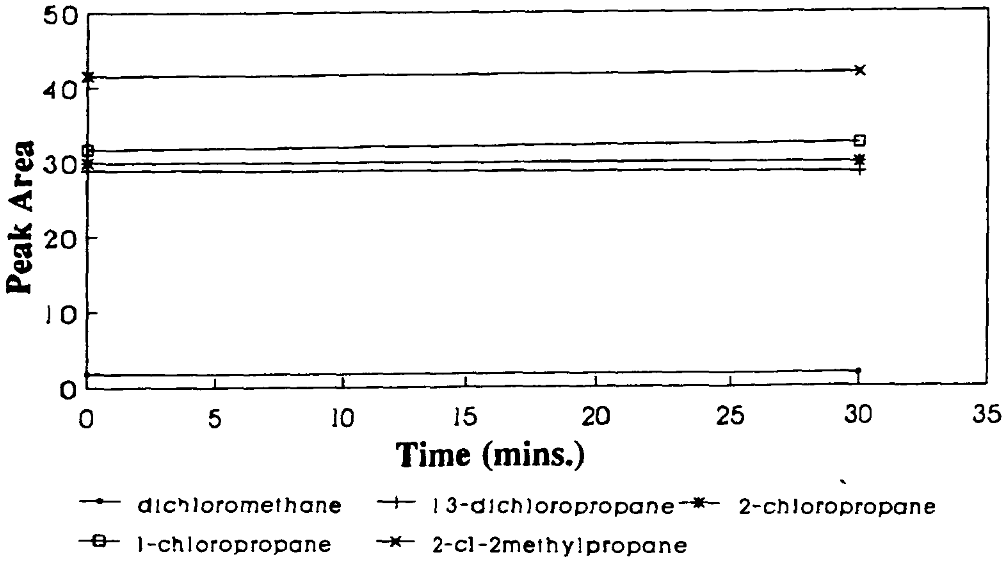


Figure 2.8: Light reaction for Cl and chloroalkanes.

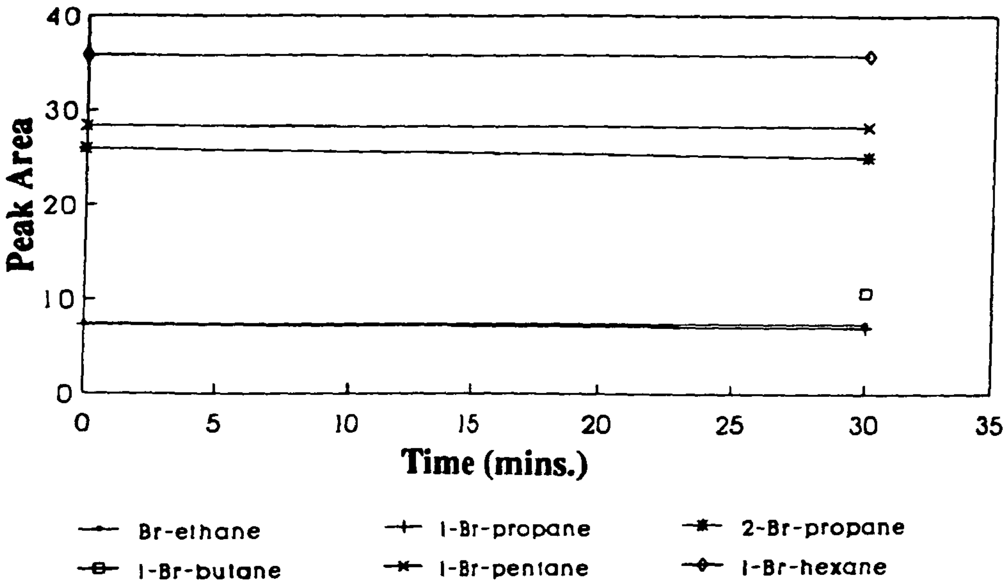


Figure 2.9: Light reaction for OH and bromoalkanes.

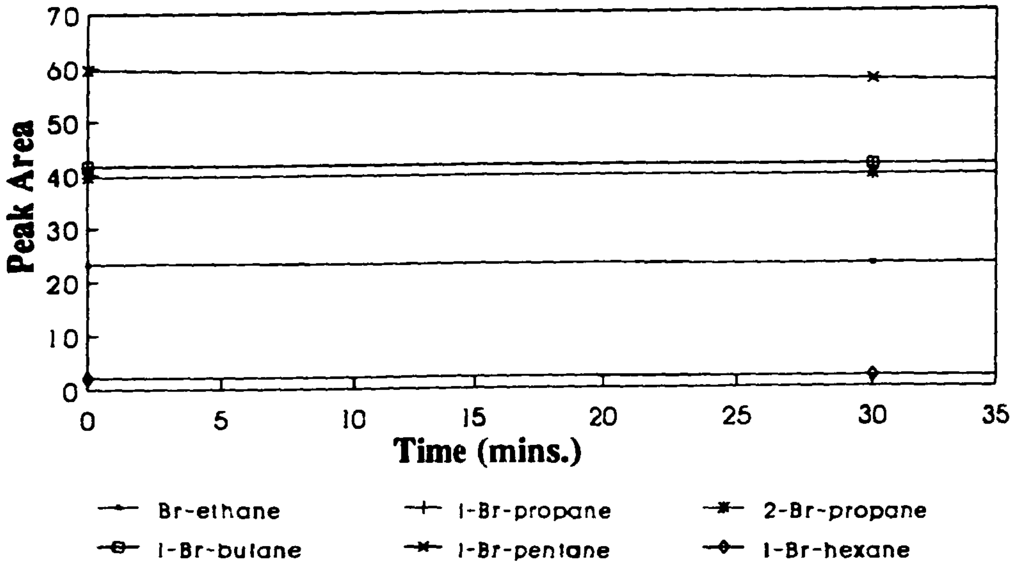


Figure 2.10: Light reaction for Cl and bromoalkanes.

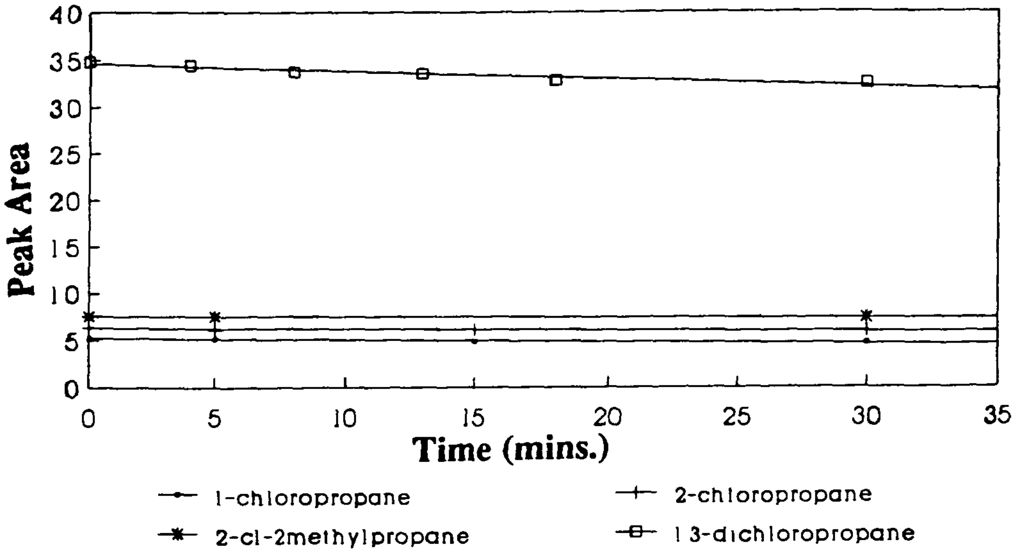


Figure 2.11: Decay curves for the reactions of OH radicals with chloroalkanes.

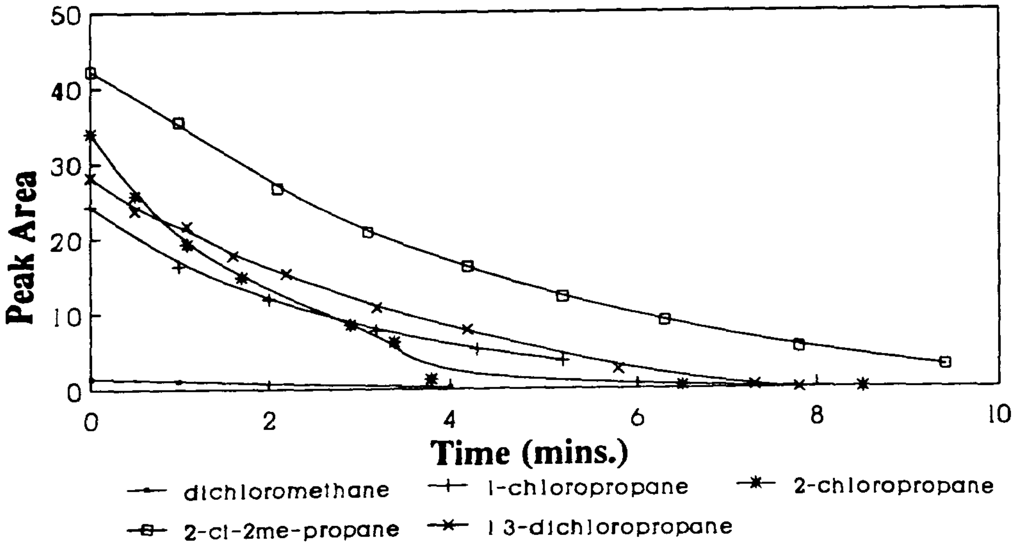


Figure 2.12: Decay curves for Cl atom reactions with chloroalkanes.

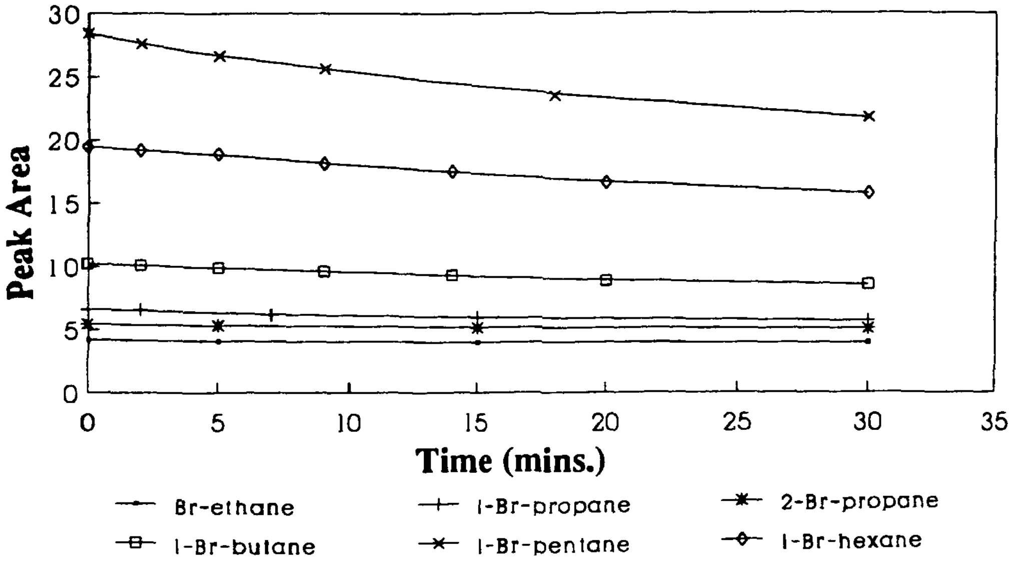


Figure 2.13: Decay curves for the reactions of OH radicals and bromoalkanes

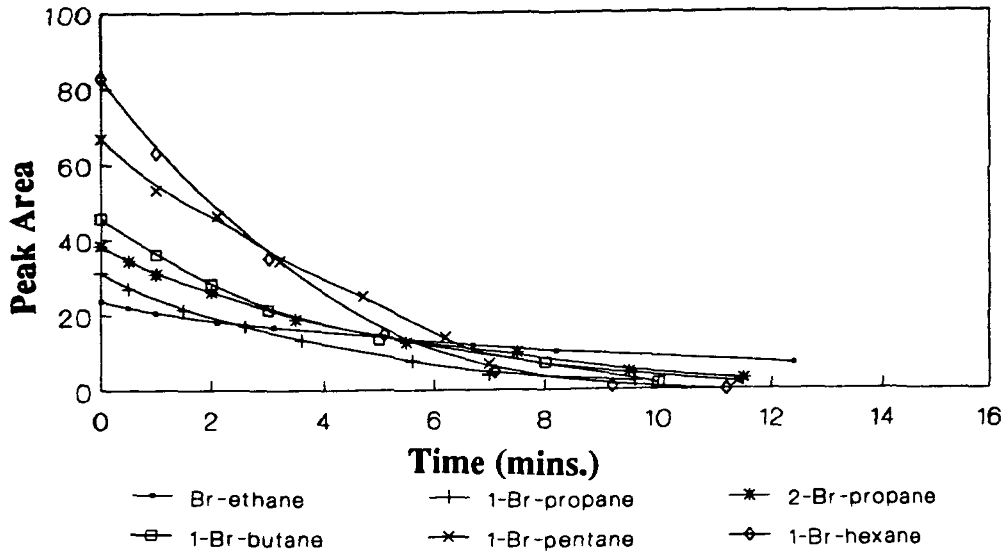


Figure 2.14: Decay curves for the reactions of Cl atoms and bromoalkanes

From the dark reactions, light reactions and decay curves (Figures 2.3 to 2.14) we concluded that for both the OH radical and Cl atom systems loss of the reference and test organics was due solely to reaction of these species with OH radicals and Cl atoms.

Representative concentration-time plots for the reactions of the haloalkanes with OH radicals and Cl atoms are shown in the form of equation 2.15 in Figures 2.15 to 2.18 except for the validation reactions and the reactions of OH + bromoethane and Cl + dichloromethane as these compounds were measured using different reference organics relative to the other organics. The plots are linear with intercepts within ± 2σ of the origin and have correlation coefficients > 0.99. The slopes of the lines can be equated to the ratio of the rate constants for the reactions of the OH radicals and Cl atoms with alkanes. The rate constant ratios k_1/k_2 were calculated using a least squares analysis of the data; k_1 was calculated from the product of k_2 and the rate constant ratio.

In the OH radical system cyclohexane was employed as the reference organic in all cases except for bromoethane and n-pentane. For the bromoethane reaction, ethane was chosen as the reference organic as it was a more suitable reference on the basis of the magnitude of its rate constant and the fact that it has approximately the same number of abstractable hydrogen atoms as bromoethane. The n-pentane reaction was used to validate our system with i-butane as the reference organic. For the OH radical reaction with 1-chloropropane three reference compounds were used (cyclohexane, n-pentane and i-butane). The reference rate constant values were calculated using the Arrhenius expressions listed by Atkinson [8] which enabled the reaction chamber temperature to be taken into account.

Ethane was used as the reference organic for the Cl atom reactions except in the reaction used to validate our system when in this case ethane was the test organic with propane as the reference organic. Propane was also used as a reference compound for the Cl + 1-bromobutane system. The rate constant value used for Cl + ethane was taken from a NASA publication [27] while the value for Cl + propane was taken from the work of Lewis et al [23]. Both reference rates were determined at similar temperatures to those in our experiments.

The errors in the reference values for the OH radical reactions were calculated by Atkinson at 298 K [8]and were ± 25% for OH + cyclohexane, i-butane and n-pentane and ± 20% for OH + ethane. For the Cl atom reactions the error in the Cl + ethane value was taken to be ± 30% [27] and ± 15% for Cl + propane [23].

Table 2.10 lists the atmospheric lifetimes for the test compounds studied with respect to both OH radical and Cl atom reactions. A globally averaged value of $7.7 \pm 1.4 \times 10^5$ OH radicals cm^{-3} was used in calculating the OH radical lifetimes [28] and a value of 1.0×10^3 Cl atoms cm^{-3} for distances up to 2 km in the marine troposphere were used to calculate Cl atom lifetimes [7].

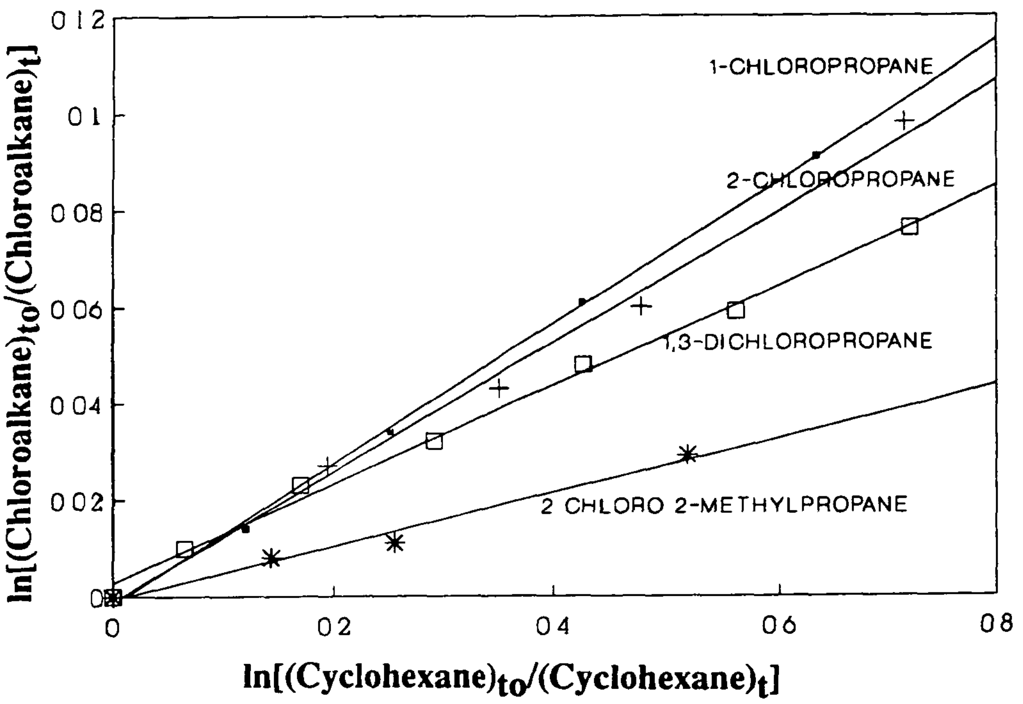


Figure 2.15: Plot of ln $[(\text{chloroalkane})_{t0}/(\text{chloroalkane})_t]$ vs ln$[(\text{cyclohexane})_{t0}/(\text{cyclohexane})_t]$ for OH radical reactions

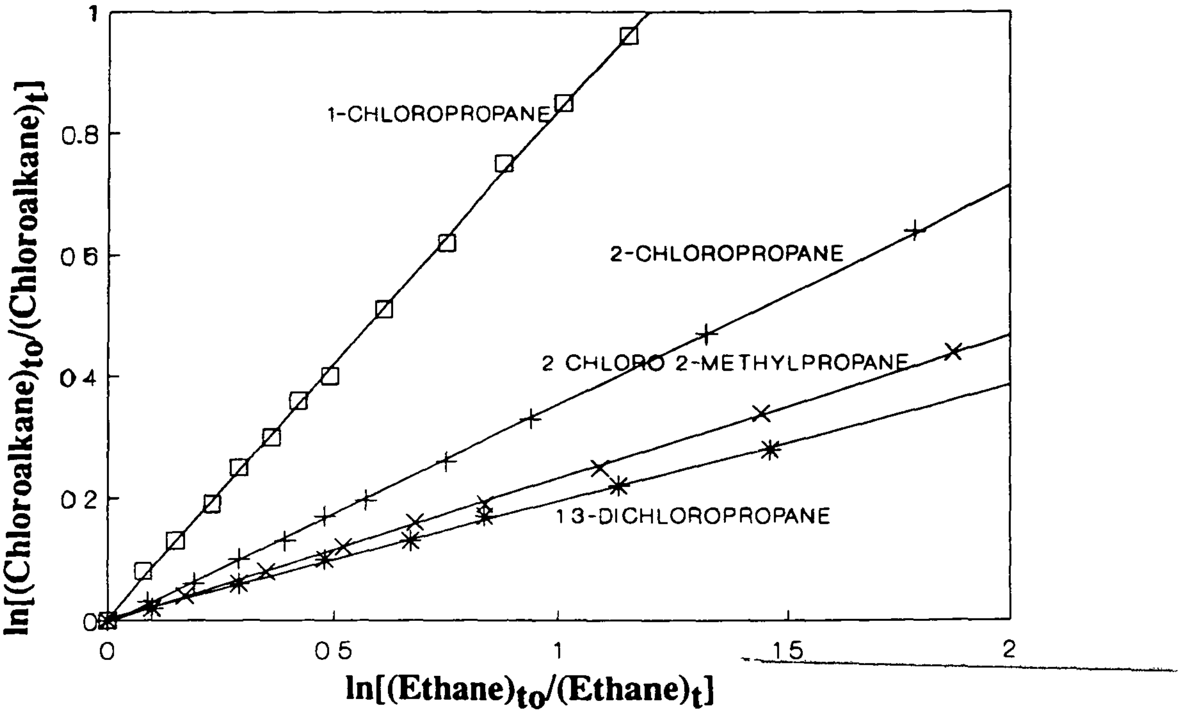


Figure 2.16: Plot of ln $[(\text{chloroalkane})_{t0}/(\text{chloroalakne})_t]$ vs ln$[(\text{ethane})_{t0}/(\text{ethane})_t]$ for Cl atom reactions

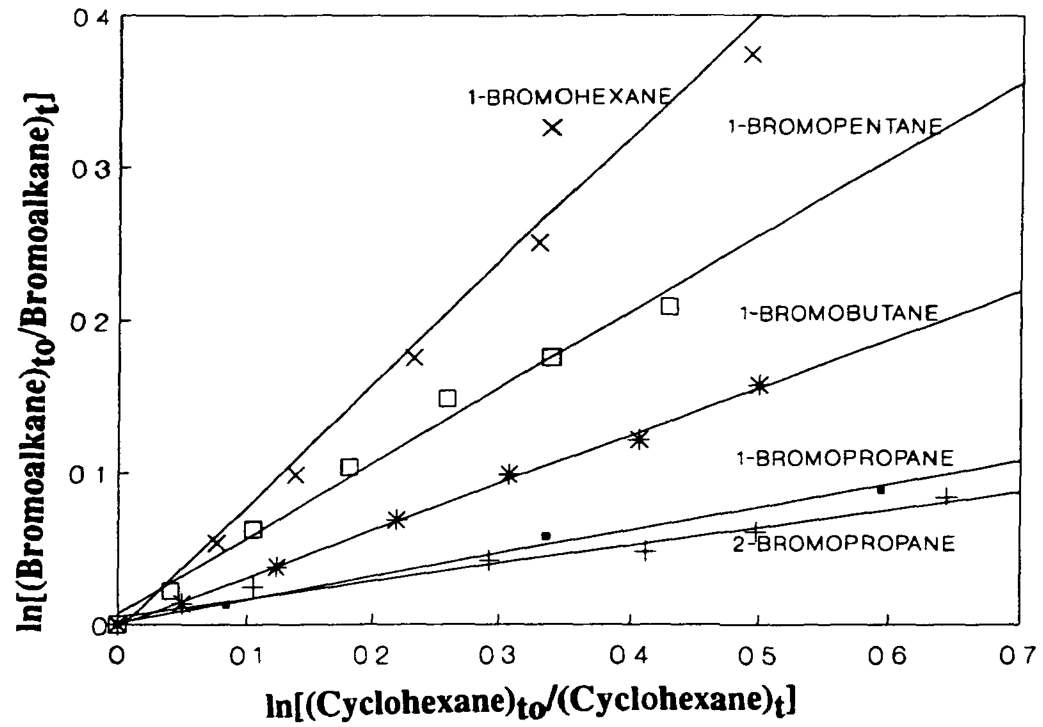


Figure 2.17: Plot of ln [(bromoalkane)$_{t0}$/(bromoalkane)$_t$] vs ln[(cyclohexane)$_{t0}$/(cyclohexane)$_t$] for OH radical reactions.

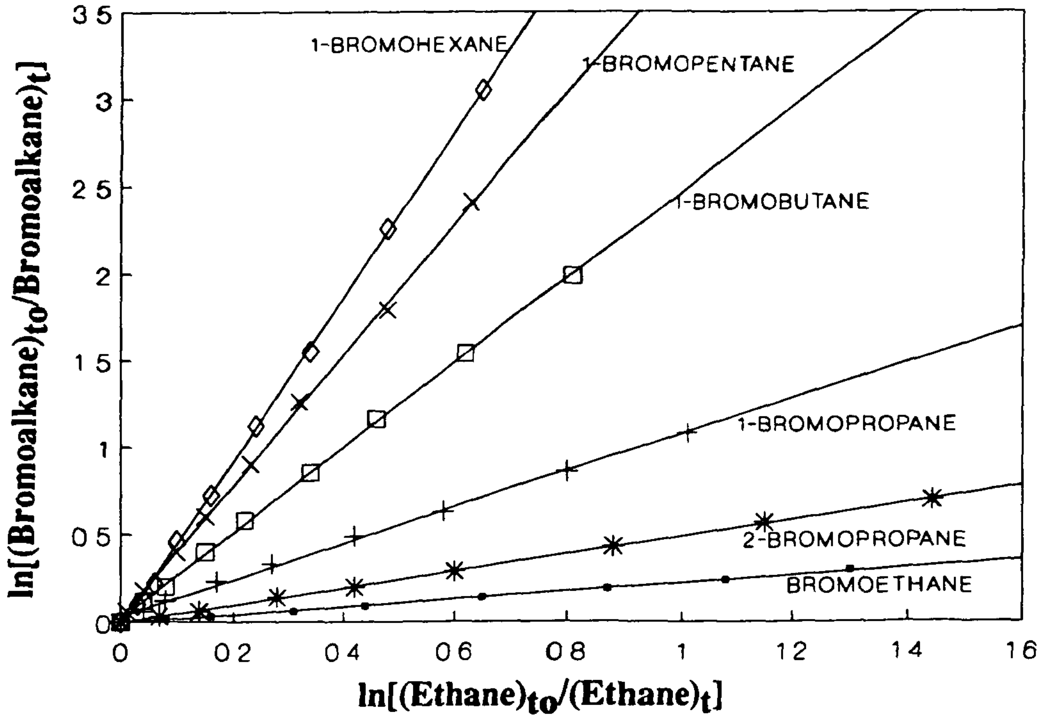


Figure 2.18: Plot of ln [(bromoalkane)$_{t0}$/(bromoalkane)$_t$] vs ln[(ethane)$_{t0}$/(ethane)$_t$] for Cl atom reactions

ORGANIC	τ_{OH}^{a} days	τ_{Cl}^{c}
Ethane		187 days
n-Pentane	3-4	
Dichloromethane	296-427^{b}	79years
1-Chloropropane	11-16	236 days
2-Chloropropane	14-20	1.6 years
1,3-Dichloropropane	16-24	3 years
2-Chloro 2-methylpropane	31-45	2.4 years
Bromoethane	51-73	2.3 years
1-Bromopropane	11-16	190 days
2-Bromopropane	14-21	1.2 years
1-Bromobutane	5-7	84 days
1-Bromopentane	3-5	48 days
1-Bromohexane	2-3	43 days

a $\tau_{OH} = 1/k[OH]$, where $[OH] = 7.7 \pm 1.4 \times 10^{5} cm^{-3}$ [28].

b rate constant value taken from [29].

c $\tau_{Cl} = 1/k[Cl]$ where $[Cl] = 1 \times 10^{3} cm^{-3}$ [7].

Table 2.10: Atmospheric lifetimes with respect to OH radicals and Cl atoms for haloalkanes studied in his work.

2.3.4 DISCUSSION

In order to validate our system and experimental technique (as these measurements were the first carried out using this apparatus) we chose to measure the rate constants for the reactions of OH + n-pentane and Cl + ethane using i-butane and propane as the reference organics respectively. Rate constants for these compounds have been extensively listed in the literature [8, 27]. The experimental values reported in this work are within the experimental errors reported in the literature, thus our experimental technique and apparatus is capable of accurately measuring rate constants for organics using the relative rate technique This observation was further substantiated when comparing rate constant measurements for OH + 1-chloropropane and Cl + 1-bromobutane using different reference organics. In both cases a second reference organic was employed as a check on the experimental measurement, as initially temperature programming was used in the chromatographic analysis of the reactant mixtures to give optimum separation of the test and reference compounds.

For the reaction of OH + 1-chloropropane using n-pentane and i-butane as the reference organics, it was felt that the reproducibility of the absolute value was not acceptable, so a third measurement using cyclohexane as the reference compound was made. From the these results it is apparent that our system is capable of a high degree of accuracy and precision.

The rate values reported by Markert et al [17] for OH radical reactions with chloroalkanes are considerably different to our measurements i.e. a difference of 26% and 53% for 1-chloropropane and 2-chloropropane respectively. As these measurements are the first reported for these particular compounds the discrepancy can be attributed to experimental error Similarly our value for OH + bromoethane is 30% lower than the value reported by Qui and Xing [18, 19]; however, the values do agree within the error values listed A better agreement between the result for Cl + 1-chloropropane was obtained between our result and that of Wallington [26].

One of the disadvantages of the relative rate technique compared to absolute methods is that the lowest rate constant ratio measurable for OH radical reactions is $0.25 \times 10^{-12} cm^3 molecule^{-1} s^{-1}$ [30]. Values lower than this would be difficult to measure even when using a reference organic that has a small rate constant value as the decrease in organic concentration due to reaction with the OH radicals could not be distinguished from the chromatographic reproducibility of the system. Our result of $0.25 \pm 0.05 \times 10^{-12} cm^3 molecule^{-1} s^{-1}$ for the OH + bromoethane reaction is within the minimum level of detection for this system.

Ideally one should choose a reference compound that has a similar rate value to the organic under investigation; however, this is not always possible especially in the case of OH radical reactions where a difficulty often encountered in this work was the chromatographic seperation of CH_3ONO and the reference organic at high column temperatures. This accounts for the use of cyclohexane as the reference organic in the OH + chloropropane reactions when ethane would have been a more suitable choice. As a result it was often quite difficult to monitor the change in test concentration with increasing reaction time as the change in peak area was quite small, thus samples were taken after longer photolysis times i.e. > 5 minutes to ensure that the concentration decrease could be monitored. This is reflected in the plots of equation 2.15 (Figures 2.15 to 2.18) when lines were constructed on as few as 3 points. This is contrary to the recommendations of Atkinson [31] who stated that as many samples as possible should be taken in the early stages of the reactions. Thus large errors would be incurred in the rate constant ratio values for those compounds that had long reaction times. The largest error however, is attributed to the error in the rate constant for the reference reaction which in some cases can be as high as ± 30%.

Table 2.11 lists the values for the OH radical and Cl atom rate constants for the chloropropanes and their corresponding parent alkanes.

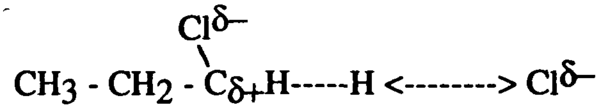
ALKANE	k_{OH}^a	REF.	k_{Cl}^a	REF.
1-Chloropropane	1.12±0.02	this work	49±15	this work
2-Chloropropane	0.92±0.23	this work	20±16	this work
1,3-Dichloropropane	0.78±0.19	this work	11±3	this work
2-Chloro 2-methylpropane	0.41±0.10	this work	13±4	this work
Propane	1.15±0.34	[8]	151±23	[23]
n-Butane	2.54±0.51	[8]	224±61	[23]
i-Butane	2.34±0.59	[8]	144±39	[24, 32]

a - units of $10^{-12} cm^3 molecule^{-1} s^{-1}$

Table 2.11: Rate constants for the reactions of chloropropanes and their parent compounds with OH radicals and Cl atoms

From these results it is observed that the presence of a Cl atom lowers the rate constant values especially if the substituents are located on the C_2 position or if there is more than one substituent present. It is interesting to note that the Cl atom rate constant values are more significantly affected by the presence and position of the Cl atoms compared to the OH radical rate values. This reflects the different factors influencing the rate of hydrogen-atom abstraction from the organics by OH radicals and Cl atoms.

The reactivity of the chloropropanes towards Cl atoms decreases dramatically with increasing Cl atom substitution and changing the Cl substituent from the C_1 to the C_2 position It has been hypothesised that the reactivity of Cl atom substituted alkanes is decreased due to a concerted effect of repulsion and electron withdrawal by the bound Cl atom with the latter effect being predominant resulting in a destabilisation of the transition state [33 - 39] i.e.:



$$CH_3 - CH_2 - \overset{Cl^{\delta-}}{C_{\delta+}}H\text{-----}H \longleftrightarrow Cl^{\delta-}$$

Also, the effect of Cl substitution on the reactivity of the organic is more pronounced for the first hydrogen-atom replaced and decreases with increasing substitution; this is reflected in the reactivities of Cl + propane, 1-chloropropane and 1,3-dichloropropane and also in i-butane and 2-chloro 2-methyl propane [24 - 30].

As previously mentioned much work has been carried out on the reactions of OH radicals with chlorinated methane and ethane compounds. For the chlorinated methane compounds, the rate of hydrogen-atom abstraction increases with increasing substitution as a result of the decrease in bond strength [40, 41]. E_a values were observed to decrease in going from CH_4 to CH_3Cl but then remain constant in going from CH_2Cl_2 to $CHCl_3$ [31] which could be due to the effects of repulsive forces operating in the transition state resulting from Cl substitution. The effect of repulsive forces are also observed for the chloroethanes.

Table 2 12 lists the rate constant values for several chlorinated ethane compounds; and indicates that the rate values decrease with increasing Cl substitution particularly if substitution occurs on the α carbon atom as the Cl atom reduces the stability of the transition state by introducing repulsive forces between the hydrogen atom to be abstracted and the approaching OH radical [46, 48, 49, 51].

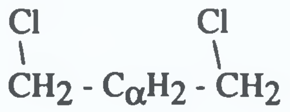
ORGANIC	kOH at 298K [$10^{12}cm^3molecule^{-1}s^{-1}$]	REFERENCE
C_2H_6	2.68	[8]
CH_2ClCH_3	4.10	[42]
	3.90	[43]
	4.30	[44]
	3.90	[45]
$CHCl_2CH_3$	2.82	[46]
	2.20	[19]
CH_2ClCH_2Cl	2.54	[47]
$CHCl_2CHCl_2$	2.30	[19]
CCl_3CH_3	0.11	[48]
	0.11	[49]
$CHCl_2CH_2Cl$	2.03	[50]

Table 2.12: Rate constant values for the reactions of OH radicals and chlorinated ethanes.

For the OH radical rate constants for the chloropropanes the presence of a Cl substituent decreases the magnitude of the rate values also and the trend of increasing the number of Cl atoms from one to two which further reduces the magnitude of the rate constants is also observed

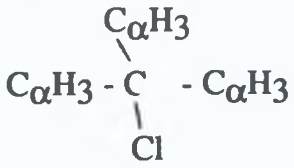
Another interesting observation is that the value of the rate constant for 1,3-dichloropropane is slightly larger than that for 2-chloro 2-methylpropane when it would be expected that on the basis of the number of Cl substituents on 1,3-dichloropropane and the number of available abstractable hydrogen atoms on 2-chloro 2-methylpropane (i.e 9 as opposed to 6) that the converse would hold.

On examining the molecular structure of these two organics it is observed that there is only one α carbon atom in 1,3-dichloropropane whereas there are three in 2-chloro 2-methylpropane:



$\overset{Cl}{CH_2} - C_\alpha H_2 - \overset{Cl}{CH_2}$

1,3-Dichloropropane



$C_\alpha H_3 - \overset{C_\alpha H_3}{\underset{Cl}{C}} - C_\alpha H_3$

2-Chloro 2-methylpropane

Figure 2.19 shows a decrease in the magnitude of the rate constant value with the number of α carbon atoms in a molecule calculated from the rate constants measured in this work. Thus the Cl atom exerts a greater influence over the 2-chloro 2-methylpropane molecule by deactivating the three α C - H bonds relative to the influence of two Cl atoms on one α carbon. The difference in the values could also be explained in terms of the relative bond strengths in the individual molecules; 1,3-dichloropropane contains four primary C - H bonds and two secondary C - H bonds whereas 2-chloro 2-methylpropane contains only primary C - H bonds. Therefore the OH radical would theoretically favour secondary hydrogen-atom abstraction.

Markert and Nielsen [17] suggested that there are two different effects on the OH radical reactivity for Cl substituted alkanes - an inductive effect which decreases the reactivity for hydrogen atom abstraction and extends to at least the β carbon atom and also a mesomeric effect which increases the reactivity of the α carbon. The inductive effect is probably the dominant effect resulting in an overall decrease in the rate constant value and a corresponding increase in the E_a values compared to n-alkanes with the same number of $-CH_2-$ groups.

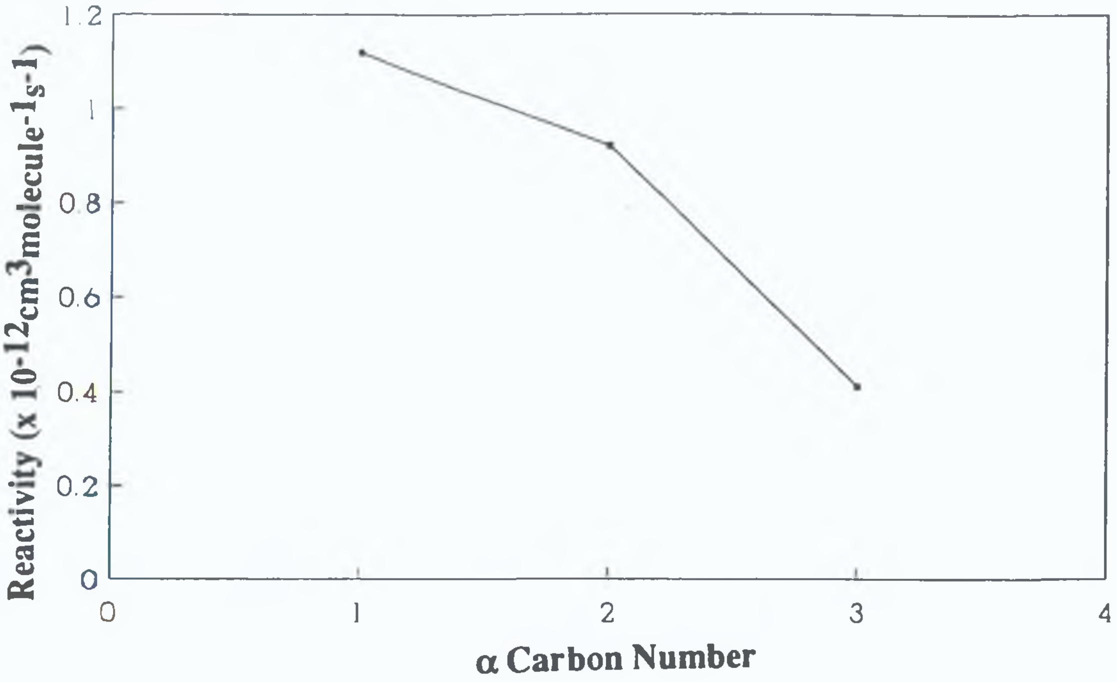


Figure 2.19: Plot of the rate constant values for chloropropanes versus the number of α carbon atoms present in the molecule.

These hypotheses made from our results are based solely on experimental rate constant values. In order to obtain a greater insight into the effects of Cl atom substitution on the rate coefficients for the reactions of OH radicals with propane a more indepth study of these reactions must be carried out.

Figures 2.20 and 2.21 illustrate OH radical and Cl atom reactivities for n-alkanes, chloroalkanes and bromoalkanes. For the OH radical reactions the presence of a bromine substituent has very little effect on the magnitude of the rate constant value whereas the chlorine substituent is observed to lower the rate constant value.

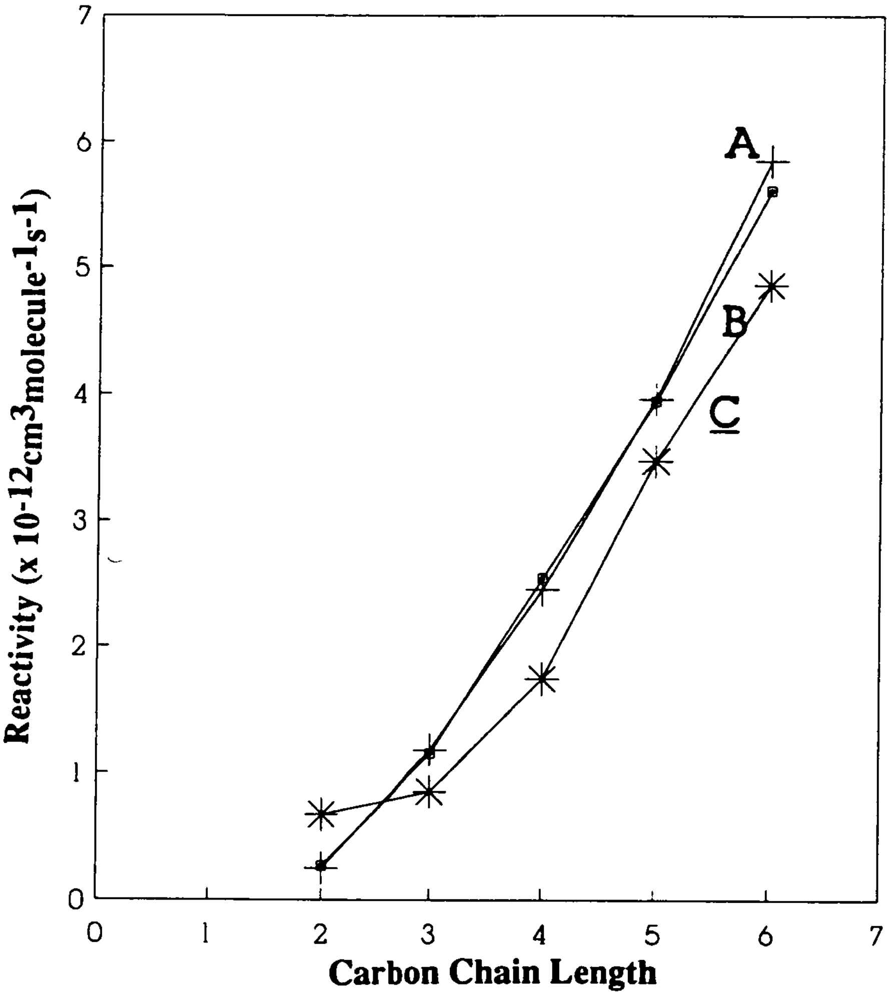


Figure 2.20: Reactivities of OH radicals towards a series of n-alkanes (+) A, bromoalkanes (■) B and chloroalkanes (∗) C. Data for the n-alkanes and chloroalkanes taken from [8] and [17] respectively.

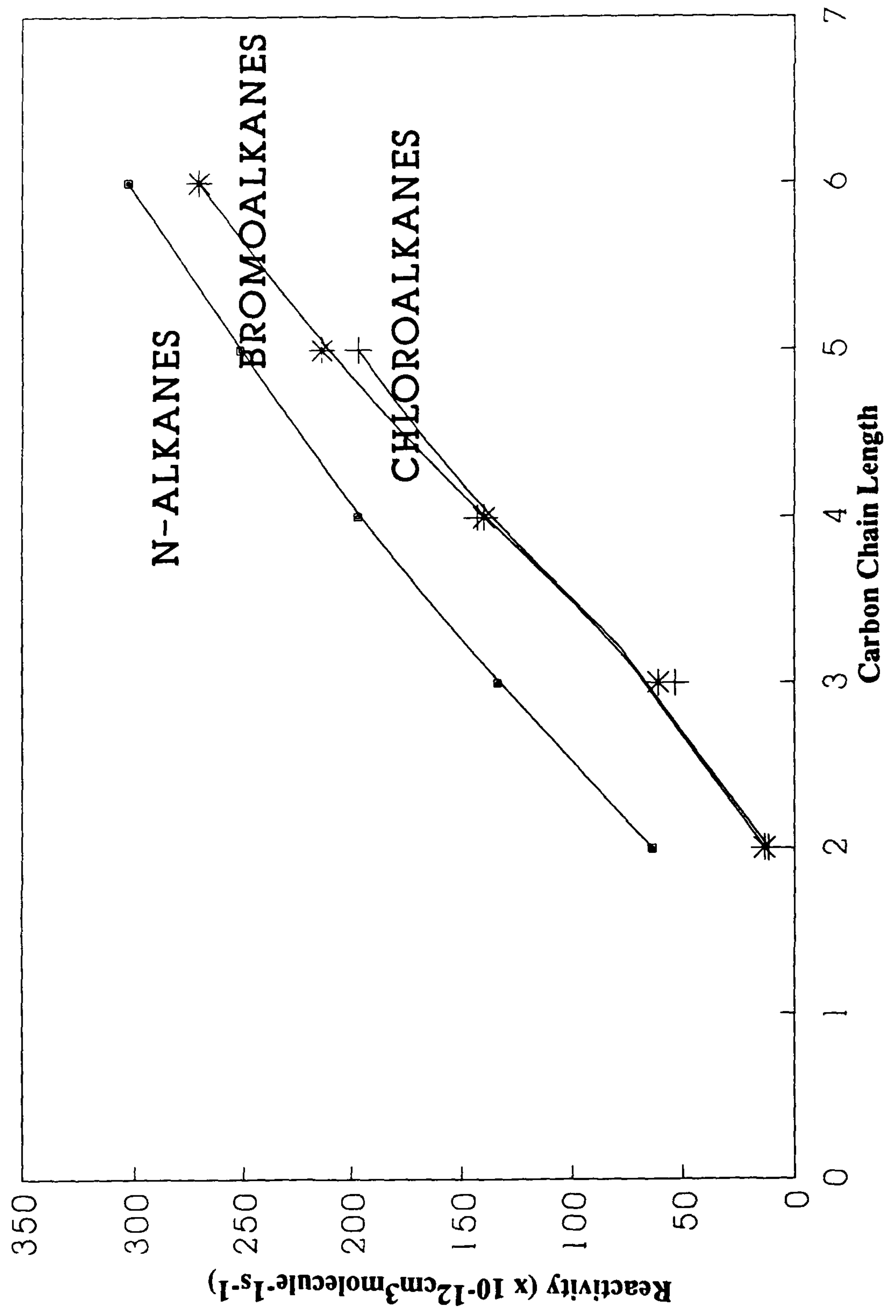


Figure 2.21: Reactivities of Cl atoms towards a series of n-alkanes, chloroalkanes and bromoalkanes The data for the n-alkanes and the chloroalkanes was taken from [24] and [26] respectively

From Figure 2.20 it is apparent that in the case of the reaction with OH radicals and chloroalkanes the Cl substituents exert more influence on the smaller alkanes which accounts for the distinct curvature of the plot. This influence then decreases with increasing chain length when the -CH_2- group rate constants become more dominant. In the case of the Cl atom reactions the presence of a halogen atom (bromine or chlorine) significantly lowers the rate constant values relative to the values for the n-alkanes with the deactivation effect being constant throughout the series. The reactivities of the bromoalkanes are similar to the chloroalkanes which is quite surprising as bromine atoms are larger and more electronegative than chlorine atoms so the rate constants would be expected to be smaller in magnitude; however, this trend has also been observed by a colleague working with halogenated ethers.

A comparison of our experimental values of the reactions of OH radicals and the 1-bromoalkanes and those calculated by Atkinson's SAR method [51] using the group values calculated by Kerr et al [15] is shown in Figure 2.22. Except for OH + bromoethane the values generally agree within ± 20%, although they are lower than the experimentally calculated values. This leads to the conclusion that the factors F(Br) and F(CH_2Br) in Atkinson's model might need to be recalculated.

Wallington [32] found that there was a linear correlation between the reactivities of the reactions of Cl atoms and OH radicals with n-alkanes. Figure 2.23 shows a plot of the rate constants for OH radical reactions with bromoalkanes against the rate constants for the Cl atom reactions with the same compounds. Figure 2.23 indicates that there is also a linear correlation for the reactivities of the bromoalkanes towards Cl atoms and OH radicals.

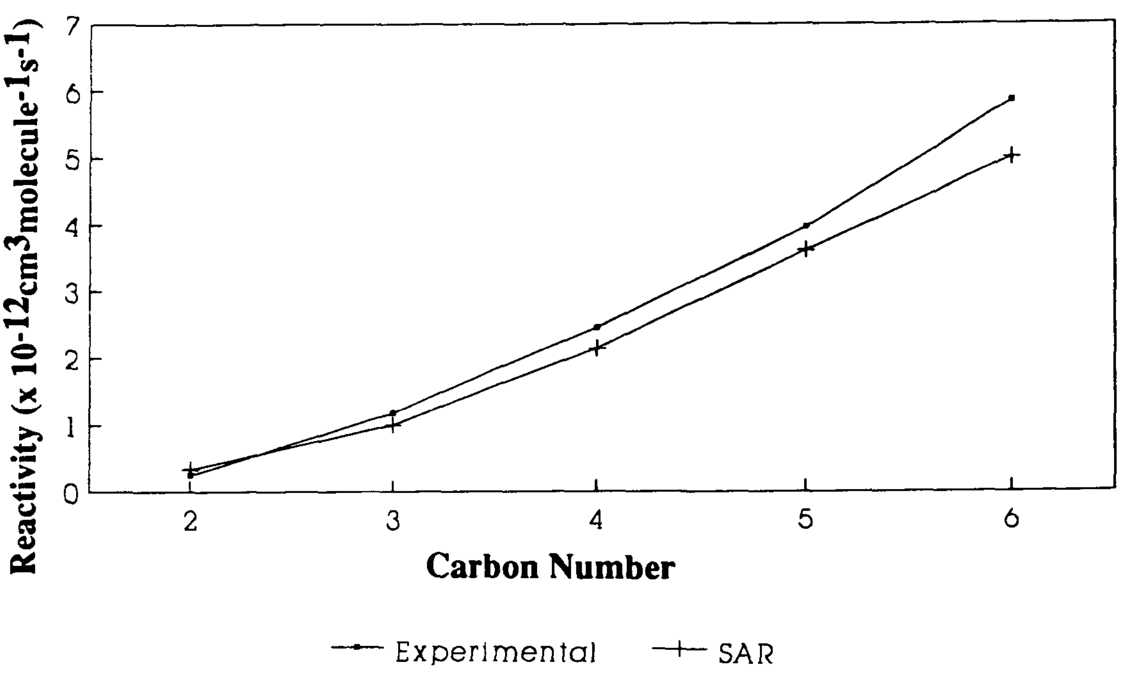


Figure 2.22: A comparison between the calculated and measured rate constants for OH + 1-bromoalkanes.

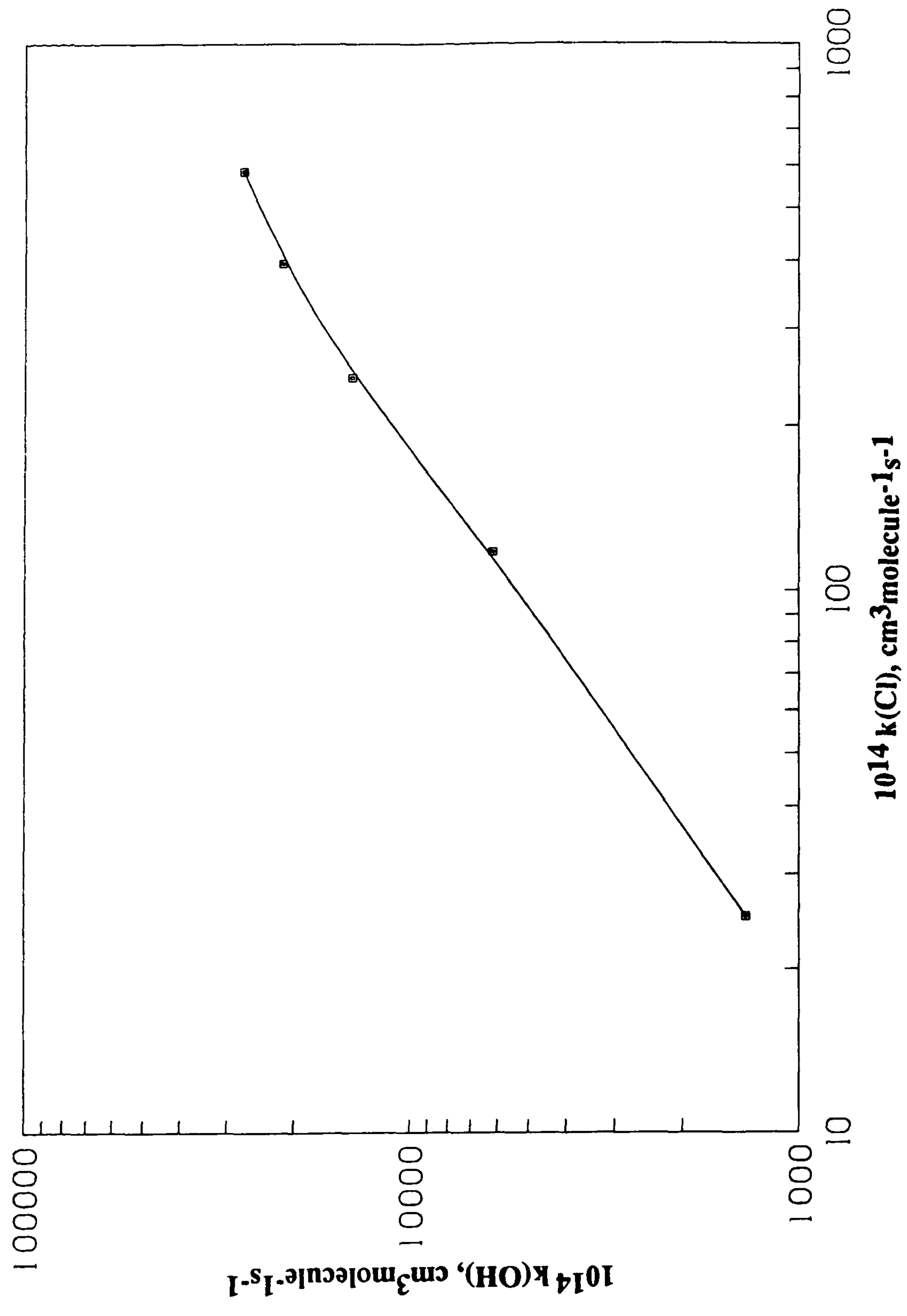


Figure 2.23: Plot of the rate constants measured in this work for the reactions of OH radicals with a series of bromoalkanes versus the corresponding rate constants for the reactions of Cl atoms.

The atmospheric lifetimes for the haloalkanes studied in this work were calculated using the expression

$$\tau = 1/k[OH]([Cl]) \qquad 1.22$$

where k is the rate constant value for the organic under investigation and [OH] or [Cl] is the global concentration of the OH radical and the Cl atom respectively. The atmospheric lifetimes for the compounds calculated in this work are listed in Table 2.10. From this data two points are noted: firstly, the atmospheric lifetimes are greater than one week except for OH + n-pentane. 1-bromobutane, 1-bromopentane and 1-bromohexane; secondly, it is observed that the reactions of the haloalkanes with Cl atoms are 10^2 - 10^3 times faster than the corresponding OH radical reactions; however, as OH radicals are approximately one thousand times more abundant in the troposphere [7] therefore the dominant reaction pathway for the haloalkanes is with OH radicals.

Dichloromethane has the longest atmospheric lifetime with a maximum of 426 days followed by bromoethane. Relative to the atmospheric lifetimes of the CFCs, halons and replacement compounds for CFCs which are in the order of years, the lifetimes of the organics studied in this work are quite insignificant and they would pose no long term threat to the ozone layer.

When quoting values for atmospheric lifetimes as we have done, several factors must be considered. Equation (1.22) assumes the sink strength is universally distributed throughout the troposphere, whereas in reality the tropospheric distribution of OH radicals and Cl atoms have as yet to be unambiguously defined. As a result the largest uncertainty in the figures comes from the OH radical and Cl atom concentrations used in the calculations. The expression also does not allow reaction temperature to be taken into account as often the less reactive halocarbons exhibit a more marked temperature dependence in their rate coefficients for OH radical attack resulting in oxidation ocurring primarily at the Earth's surface and makes chemical removal in the middle and upper troposphere relatively unimportant. Thus when using this expression to calculate tropospheric lifetimes it must be realised that the figures generated are not absolute values and are subject to several uncertainties.

2.3.5 CONCLUSION

Tables 2.8 and 2.9 list the rate constant values for the organics studied in this work along with relevant literature data. The values calculated for the validation reactions show excellent agreement with literature values indicating that our experimental technique and apparatus was capable of accurate and precise rate constant measurements. The major sources of error in our results were from the reference organic rate constant values.

The major factors affecting the reactivity of OH radicals and Cl atoms with haloalkanes appears to be inductive effects occurring in the transition state as a result of halogen atom substitution (Cl and Br). These effects were more pronounced for the Cl atom reactions due to the electronegativity of the halogen substituents and the incoming Cl atom. In the case of the OH radical reactions the reactivities of the alkanes were not adversly effected by the presence of Br substituents whereas the reactivities for the chloroalkanes were reduced.

The atmospheric lifetimes for the haloalkanes were calculated for both OH radical and Cl atom reactions. The values indicate that the major atmospheric reaction pathway is via reaction with OH radicals. The values are low enough to ensure that the compounds would not be a significant threat to the ozone layer.

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2.4

THE REACTION OF OH RADICALS AND Cl ATOMS WITH A SERIES OF KETONES

2.4.1 INTRODUCTION

The atmospheric study of carbonyl compounds has not received as much attention in the past as has for example alkanes or alkenes. However, it has recently been recognised that carbonyl compounds are important species in tropospheric chemistry because they are the products of the first photooxidation stage of almost all organic compounds emitted into the atmosphere [1]. Carlier estimated that secondary aldehydes and ketones account for about 7/8 of the total carbonyl compounds in the polluted air above Los Angeles despite the source strength of the primary compounds.

The production of carbonyl compounds including ketones in the troposphere is primarily controlled by the formation of free radicals produced as a result of the photooxidation of organic compounds in the troposphere. For example the photooxidation of alkanes by reaction with OH radicals produces alkyl radicals (R) which react with oxygen to form alkylperoxy radicals (RO_2) and in the presence of NO alkoxy radicals are produced (RO) i.e.:

$$RH + OH \text{ -------> } H_2O + R \qquad 2.44$$

$$R + O_2 \text{ -------> } RO_2 \qquad 2.45$$

$$RO_2 + NO \text{ -------> } RO + NO_2 \qquad 2.46$$

The RO radical can under go three reactions which will result in the formation of ketones [2]. A decomposition reaction, an oxygen abstraction of a hydrogen atom attached to the alkoxy carbon position which occurs only for primary and secondary alkoxy radicals as tertiary radicals do not contain abstractable hydrogen atoms and an internal hydrogen atom abstraction by the O radical center which is only important in species with greater than four carbons present [3]. Radical production is controlled by the concentration of the sink species (OH, Cl, O_3, NO_3 etc.) and on the rate constants between the sink species and the organics in the troposphere Table 2.13 illustrates the major reaction products in the gas phase reactions of some alkanes under simulated atmospheric conditions [3].

ALKANE	KETONE
Propane	2-Propanone
n-Butane	2-Butanone
2-Methylpropane	2-Propanone
n-Pentane	2-Pentanone 3-Pentanone
2-Methylbutane	2-Propanone 3-Methyl-2-propanone
n-Hexane	5-Hydroxy-2-hexanone 3-Hexanone
2-Methylpentane	2-Methyl-3-pentanone

Table 2.13: Major reaction products from the gas phase reactions of alkanes under atmospheric conditions [3].

Factors influencing the production of ketones due to the photooxidation of alkanes include ambient temperature conditions during formation and also the transport, formation and decomposition rates of the alkoxy radicals. Because of the widely varying atmospheric lifetimes of the precursor hydrocarbons, the production of the ketone products may exceed their estimated lifetimes which would result in a steady-state concentration of ketones being present in the atmosphere.

Other sources of carbonyl compounds in the troposphere result from natural and anthropogenic sources. In natural atmospheres the sources of carbonyl compounds are primarily of biological origin including volcanic eruptions, forest fires and animal excretae [1]. Anthropogenic sources include rubbish incineration, industrial and domestic heating, motor vehicle traffic, solvent evaporation and exploitation of fossil fuels for energy production.

Carbonyl compounds present in the troposphere can either under go photolysis or reaction with typical sink species (OH, O_3, NO_3, Cl). Photolysis reactions would be considered to be of minor importance [4]; also, reactions with O_3 and NO_3 are very slow ($< 10^{-20}$ cm^{3}molecule^{-1}s^{-1} for O_3 reactions and 10^{-17} - 10^{-16} cm^{3}molecule^{-1}s^{-1} for NO_3 reactions) and have a negligible contribution to the ketone loss process in the troposphere [4, 5]. Therefore, the major loss process for ketones in the troposphere is via reaction with OH radicals [1, 4, 6].

The importance of OH radical degradation of ketones in tropospheric chemistry has prompted investigations into this area [2, 7 - 10] which have been summarised by Atkinson [11].

The reaction of OH radicals with ketones proceeds in a similar fashion to the reaction with alkanes i.e. via a hydrogen-atom abstraction mechanism; however, there is an enhancement in reactivity at the β and possibly the γ positions relative to the C=O group which has been attributed to the formation of a six membered ring adduct prior to hydrogen atom abstraction [12]. It is the aim of this section of work to provide additional rate constant data for OH radical reactions with ketones which will give a further insight into the mechanistic influences of the C=O group on the rate of hydrogen-atom abstraction by OH radicals.

As a result of the proposal by Singh [13] it has been accepted that Cl atom reactions in the troposphere must be a consideration in determining the fate of organics in the troposphere. To date there have been no published kinetic data on the reactions of Cl atoms with ketones.

This body of work is a relative rate study of the reactions of OH radicals and Cl atoms with aliphatic ketones and cyclic ketones. The results will serve to increase the current data base of information on OH radical reactions with carbonyl compounds and will also establish a new data base of information with respect to Cl atom reactions. Both sets of results will be used to study factors affecting the reactivity of the reactions and to establish the relationship between structure and reactivity.

2.4.2 EXPERIMENTAL

Only specific details relating to the analysis of the ketone compounds are discussed in this section as the experimental procedures employed to determine the OH radical and Cl atom rate constants have previously been discussed in Sections 2.2. Table 2.14 lists the compounds studied along with their respective purities and suppliers. All compounds were used without further purification and were throughly degassed using the freeze-pump-thaw method prior to use. Sample mixtures were prepared and the smog chamber filled as outlined in Section 2.2.

The test and reference organics used along with the analytical conditions uesd to achieve optimum seperation of the analytes for the OH radical and Cl atom systems are listed in Tables 2.15 and 2.16.

ORGANIC	PURITY (%)	SUPPLIER
Cyclopentane	99+	B.D.H
Cyclohexane	99+	Aldrich Chemicals
Cyclobutanone	99	Aldrich Chemicals
Cyclopentanone	99+	Aldrich Chemicals
Cyclohexanone	99.5	Riedel-de-Haen
Cycloheptanone	99	Aldrich Chemicals
2-Methyl-cyclopentanone	98	Aldrich Chemicals
2-Methyl-cyclohexanone	98	Aldrich Chemicals
4-Methyl-cyclohexanone	98	Aldrich Chemicals
3-Methyl-2-butanone	99	Aldrich Chemicals
3-Methyl-2-pentanone	97	Aldrich Chemicals
2-Methyl-3-pentanone	97	Aldrich Chemicals
2-Methyl-3-hexanone	99	Aldrich Chemicals
5-Methyl-2-hexanone	99	Aldrich Chemicals
2-Methyl-3-heptanone	99	Aldrich Chemicals
5-Methyl-3-heptanone	99	Aldrich Chemicals

Table 2.14: Purities and suppliers for the ketones studied in this work.

ORGANIC[a]	REACTION TEMP. (K)	COL. TEMP (K)
Cyclopentanone	305	383
Cyclohexanone[b]	306	T.P[c]
Cycloheptanone	304	T.P[d]
2-Methylcyclopentanone	305	373
2-Methylcyclohexanone	307	T.P[e]
4-Methylcyclohexanone	305	T.P[f]
3-Methyl 2-butanone	307	363
3-Methyl 2-pentanone	307	353
2-Methyl 3-pentanone	307	363
2-Methyl 3-hexanone	307	363
5-Methyl 2-hexanone	305	373
2-Methyl 3-heptanone	307	373
5-Methyl 2-heptanone	305	373

a reference = cyclohexane

b reference = cyclopentane

c T.P. initial temp. = 343K, final temp. = 383K.

d T.P initial temp. = 383K, final temp. += 403K.

e T.P. initial temp. = 373K, final temp. = 403K.

f T P: initial temp = 373K, final temp. = 413K.

Table 2.15: Analytical conditions for the reactions of OH radicals and ketones. [N$_2$ flow = 45±1 ml min^{-1}, injector temp. = 473 K, detector temp. = 523 K Column, 10% PEG on Chromosorb W AW (100-120μm)]

ORGANIC	REFERENCE ORGANIC	COL. TEMP.(K)
Cyclobutanone	Cyclopentane	383
	Ethane	373
Cyclopentanone	Cyclopentane	383
	Ethane	393
Cyclohexanone	Cyclopentane	383
	n-Butane	393
Cycloheptanone	Cyclopentane	403
	n-Butane	403
2-Methylcyclopentanone	n-Butane	383
2-Methylcyclohexanone	n-Butane	393
4-Methylcyclohexanone	n-Butane	T.P[a]
3-Methyl 2-butanone	Ethane	363
3-Methyl 2-pentanone	Ethane	353
2-Methyl 3-pentanone	Ethane	363
2-Methyl 3-hexanone	n-Butane	373
5-Methyl 2-hexanone	n-Butane	383
2-Methyl 3-heptanone	n-Butane	383
5-Methyl 3-heptanone	n-Butane	383

[a] T.P: initial temp. = 368 K, final temp. = 413 K.

Table 2.16: Analytical conditions for the reactions of Cl atoms and ketones at 298 ± 2K. [N_2 flow = 45±1ml min^{-1}, injector temp. = 473 K, detector temp. = 523 K, Column = 10% PEG on Chromosorb W AW (100-120 μm)]

2.4.3 RESULTS

To validate our experimental procedure we remeasured the rate constants for OH + cyclohexanone and cyclopentanone using cyclopentane and cyclohexane as the reference organics respectively. As there are no rate values listed for the reactions of Cl atoms with ketones in the literature, these were the only validation reactions carried out. The relative rate constant ratios, their absolute rate constant values and relevant literature data for the reactions of OH radicals and Cl atoms with the ketones studied are listed in Tables 2.17 and 2.18.

To ensure that the only removal of the test and reference organic in the system was by reaction with either OH radicals or Cl atoms and not as a result of direct photolysis by the lamps or by reaction with either $CH_3ONO\backslash NO$ or Cl_2, light and dark reactions were carried out prior to determining the rate constant ratios. Typical light reaction profiles are illustrated in Figures 2.24 - 2.27 and dark reaction profiles are shown in Figures 2.28 - 2.31 for aliphatic and cyclic ketones. As a test for secondary reactions occurring as a result of the reaction of either the test or reference organic with OH radicals or Cl atoms, decay profiles were obtained of mixtures of either the test or reference organic and $CH_3ONO\backslash NO$ or Cl_2. These profiles are illustrated in Figures 2.32 - 2.35.

KETONE	$k_1/k_2^{a,b}$	T (K)	$k^{e,f}$	Literature Values [11]^{f}
cyclobutanone				0.87±0.06
cyclopentanone	0.352±0 013^{c}	305	2 69±0.7	2.94±0.2
cyclohexanone	1.116±0.023^{d}	307	5.94±1.2	6.39±0.5
cycloheptanone	1 25±0.044	306	9.58±2.4	
2-methylcyclopentanone	0.764±0.02^{c}	304	5.82±1.5	
2-methylcyclohexanone	0.959±0 024	305	7.33±1.8	
4-methylcyclohexanone	0.934±0 028	303	7.1±1.8	
3-methyl-2-butanone	0.255±0 011	307	1.96±0.5	
3-methyl-2-pentanone	0 871±0 009	307	6.70±1.7	
2-methyl-3-pentanone	0 586±0 21^{c}	307	4.51±1.1	
2-methyl-3-hexanone	0 995±0 019	307	7.65±1.91	
5-methyl-2-hexanone	1.761±0 053	305	13.45±3.4	
2-methyl-3-heptanone	1 601±0 045	307	12.31±3.0	
5-methyl-3-heptanone	3.599±0.144	305	27 5±6.9	

a errors quoted are ± 2σ from the least squares analysis of the data

b reference - cyclohexane

c errors quoted are calculated from the chromatographic reproducibility of the data.

d reference - cyclopentane

e errors quoted includes the errors in the reference value. (±25% for cyclohexane and cyclopentane at 298K calculated form [11]).

f units of 10^{-12}cm^{3}molecule^{-1}.

Table 2.17: Rate constant ratios, absolute rates and literature values for the reactions of OH radicals with aliphatic and cyclic ketones.

KETONE	$k_1/k_2{}^{a}$	$k^{g,h}$
Cyclobutanone	$0\ 104\pm0.003^{b}$	31 ± 9
	$0\ 104\pm0.003^{c}$	27 ± 1
Cyclopentanone	$1\ 85\pm0.07^{b}$	105 ± 32
	0.293 ± 0.013^{c}	91 ± 4
Cyclohexanone	0.778 ± 0.051^{d}	175 ± 26
	0.608 ± 0.019^{c}	156 ± 7
Cycloheptanone	$1.323\pm0.04^{d,\ f}$	297 ± 45
	$0.609\pm0.01b^{e}$	189 ± 9
2-Methylcyclopentanone	$0.721\pm0.027^{d,\ f}$	162 ± 24
2-Methylcyclohexanone	$0\ 994\pm0.016^{d,\ f}$	224 ± 34
4-Methylcyclohexanone	$0.866\pm0.042^{d,\ f}$	195 ± 29
3-Methyl-2-butanone	1.241 ± 0.058^{b}	71 ± 21
3-Methyl-2-pentanone	$2.42\pm0.043^{b,\ f}$	138 ± 41
2-Methyl-3-pentanone	1.987 ± 0.055^{b}	113 ± 34
2-Methyl-3-hexanone	$0\ 933\pm0\ 026^{d}$	210 ± 31
5-Methyl-2-hexanone	$0\ 929\pm0\ 028^{d}$	209 ± 31
2-Methyl-3-heptanone	$1.22\pm0\ 05^{d}$	275 ± 41
5-Methyl-3-heptanone	$1.157\pm0\ 042^{d}$	260 ± 39

a errors quoted were calculated from the chromatographic reproducibility of the data.

b reference ethane.

c reference cyclopentane.

d reference n-butane

e reference cyclohexane.

f errors are $\pm 2\sigma$ from the least squares analysis of the data.

g units of $10^{-12}\text{cm}^{3}\text{molecule}^{-1}\text{s}^{-1}$

h errors include errors in the reference value.

Table 2.18: Rate constants and absolute values for the reactions of ketones and cycloketones with Cl atoms.

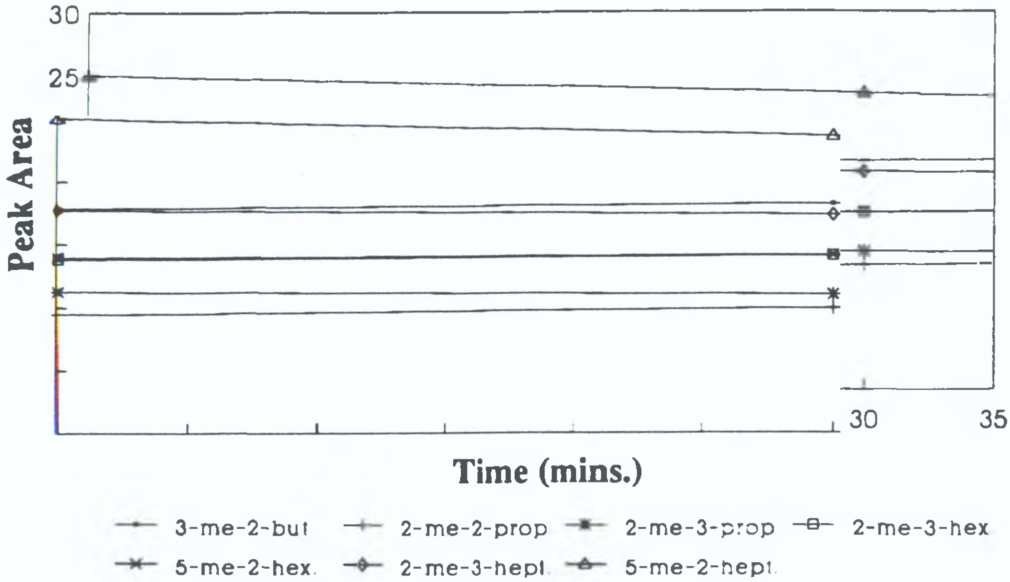

Figure 2.24: Light reactions for the OH radical reactions with ketones.

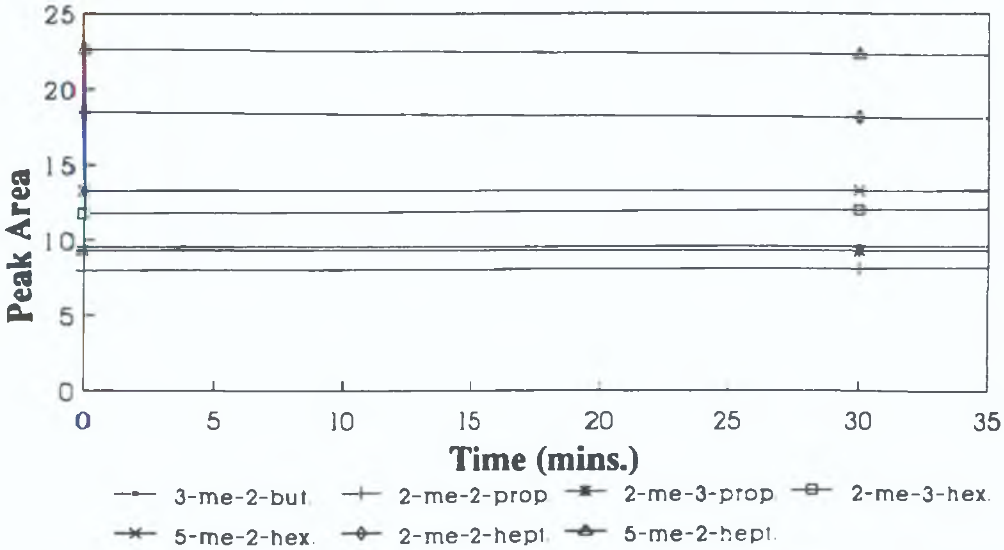

Figure 2.25: Light reactions for the Cl atom reactions with ketones.

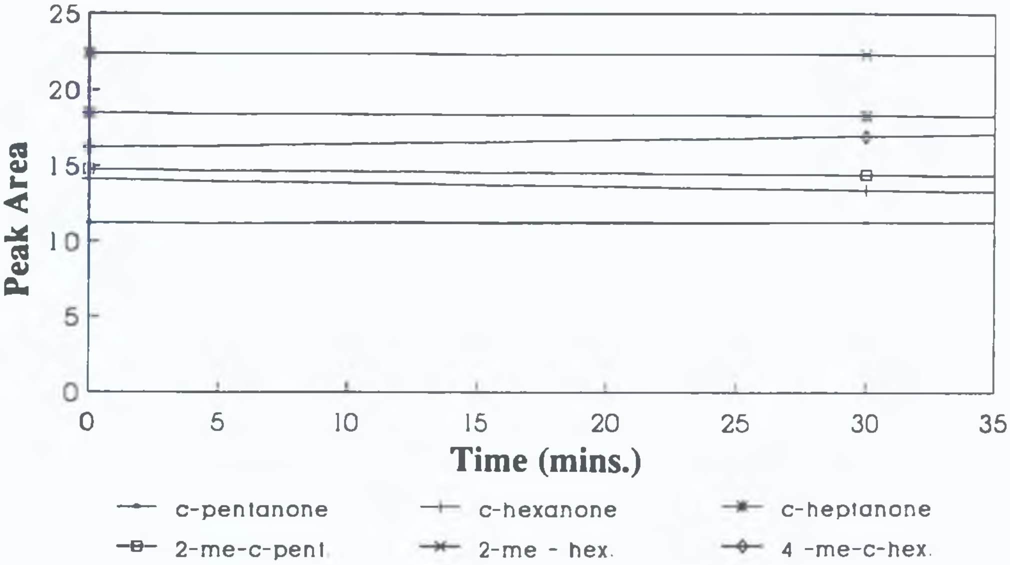

Figure 2.26: Light reaction for the reaction of OH radicals with cyclic ketones.

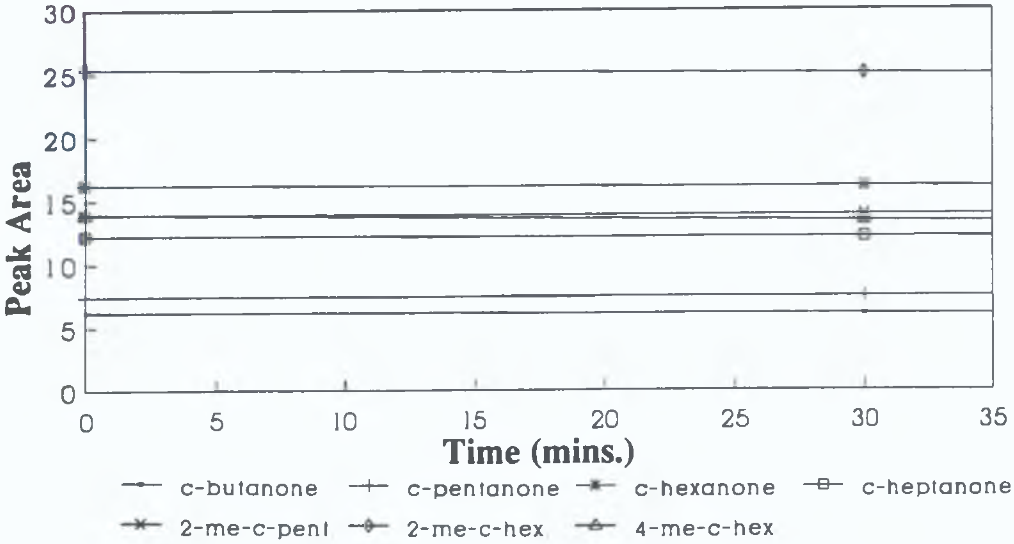

Figure 2.27: Light reaction for Cl atom reactions with cyclic ketones.

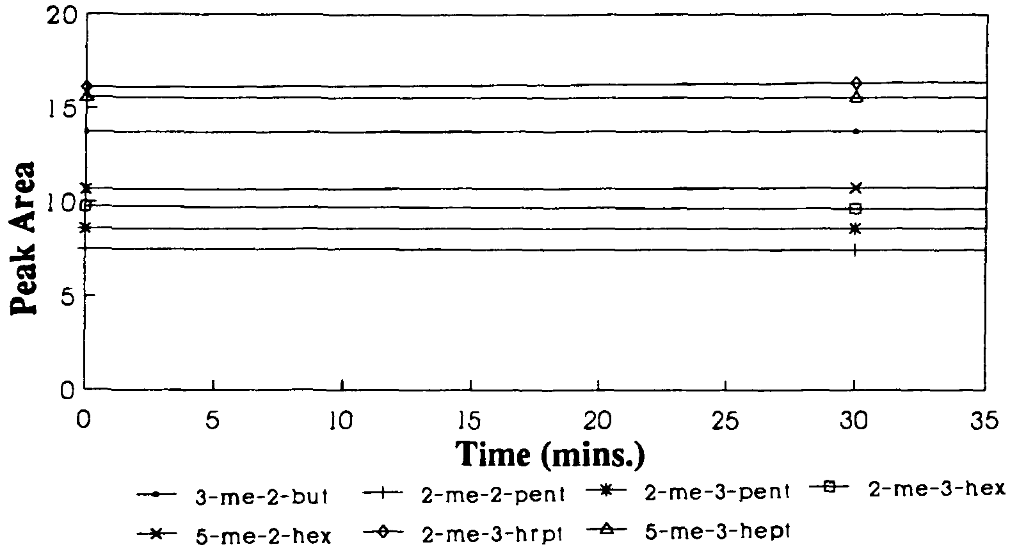

Figure 2.28: Dark reaction for the reaction of OH radicals and ketones.

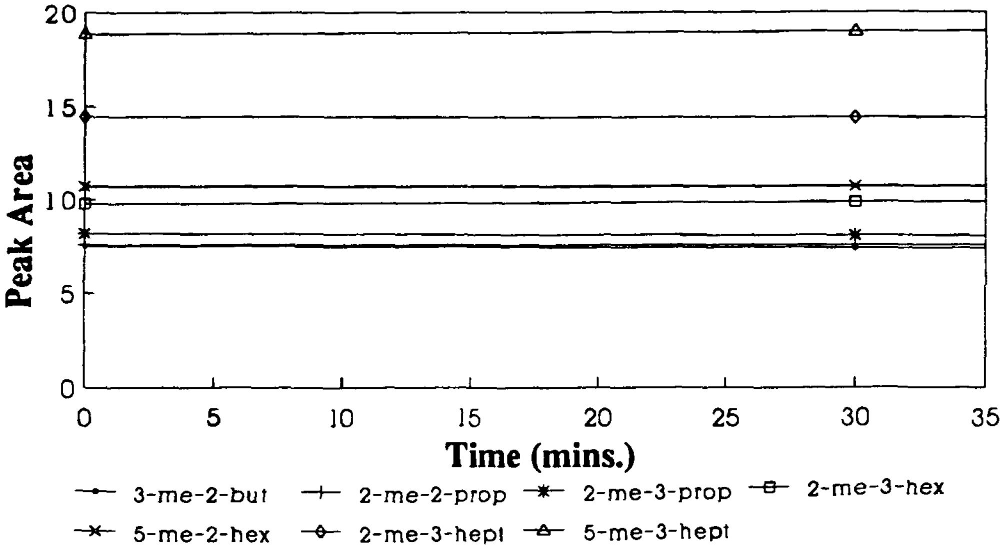

Figure 2.29: Dark reaction for Cl atom reactions with ketones.

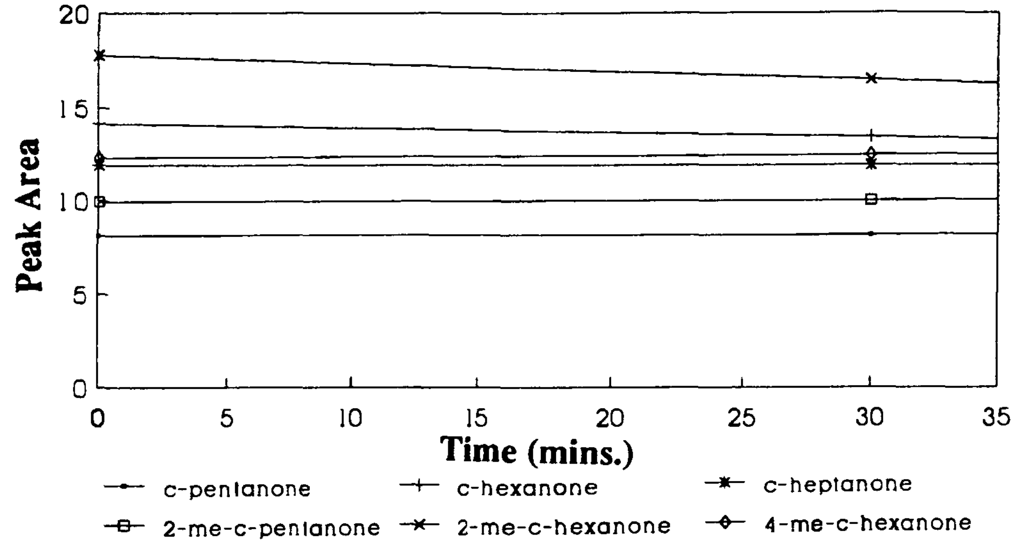

Figure 2.30: Dark reaction for OH radicals and cyclic ketones.

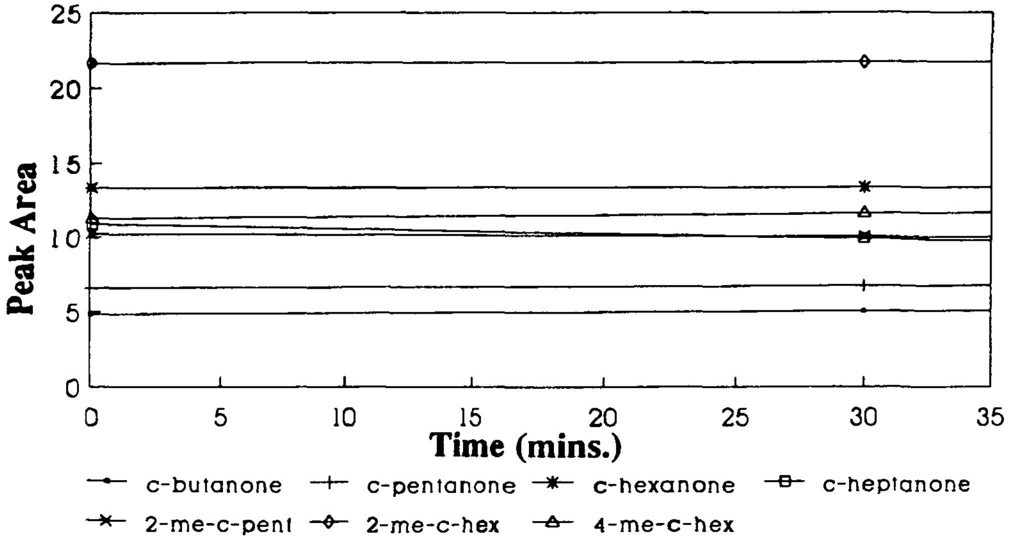

Figure 2.31: Dark reaction for Cl atoms with cyclic ketones

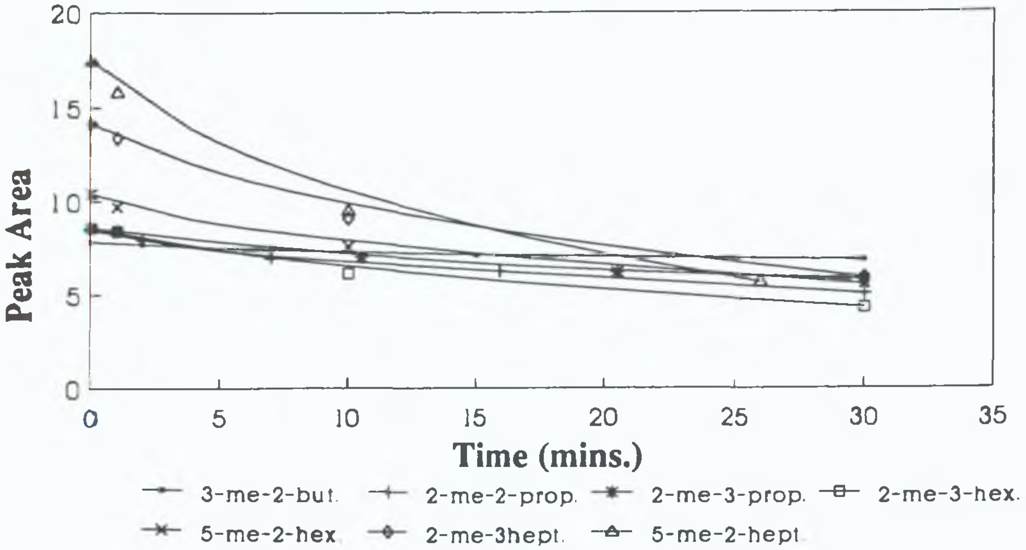

Figure 2.32: Decay curves for the reactions of OH radicals with ketones.

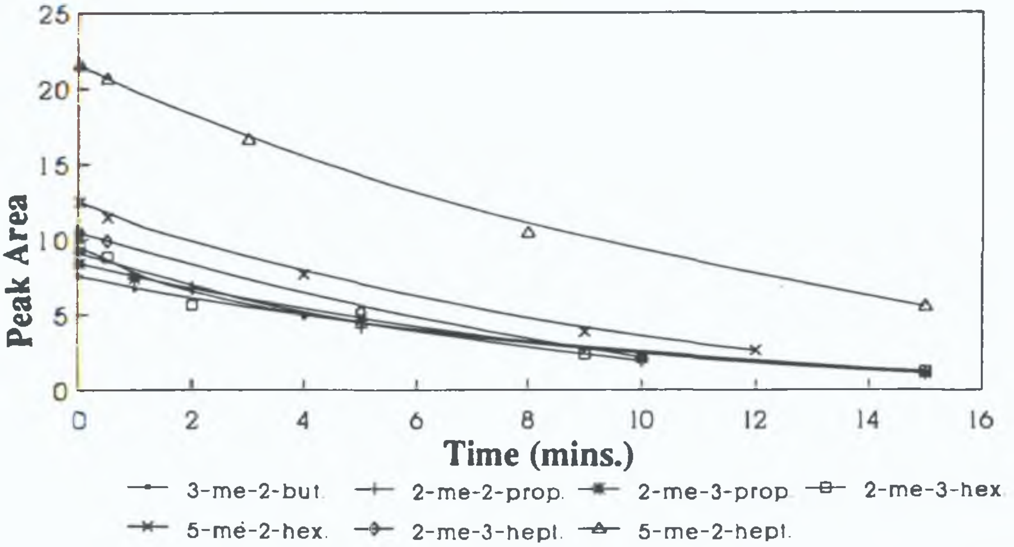

Figure 2.33: Decay curves for the reactions of Cl atoms with ketones.

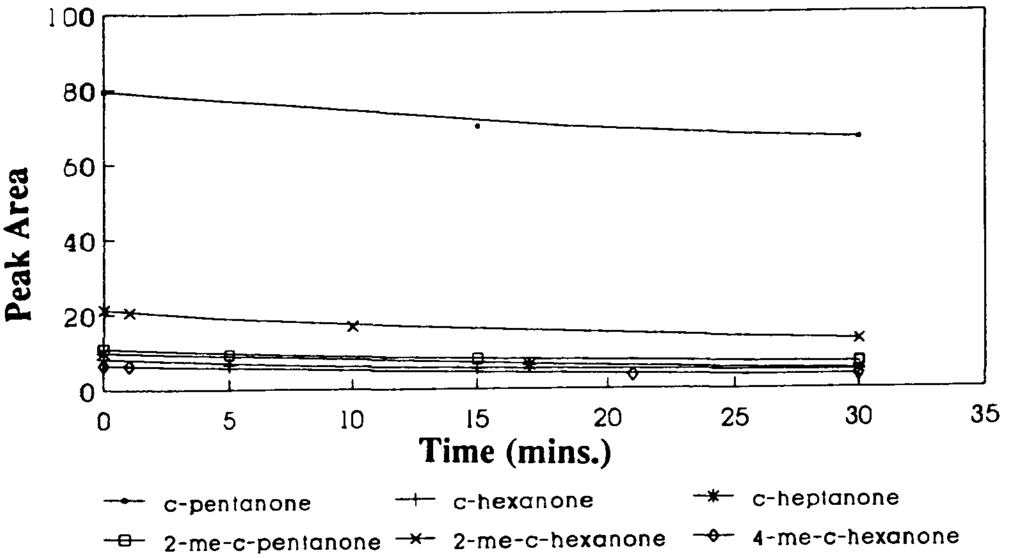

Figure 2.34: Decay profiles for OH radicals with cyclic ketones.

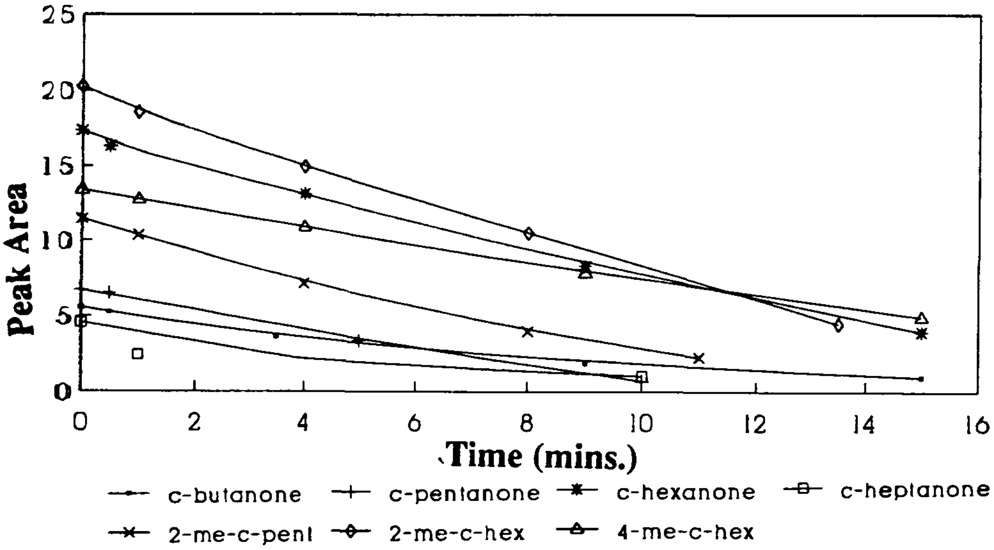

Figure 2.35: Decay profiles for the reactions of Cl atoms with cyclic ketones

Representative concentration-time plots for the reactions of aliphatic and cyclic ketones with OH radicals and Cl atoms are illustrated in the form of equation 2.15 in Figures 2.36 to 2.40. The rate constant ratios were calculated using a least squares analysis fo the concentration-time plots and the ratio values were placed on an absolute basis by calculating the product of the rate constant ratio (k_1/k_2) and the reference rate constant value (k_2).

Cyclohexane was used as the reference organic for the OH radical reactions except in the case of the OH + cyclohexanone reaction when cyclopentane was used. The reference rate constant value for cyclohexane was calculated from the Arrhenius expression quoted by Atkinson [11] which allowed the chamber temperature to be taken into consideration. For the Cl atom reactions ethane was used as the reference organic for the Cl + 3-methyl-2-butanone, 3-methyl-2-pentanone and 2-methyl-3-pentanone reactions while n-butane was used for the remainder of the organics. The rate constant value for Cl + ethane was taken from [14] and the rate value for Cl + propane was taken from [15]. Both reference rates were determined at temperatures similar to those used in our experiments. Cyclopentane was also used as the reference organic for the Cl atom reactions with the cycloketones; as there were no rate values for this organic listed in the literature we measured the rate constant using our system with cyclohexane as the reference organic.

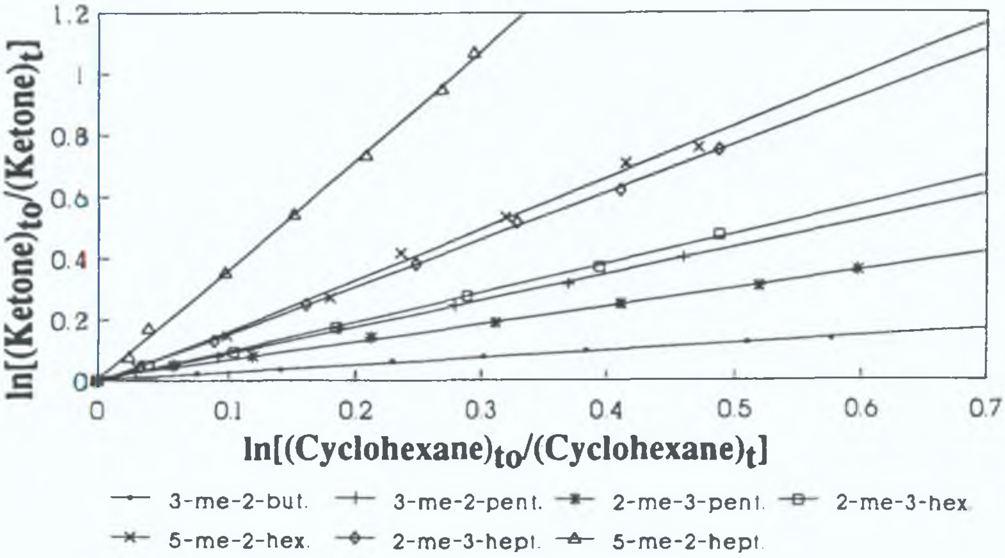

Figure 2.35: Plot of ln[(ketone)$_{to}$/(ketone)$_t$] vs ln[(cyclohexane)$_{to}$/(cyclohexane)$_t$] for OH radical reactions.

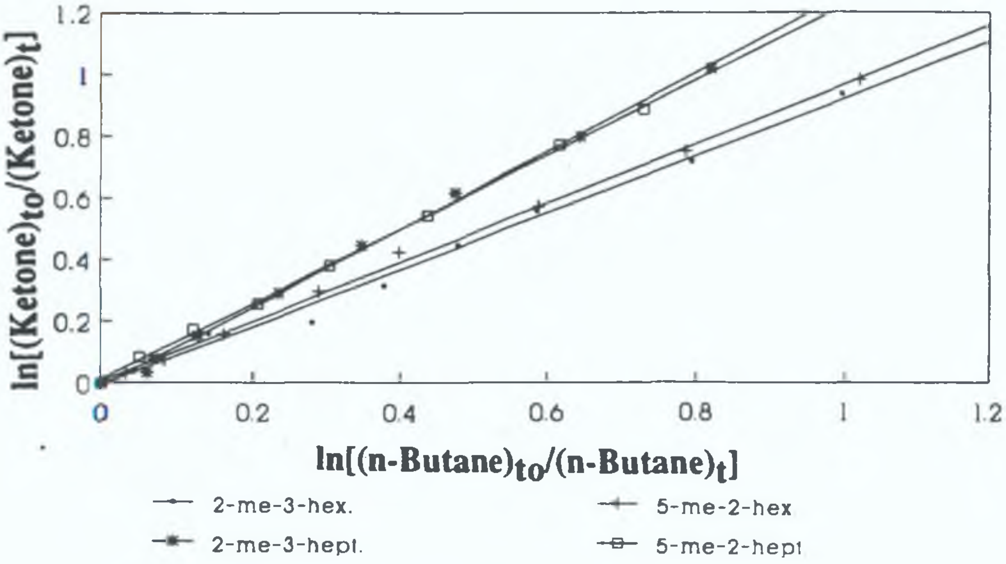

Figure 2.36: Plot of ln[(ketone)$_{to}$/(ketone)$_t$] vs ln[(n-butane)$_{to}$/(n-butane)$_t$] for Cl atom reactions.

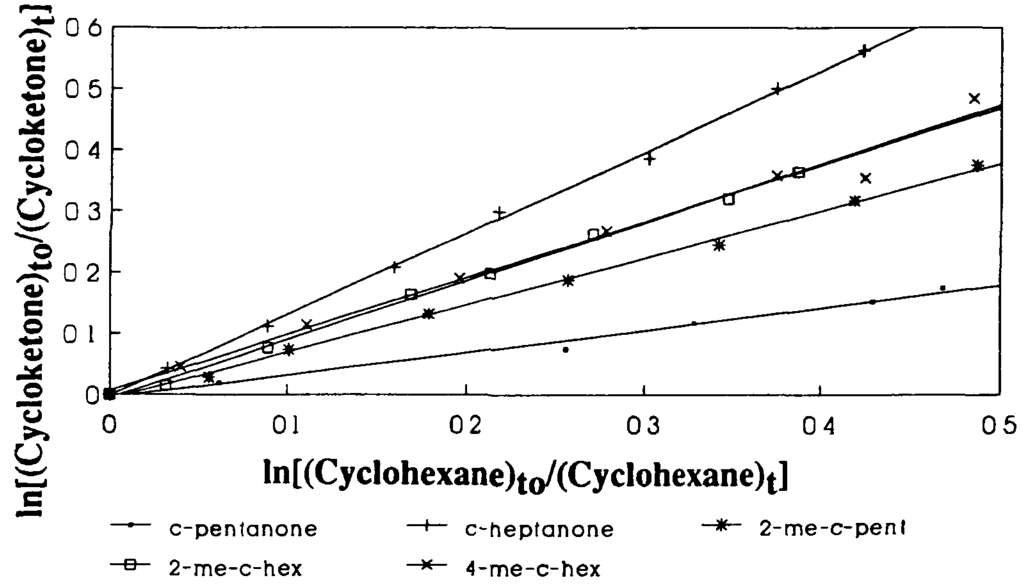

Figure 2.37: Plot of ln[(cycloketone)$_{t0}$/(cycloketone)$_t$] vs ln[(cyclohexane)$_{t0}$/(cyclohexane)$_t$] for OH radical reactions.

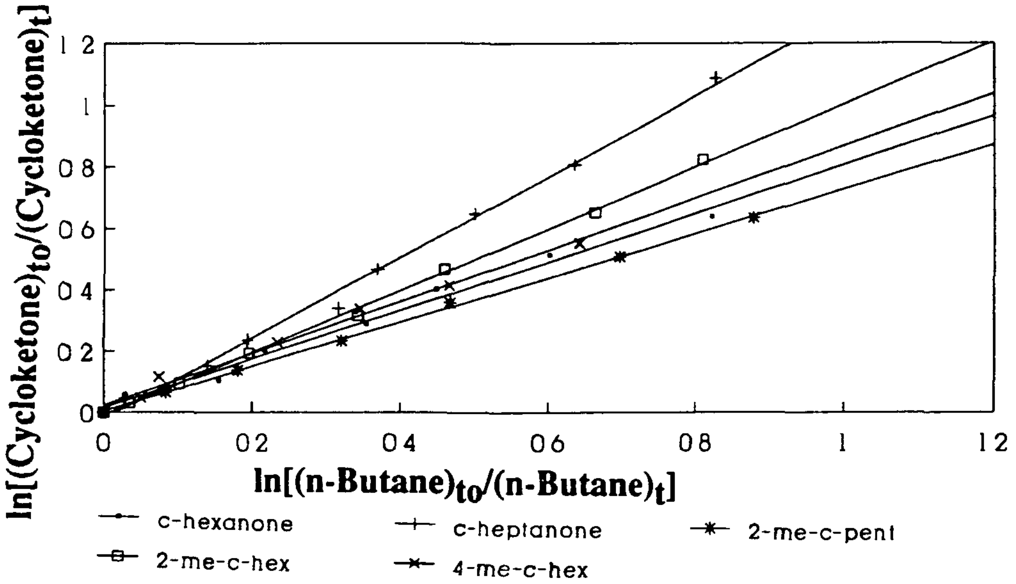

Figure 2.38: Plot of ln[(cycloketone)$_{t0}$/(cycloketone)$_t$] vs ln[(n-butane)$_{t0}$/(n-butane)$_t$] for Cl atom reactions

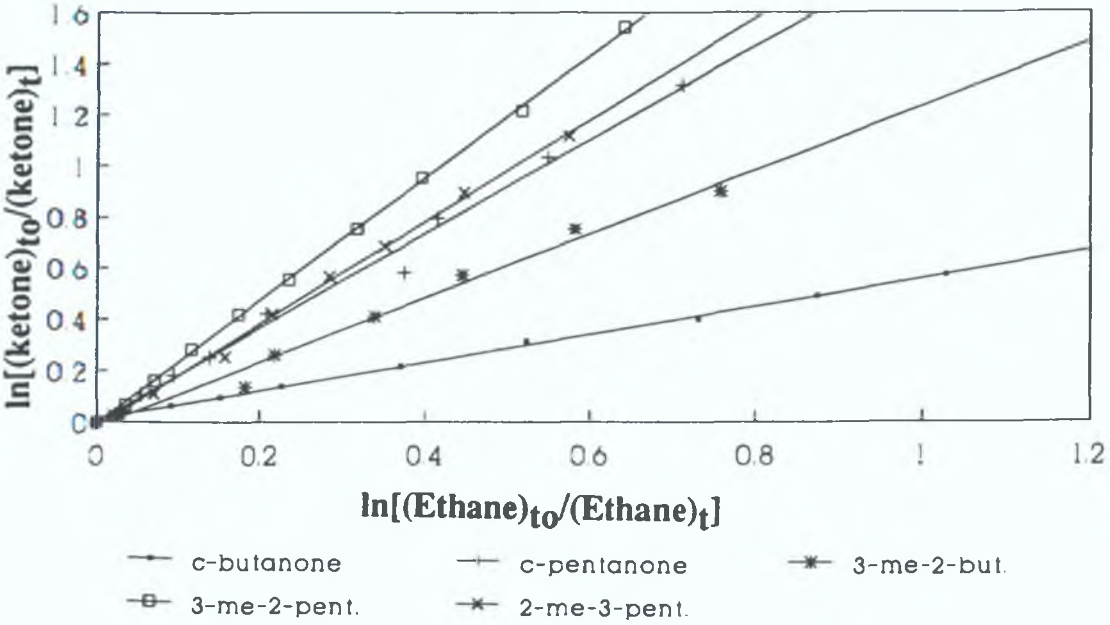

Figure 2.39: Plots of $\ln[(\text{ketone})_{to}/(\text{ketone})_t]$ vs $\ln[(\text{ethane})_{to}/(\text{ethane})_t]$ and $\ln[(\text{cycloketone})_{to}/(\text{cycloketone})_t]$ vs $\ln[(\text{ethane})_{to}/(\text{ethane})_t]$ for Cl atom reactions.

The errors in the reference rate constant data for the OH radical reactions were calculated by Atkinson [11] at 298K and were 25% for OH + cyclohexane and cyclopentane. The errors for the Cl atom reactions wre taken as: ± 30% for Cl + ethane [16], ± 15% for n-butane [15], ± 4.5% for Cl + cyclohexane [17] and ± 5% for Cl + cyclopentane [this work].

Table 2.19 lists the atmospheric lifetimes for the test compounds studied in this work for both OH radical and Cl atom reactions. A value of 7.7 ± 1.4 OH radicals cm^{-3} was used to calculate the atmospheric lifetimes with respect to OH radical reactions. This value was calculated over a seven year period and

KETONE	τ_{OH}[a] (hours)	τ_{Cl}[b] (days)
Cyclobutanone	113-164	1year
Cyclopentanone	113-164	110
Cyclohexanone	51-74	66
Cycloheptanone	32-46	39
2-Methylcyclopentanone	52-76	71
2-Methylcyclohexanone	42-60	52
4-Methylcyclohexanone	43-62	59
3-Methyl-2-butanone	155-225	163
3-Methyl-2-pentanone	46 66	84
2-Methyl-3-pentanone	68-98	102
2-Methyl-3-hexanone	40-58	55
5-Methyl-2-hexanone	23-33	55
2-Methyl-3-heptanone	25-36	42
5-Methyl-3-heptanone	11-16	45

a $\tau = 1/k[OH]$; $[OH] = 7.7 \pm 1\ 4 \times 10^5$ cm^{-3} [18].
b $\tau = 1/k[Cl]$; $[Cl] = 1 \times 10^3$ cm^{-3} [13].

Table 2.19: Atmospheric lifetimes for the OH radical and Cl atom reactions with ketones and cycloketones used in this work.

represents a globally avaraged value [18]. A value of 1 x 10^3 Cl atoms cm^3 was used to calculate the atmospheric lifetimes for the Cl atom lifetimes [13].

2.4.4 DISCUSSION

The kinetic data on ketones contained in this section of work is among the first reported using the relative rate technique in conjunction with a smog chamber. Although we had previously carried out validation reactions on our equipment and experimental technique as described in Section 2.3, I felt that this procedure was again necessary considering the difficulty in obtaining "clean" samples while cleaning the bag; another consideration was the potential problem of first-order wall losses of the ketones during irradiation which had been observed by Atkinson [7]. Of the organics we chose to study, two of these had previously been examined i.e cyclopentanone and cyclohexanone using an absolute technique [11]. There is excellent agreement (<10%) between these values and those calculated in this work (refer to Table 2.17) which indicated that our system was functioning to a high degree of accuracy. As there are no published data for Cl atom reactions with ketones or cycloketones these reactions were the only validation reactions carried out at this point.

The relative rate constants and their absolute values for both the Cl atom and OH radical reactions are listed in Tables 2.17 and 2 18. For the OH radical reactions the errors in the rate constant ratios represent ± 2σ from the least squares analysis of the data. In some cases i.e. OH + cyclopentanone, 2-methyl-cyclopentanone and 2-methyl-3-pentanone and for the majority of the Cl atom reactions, the errors quoted for the rate constant ratios were calculated from the chromatographic reproducibility of the data, that is samples were taken over a fixed time period usually sixty minutes and the reproducibility of the data calculated. In cases where the chromatographic reproducibility exceeded the ± 2σ value from the least squares analysis of the data this value was quoted as the overall error on the rate constant ratio. In most cases the errors in the ratio values do not exceed ± 5%. The errors in the absolute values include the errors in the reference values.

To ensure that the only reactions taking place in our system were between the organics and either OH radicals or Cl atoms, the stability of the organics was monitored both in the dark (to determine whether the compounds reacted with either $CH_3ONO\backslash NO$ or Cl_2) and in the presence of radiation (to establish whether the organic reactants themselves could undergo photolysis by the lamps). From Figures 2.23 to 2.30 it was concluded that the only reactions taking place in the chamber were between the reactants and OH radicals or Cl atoms depending on which system was being studied. Decay curves for each test and reference organic were also used to eliminate potential problems due to the formation of secondary products which may interfere with the chromatographic analysis of the reactant mixtures (Figures 2.31 - 2.34). In cases where interferences were detected either the chromatographic conditions or the choice of reference organic was altered. This was the case for the OH + cyclohexanone reaction where a product arising from the photolysis of cyclohexane could not be chromatographically separated from the cyclohexanone peak; this accounts for the use of cyclopentane as the reference organic. From the decay profiles, which gave a rough indication of the degree of reaction i.e. fast or slow over the time scale of the experiments, the optimum analytical conditions were established and were then used to monitor the reactant concentrations during the reactions with OH radicals and Cl atoms.

The reference organics used for the OH radical systems were cyclopentane and cyclohexane; for the Cl atom reactions ethane and n-butane were used, however, cyclopentane was also used in the cyclic ketone reactions. As the rate value for this organic had not been cited in the literature we calculated the rate constant value using cyclohexane as the reference organic using our system. On examining the absolute values listed in Table 2.18 for the Cl + cyclic ketone reactions, it is apparent that there are large differences between the rates calculated using both ethane and cyclopentane as the reference organics. The most reliable reference is considered to be ethane as the rate constant value is the average value calculated from several absolute measurements [15] whereas the rate value for cyclopentane was calculated using a reference that had only been measured twice using using the relative rate technique [17, 19].

The rate constant ratios were calculated from the slopes of the plots illustrated in Figures 2 35 - 2.39 which were analysed using a least squares method. All plots were linear with zero intercepts and correlation coefficients > 0 99 indicating the high degree of precision of our data. From the rate constant ratios the absolute values were subsequently calculated from the product of the reference value (k_2) and the ratio value (k_1/k_2).

Having determined the rate constants for the OH radical and Cl atom reactions with ketones and cyclic ketones, it is possible to investigate the effects of molecular structure on the reactivity. As the OH radical reactions have to a certain extent received more attention in the literature I propose to concentrate on these reactions first.

Table 2.20 shows the rate constant values for the reactions of OH radicals with a series of ket-2-ones, methyl ketones (studied in this work) and the parent alkanes.

It is interesting to observe that for the ket-2-ones (except 2-butanone) the rates are all higher than the respective n-alkanes; this has been attributed to the presence of the C=O group [7]. The position of the carbonyl group also affects the reactivity i.e. 2-pentanone and 2-hexanone are correspondingly faster than 3-pentanone and 3-hexanone which is attributed to the decativating effect of the carbonyl group on the α position and the activating effect at the β and γ positions relative to the C=O group. This enhancement of reactivity is thought to be due to the formation of an adduct species [12] which facilitates hydrogen-atom abstraction by OH radicals.

ORGANIC	k_{OH} at 298K[a]	REFERENCE
Butane	2.54±0.51	11
2-Butanone	1.2±0.02, 0.95±0.09	11
	0.97±0.17, 1.15±0.10	
3-Methyl-2-butanone	1.96±0.5	This Work
Pentane	3.94±0.99	11
2-Pentanone	4.74±0.14,4.0±0.19	11
3-Methyl-2-pentanone	6.7±1.7	This Work
3-Pentanone	1.85±3.3, 2.74±1.3	11
2-Methyl-3-pentanone	4.51±1.1	This Work
Hexane	5.61±1.40	11
2-Hexanone	9.16±0.61, 6.64±0.56	11
5-Methyl-2-Hexanone	13.45±3.4	This Work
3-Hexanone	6.96±0.29	11
2-Methyl-3-Hexanone	7.65±1.91	This Work
Heptane	7.15±1.79	11
2-Heptanone	8.67±0.84	11
2-Methyl-3-Heptanone	12.31±3.0	This Work
5-Methyl-3-heptanone	27.5±6.9	This Work

[a] units of 10^{-12}cm^{3}molecule^{-1}s^{-1}.

Table 2.20: Rate constants for the reaction of OH radicals with n-alkanes, ket-2-ones and methyl ketones at 298 K.

Our results further substantiate this ring formation as the magnitude of the rate constants for the methyl ketones are all larger relative to the values for the ket-2-ones. In all cases except the OH + 5-methyl-3-heptanone, the additional CH_3 groups are situated at the β position to the carbonyl group; in the case of 5-methyl-3-heptanone the CH_3 group is located at the γ position resulting in the reactivity being greater than twice that for OH + 2-methyl-3-heptanone.

Table 2.21 lists the rate values for a series of cycloalkanes, cyclic ketones and some methyl-cycloketones which were studied in this work. From the data it is apparent that the cyclic ketones are less reactive compared to the cycloalkanes which could be due to the presence of the carbonyl group and the fact that the formation of an adduct species is impossible due to the physical structure of these organics. A comparison of the room temperature reactivities per $-CH_2-$ group for both the cycloalkanes and the cycloketones are listed in Table 2.22. This shows that there is essentially no difference in both sets of values especially when the experimental error is taken onto consideration. These values indicate that there is probably no enhancement of reactivity at the β position in the cyclic ketones; a similar conclusion was reached by Dagaut et al in his study of OH radical reactions with some cyclic ketones [20]. In the case where there is a methyl group present, the reactivity of the organics increases accordingly.

ORGANIC	TEMP (K)	k_{OH} x10^{12}cm^{3}molec.$^{-1}$s^{-1}	REFERENCE
Cyclobutane	298	1.2±0.3	[11]
Cyclobutanone	298	0.87±0.06	[11]
Cyclopentane	305	5.28±1.1	[11]
Cyclopentanone	305	2.69±0.7	This Work
2-Methylcyclopentanone	304	5.82±1.5	This Work
Cyclohexane	306	7.67±1.9	[11]
Cyclohexanone	307	5.94±1.2	This Work
2-Methylcyclohexanone	305	7.33±1.8	This Work
4-Methylcyclohexanone	305	7.10±1.8	This Work
Cycloheptane	300	12.45±2.0	[11]
Cycloheptanone	306	9.58±2.4	This Work

Table 2.21: A comparison of the OH radical rate constants for cycloalkanes and cyclic-ketones

ORGANIC	ALKANE		KETONE	
	k_{OH}	$-CH_2-$ REACTIVITY	k_{OH}	$-CH_2-$ REACTIVITY
	x10^{12}cm^{3}molec.$^{-1}$s^{-1}		x10^{12}cm^{3}molec.$^{-1}$s^{-1}	
c-But.	1.2±0.3	0.3±0.08	0.87±0.06	0.29±0.02
c-Pent.	5.16±1.03	1.03±0.21	2.69±0.67	0.67±0.17
c-Hex.	7.49±1.87	1.25±0.31	5.94±0.12	1.19±0.02
c-Hept	11.8±0.2	1.48±0.03	9.58±2.4	1.60±0.40

Table 2.22: OH radical rate constants and $-CH_2-$ group reactivities for cycloalkanes [11] and cycloketones [this work].

A comparison between our data and the data calculated using Atkinson's SAR estimation technique [21] using the updated values for k_{prim}, k_{sec} and k_{tert} as calculated by Kerr [22] (refer to Table 2 23) shows that the reactivities for the cyclic-ketones are overestimated while the reactivities for the methyl ketones are underestimated. The substituent factors F(X) used to calculate these reactivities do not consider the activating or deactivating effect due to the presence of the carbonyl function which results in large discrepancies between the experimental and estimated values especially in the case of the larger ketone molecules (2-methyl-3-hexanone, 5-methyl-2-hexanone, 2-methyl-3-heptanone and 5-methyl-3-heptanone) which contain groups at the γ and δ positions and based on previous results indications are that these groups would be more reactive compared to those groups located at the α position.

Atkinson [7] and Wallington [12] both calculated group reactivities for ketones based on the reactivities of a series of ket-2-ones (see Table 2.24). Atkinson assumed that the hydrogen-atom abstraction rate from the primary C - H bonds occurred at a similar rate as in alkanes i.e. 2 x $10^{-13}cm^3molecule^{-1}s^{-1}$ and thus calculated only the reactivities of $-CH_2-$ and >CH- groups at α and β positions in the organics, whereas Wallington's calculations show the variation in reactivity of both $-CH_3$ and $-CH_2-$ groups at α and β positions; these reactivities were updated as more kinetic data became available [20].

KETONE	k_{OH}[a]	REF.	SAR[a, b]
Cyclobutanone	0.87±0.06	11	1.23
Cyclopentanone	2.69±0.7	This Work	6.22
Cyclohexanone	5.82±1.5	This Work	7.23
Cycloheptanone	5.94±1.2	This Work	9.17
2-Methylcyclopentanone	7.33±1.8	This Work	9.57
2-Methylcyclohexanone	7.10±1.8	This Work	11.10
4-Methylcyclohexanone	9.58±2.4	This Work	10.56
3-Methyl-2-butanone	1.96±0.5	This Work	1.93
3-Methyl-2-pentanone	6.70±1.7	This Work	3.43
2-Methyl-3-pentanone	4.51±1.1	This Work	2.92
2-Methyl-3-hexanone	7.65±1.91	This Work	6.31
5-Methyl-2-hexanone	13.45±3.4	This Work	8.49
2-Methyl-3-heptanone	12.31±3.0	This Work	8.66
5-Methyl-3-heptanone	27.50±6.9	This Work	13.78

a units of $10^{-12} cm^{3} molecule^{-1} s^{-1}$.

b calculated from work of Atkinson [21].

Table 2.23: A comparison between experimental values and values calculated using the SAR estimation technique for OH radical reactions with a series of methyl ketones and cycloketones.

POSITION	REACTIVITY $x10^{12}cm^3molec.^{-1}s^{-1}$		
	$-CH_3$	$-CH_2-$	$>CH-$
α	0.11[20]	0.73 [7] 0.91[20]	2.3[7]
β	0.37[20]	3.6[7] 3.46[20]	13.0[7]
γ	<0.37[20]	---	---

Table 2.24: Group reactivities for the reactions of OH radicals with ket-2-ones as calculated by Atkinson [7] and Wallington [20].

From our results it was possible to calculate the reactivity of >CH- groups at the α and γ positions in the methyl ketones using both Atkinson's and Wallington's values for the $-CH_3$ and $-CH_2-$ groups. These values are listed in Table 2.25.

Atkinson's assumption that the reactivity of the CH_3 group is identical in both ketones and alkanes is not valid in light of the present conclusions therefore it would be more acceptable to chose the results based on Wallington's calculations.

It is unfortunate that the choice of organics in this work did not facilitate the calculation of β >CH- reactivities however it is apparent that the reactivity at the γ position is much greater than at the α position. This suggests that the influence of the carbonyl group reaches to two carbon atoms from the carbonyl group, however only further investigations in this area will support this statement.

ORGANIC	METHOD	REACTIVITY^a	
		αCH	γCH
3-Methyl-2-butanone	Atkinson Wallington	1.36 1.11	
3-Methyl-2-pentanone	Atkinson Wallington	2.50 2.39	
2-Methyl-3-pentanone	Atkinson Wallington	0.31 2.56	
2-Methyl-3-hexanone	Atkinson Wallington	2.73 3.02	
5-Methyl-2-hexanone	Atkinson Wallington		8 52 8.23
2-Methyl-3-heptanone	Atkinson Wallington	3.75 5.04	
5-Methyl-3-heptanone	Atkinson Wallington		21.85 21.25

a units of $10^{12}cm^3molecule^{-1}s^{-1}$.

Table 2.25: >CH- reactivities at the α and the γ position in methyl ketones calculated using $-CH_3$ and $-CH_2-$ reactivities calculated by Atkinson [7] and Wallington [20].

A compromise between Atkinson's SAR technique [21] and the group reactivity method calculated by Wallington [12, 20] would probably give the most effective method for predicting rate constants for the reactions of OH radicals with ketones by calculating k_{prim}, k_{sec} and k_{tert} and substituent factors F(X) which take the activating or deactivating effect of the carbonyl function into account

To date there has been no published information available on the reaction of Cl atoms with ketones. It is reasonable to assume however, that these reactions should proceed via a hydrogen-atom abstraction reaction in a similar fashion to the OH radical reactions with ketones as both species are electrophilic. Whether or not an adduct species is formed in the transition state remains to be seen. Table 2.26 shows a comparison of the reactivities for the reactions of Cl atoms with a series of n-alkanes, ket-2-ones and the methyl ketones studied in this work. converse to the OH radical reactivities, the rate values for the ket-2-ones are greater than those for the analagous alkanes; however, the rates for pentan-2-one and hexan-2-one are greater than the values for pentan-3-one and hexan-3-one. The reactivities for the methyl ketones are larger than the rates for the ketones. These results would suggest that that the presence of the carbonyl group also adversly influences the Cl atom reactivities but the formation of an adduct species is questionable.

As expected, the reactivities of the cyclic ketones with Cl atoms are less than the reactivities for Cl atom reactions with cycloalkanes. Table 2.27 lists these reactivities along with the reactivity per -CH_2- group. Unlike the OH radical reactions the -CH_2- reactivities for the cyclic ketones are less than the values for the cycloalkanes. This could be due the the greater influence of the carbonyl function over the molecules and that the presence of an oxygen atom would have a repelling effect on the incoming Cl atom.

ORGANIC	k_{Cl} x10^{11}cm^{3}molec.$^{-1}$s^{-1}	REFERENCE
n-Butane	22.5±3.4	16
2-Butanone	32.1±5.6	23
3-Methylbutanone	7.10±2.1	This Work
n-pentane	31.0±1.6	19
	25.2±1.2	17
2-Pentanone	10.17±1.75	23
3-Methyl-2-butanone	13.8±4.1	This Work
3-Pentanone	7.06±1.34	23
2-Methyl-3-pentanone	11.3±3.4	This Work
n-Hexane	34.5±2.3	19
	30.3±0.6	17
2-Hexanone	18.94±3.22	23
5-Methyl-2-Hexanone	20.9±3.1	This Work
3-Hexanone	14.8±3.8	23
2-Methyl-3-hexanone	21.0±3.1	This Work
n-Heptane	34.1±1.2	17
2-Heptanone	23.54±3.97	23
2-Methyl-3-heptanone	27.5±4.1	This Work
5-Methyl-3-heptanone	26.0±3.9	This Work

Table 2.26: A comparison of the rate constant values for the reactions of Cl atoms with n-alkanes, ketones and methyl ketones.

ORGANIC	k_{Cl}^{a}	REF.	$-CH_2-$ REACTIVITY^{a}
Cyclobutane	-------	Not Available	
Cyclobutanone	3 1±0.9	This Work	1.03±0.3
Cyclopentane	25.7±1 2	This Work	5.17±0.24
Cyclopentanone	10.5±3.2	This Work	2.63±0.80
2-Methyl cyclopentanone	16 2±2 4	This Work	
Cyclohexane	36.1±1 5	[19]	5 6±0.25^{b}
	31.1±1 4	[16]	
Cyclohexanone	17.5±2 6	This Work	3.5±0.15
2-Methyl cyclohexanone	22.4±3 4	This Work	
4-Methyl cyclohexanone	19.5±2.9	This Work	
Cycloheptane	-------	Not Available	
Cycloheptanone	29 7±4.5	This Work	4.95±0.75

a units of $10^{11}cm^{3}molecule^{-1}s^{-1}$

b calculated from the average of the results from [7] and [17]

Table 2.27: A comparison of the rate constant values for the reactions of cycloalkanes and cyclic ketones and the reactivities of the rate constants per $-CH_2-$ group.

McLoughlin [23] used Wallington's group reactivity theory [12] to calculate the reactivities of the aliphatic chains for the Cl atom reactions with the ket-2-one organics (refer to Table 2.28) and also the reactivity of the -CH_2- groups at the α, β, γ and δ positions in the ketones (Table 2.29). From these results the >CH- reactivities at the α and the γ positions can be calculated from our rate values of the Cl atom reactions with the methyl ketones, these values are listed in Table 2.30.

R	$k_{CH_3(CO)R}$ $\times 10^{11} cm^3 molec^{-1} s^{-1}$
CH_3	0.05
C_2H_5	3.16
C_3H_7	10.12
C_4H_9	18.89
C_5H_{11}	23.49

Table 2.28: The reactivity of linear aliphatic chains in ketones calculated from the Cl atom rate constants measured by McLoughlin [23].

POSITION RELATIVE TO C=O GROUP	REACTION RATES $x10^{11}cm^3molec.^{-1}s^{-1}$	
	$-CH_3$	$-CH_2-$
α	0.05	3.06
β	0.05	7.01
γ	0.05	8.77
δ	0.05	4.66

Table 2.29: The reactivities of $-CH_3$ and $-CH_2-$ groups in ketones as calculated by McLoughlin [23] for Cl atom reactions with aliphatic ketones.

KETONE	REACTIVITY $x10^{11}cm^3molec.^{-1}s^{-1}$	
	α CH	γ CH
3-Methyl-2-butanone	6.95	
3-Methyl-2-pentanone	6.64	
2-Methyl-3-pentanone	8.04	
2-Methyl-3-hexanone	9.88	
5-Methyl-2-hexanone		10.68
2-Methyl-3-heptanone	8.51	
5-Methyl-3-heptanone		15.02

Table 2.30: >CH- reactivities at the α and γ positions in methyl ketones calculated in this work.

As with the OH radical reactions the reactivities of the >CH- group are larger in the γ position compared to the α position; however it must be considered that in these calculations the $-CH_3$ reactivities were assumed to remain constant when the reactivity would more than likely vary from position to position. To verify this assumption more kinetic studies of this nature must be carried out.

When comparing the reactivities of the OH radical reactions and the Cl atom reactions with the ketones studied in this work it is apparent that the magnitude of the reactivities for the Cl atom reactions are at least ten times greater than for the corresponding OH radical reactivities. This has been attributed to the fact that the preexponential A factor for Cl atom reactions is a magnitude larger than the value calculated for OH radical reactions [25].

Table 2.19 lists the atmospheric lifetimes calculated for the Cl atom and OH radical reactions with the ketones studied in this work. Although the lifetimes with respect to the Cl atom reactions are much larger compared to the OH radical lifetimes the fact that OH radicals are approximately 1000 times more abundant in the troposphere [13] ensures that the removal mechanisms for the ketones will be predominantly by reaction with OH radicals.

The OH radical lifetimes for the ketones are very short with the maximum lifetime being 225 hours (approximately 10 days) for 3-methyl-2-butanone; therefore these compounds will be rapidly removed before they can be transported to higher regions of the atmosphere. It must be stressed however, that these values are subject to several uncertainties which includes the rate of formation of these compounds in the troposphere as the result of the photooxidation of primary pollutants in the atmosphere.

2.4.5 CONCLUSION

Using a smog chamber in conjunction with the relative rate technique, accurate and precise rate constants were measured for the reactions of OH radicals and Cl atoms with a series of aliaphtic and cyclic ketones. Atmospheric lifetimes for these organics were calculated from the rate constants measured in this work. The rate constants for the Cl atom reactions were 10 to 30 times faster compared to the OH radical reactions; however, as OH radicals are more abundant in the troposphere the dominant loss process for these organics will be via reaction with OH radicals. The tropospheric lifetimes are small ensuring that these compounds will be rapidly removed from the troposphere.

The data obtained in this work supports previous conclusions that an adduct species is formed in the transition stage of the hydrogen-atom abstraction reactions involving ketones and OH radicals as the reactivities for the methyl ketones (where a methyl group was introduced at the β position relative to the carbonyl functional group) were correspondingly larger than the ket-2-ones; low reactivities for cyclic $-CH_2-$ groups were also calculated which further supports our statement in that the formation of an adduct species would be impossible in these cases. From our results we calculated that the reactivities for tertiary hydrogen-atom abstraction are greater in the γ position relative to the α position in ketone compounds.

We also concluded that the formation of an adduct species in the Cl atom reactions with the ketones is questionable due to the difference in reactivity trends observed for the OH radical and Cl atom reactions; this may be as a result of an oxygen atom in the carbonyl group which would have a repelling effect on the incoming Cl atom; this would account also for the decrease in the group reactivities for the cyclic ketones compared to the cycloalkanes.

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CHAPTER 3

A FEASIBILITY STUDY OF THE PERFORMANCE OF A PEAT BIOFILTER IN THE REMOVAL OF DICHLOROMETHANE FROM AN ARTIFICIAL GAS STREAM

3.1 INTRODUCTION

With increasing global environmental problems, stronger regulations are being implemented in the industrial sector with regard to the control of emissions of waste into the atmosphere; as a result, environmental research in the area of emissions of toxic and odorous compounds into the atmosphere has increased. Traditionally, gaseous pollutants emitted by industrial or agricultural sources were considered a nuisance primarily due to the strong smell associated with them. However, due to increased awareness, gaseous pollutants are now considered as potential health hazards and also damaging to the Earth's atmosphere, especially if the waste gases contain halogenated compounds.

Many branches of industry produce waste gases which contain odorous organic or inorganic components which can be of synthetic or natural origin. Synthetic pollutants are products from chemical and processing industries e.g. paint and dye companies and pharmaceutical industries. Odorous components of natural origin generally originate from the food industry e.g. sugar factories, sewage treatment works and breweries.

An important category of toxic compounds emitted from industrial sources are volatile organic compounds (VOCs). While these compounds are often carcinogenic (e.g. benzene) the main concern about VOCs is in the formation of photochemical oxidants. Some halogenated organics such as CFCs can cause perturbations in the Earth's atmosphere resulting in the depletion of the ozone layer.

Chlorinated hydrocarbons are an important category of VOCs and are produced in enormous quantities every year throughout the world. These organics are widely used in industry as solvents, degreasing agents, pesticides and intermediate compounds in production processes. For example. the production volumes of some chlorinated organic compounds in the U.S. in 1991 are listed in Table 3.2 [1]. Because of the volatility of VOCs, the quality of air emissions are an important consideration for those industries that both manufacture and use these organics.

ORGANIC	tonnes x 10^3
Carbon tetrachloride	na[a] (188 in 1990)
Chloroform	na[a] (220 in 1990)
Ethyl chloride	na[a] (66 in 1990)
Ethylene dichloride	6,327
Methyl chloride	356
Methylchloroform	295
Methylene chloride	177

na - not available

Table 3.1: Volume of chlorinated organic compounds produced in the U.S. in 1991 [1].

A number of methods are available to eliminate odorous and toxic components from waste gas streams. These methods may be classified as:

(a) gas phase methods
(b) liquid phase removal systems
(c) solid phase removal systems
(d) combustion systems

Gas phase methods include scrubbing with chlorine, ozone, hypochlorite or permanganate. These methods are rapid and remove approximately 95% of reactive VOCs in waste gases; however, this method can be ineffective for slowly reacting compounds. In addition, the chemical oxidants are corrosive and hazardous and the method itself is expensive to implement [2]. Another technique in this category is masking odorous smells by using a more acceptable odour which quite often causes an even more unpleasant smell.

In the case of liquid phase emission control systems, the pollutants are in contact with a liquid phase in which the pollutants are absorbed. This method is most effective when the waste compound is soluble in the liquid phase however, the rate of elimination can be increased when the absorption process is followed by a chemical reaction i.e. an oxidation reaction

Biological regeneration processes which are also included in this category have been available since the 1960's [3] Under aerobic conditions (in the presence of oxygen) many odorous compounds of organic and inorganic origin as well as VOC's are oxidised by suitable microorganisms The microbial population can be dispersed in the liquid phase (bioscrubbers) or immobilised on a carrier material which is surrounded by a liquid phase (trickling filter columns).

In solid phase control systems the waste gas is in contact with a solid phase where the waste molecules are bound to the surface of the adsorbent by physical or chemical adsorption and are then eliminated from the waste gas. Activated carbon can be used as the solid phase and is particularly useful for odorous compounds. Activated carbon can adsorb 90-95% of the incoming waste components [2]; however, a major disadvantage of this method is saturation of the adsorbent which necessitates regeneration of the carbon material. This is an expensive process and quite often the material is dumped as solid waste which creates further elimination problems.

Biological filtration methods have also been introduced into this field where the filter beds contain an appropriate filter material such as compost, sludge or soil. Microorganisms may grow on this support material and use the waste compounds adsorbed in the bed as a carbon source, resulting in a continuous regeneration of the filter material which prevents ageing and permits a high biological activity which can be maintained over long periods of time (years). Biofiltration removes 80% to greater than 99% of a very wide range of VOCs depending on their chemical and biological reactivity [2].

Organic compounds can be incinerated to carbon dioxide and water at high temperatures with a 99% removal rate [2]. This removal method is very costly as it requires large amounts of fuel and often produces NO_X and HCl which are atmospherically undesirable species. In Ireland, toxic waste materials have to be shipped to England to be incinerated which further increases the cost of this process. Catalytic oxidation systems can also be used to eliminate organic compounds from waste gases; however, this method is only applicable to a few well defined waste gases due to poisioning of the catalyst by certain compounds.

Most of the available techniques for controlling gaseous emissions are highly capital intensive and may have very high operating costs. In general biological methods of emissions control have lower capital and running costs than competing technologies and may have the added advantage of not producing a new waste stream.

In spite of the ability of nature to recycle waste materials and to purify itself, the increasing demand placed on the Earth's environment during the last decades by large amounts of waste and pollutants could threaten the capacity of the natural systems to recover and maintain an environmental equilibrium. Biodegradation techniques could provide the means to ease the problem of pollution and ultimately preserve the environment. Biodegradation techniques are versatile and can be used at various stages of waste treatment, and also have cost advantages compared to competing methods of emissions control.

The principle of purifying air by contacting it with a microbial population has been known for some time. In 1953 a soil system was used for the treatment of odorous sewer gas in Long Beach California; in Europe, the first attempts (also with soil filters) were made in Gineva-Vilette, Switzerland, for the treatment of exhaust air from compost works. "Biofiltration", which is the generic name for the process, has since become a popular method of eliminating waste from agricultural sources in Germany and the Netherlands [4]. Because of the microbiological developments and technological research, interest in biological gas treatment systems is increasing. Biological methods have some specific advantages over conventional chemical and physico-chemical treatments.

Biological systems require little maintenance, are inexpensive to run as they use microbial rather than thermal or chemical oxidation and in the case of the biofilter system, natural filter materials are used as opposed to synthetic materials. Biological methods also actually remove the waste substrates as opposed to shifting the pollution problem to another phase like incineration methods and adsorption by activated carbon.

The three most common biological methods in use today are bioscrubbers, biotrickling filters and biofilters. They can be distinguished by the behaviour of the liquid phase (which is either continually moving or stationary) in the contact apparatus and the microorganisms can either be freely dispersed in the aqueous phase or immobilised on a carrier or a packing material.

In the bioscrubber system, the microbial population is freely dispersed in the water phase. The removal process is divided into two steps: (a) an absorption phase in a scrubber compartment where the water soluble components present in the waste gas are transferred to the liquid phase by contacting both phases intensively in a contact apparatus e.g. a spray column; and (b) a regeneration phase in an activated sludge tank where the water absorbed substances are oxidised and eliminated from the liquid phase. Physical and chemical conditions (e.g. temperature, pH, carbon to nitrogen to phosphorous ratio) in the scrubber need to be monitored to ensure optimal microbial oxidation.

A biotrickling filter consists of a column filled with a packing material which has a low specific area (100 - 300 m^2m^{-3}) in order to create a large void area for the gases passage; this minimises the pressure drop across the system and prevents obstruction of the void space by biological growths. Water containing essential inorganic nutrients is continuously supplied at the top of the column and distributed homogeneously within the filter. The water flows down the system and forms a thin film which surrounds the packing material and wets the biolayer. The waste gas is forced to flow counter-currently through the cloumn in order to obtain the greatest rate of absorption. Water soluble components are transferred to the liquid phase from which they diffuse to the biolayer where they are degraded by the microorganisms. The surface films are sloughed off continuously and as a result the drain water has to be kept separate from surplus biomass before it is recirculated. Due to evaporation, fresh water has to be supplied continuously to the system. In contrast to the bioscrubber method, the absorption process and regeneration is carried out simultaneously in one process apparatus.

A biofilter is the simplest of the biological emission control systems. In a biofilter the microorganisms are attached to a suitable packing material which contains the necessary nutrients for growth; the material may also contain additives (twigs/heather) to improve the filter packing structure. For the optimal operation of a biofilter, a minimum water content in the packing material is required because the microbial growth takes place in a "biolayer" around the packing material. A concentration gradient is created in the biolayer when air flows through the biofilter as there is a continuous mass transfer between the gas phase and the biolayer. Volatile pollutants present in the waste gas are partially dissolved in the biolayer and are degraded aerobically by microbial activity. The metabolic products then diffuse into the gas phase and leave the bed with the exit gas.

The nutrients necessary for maintaining microbial growth are supplied by the filter material, the most common materials being humus, compost, wood chips, peat and other related substances. The packing particles of a biofilter are usually of a size that provides both a reasonable adsorption surface and an acceptable flow resistance.

Depending on the nature of the organic compounds present in the waste gas, the filter bed sometimes needs innoculation with appropriate microorganisms to start biological activity. For components which are easily biodegradable, an activated sludge-suspension from a municipal waste water treatment plant may be used for the innoculation, as activated sludges contain a variety of microorganisms which are capable of eliminating a broad spectrum of organic compounds. When treating waste gases containing poorly degradable compounds or xenobiotics (man-made compounds) the filter material will need to be innoculated with specially cultivated microorganisms.

Bioscrubbers and biotrickling filters are more energy intensive than biofilters as water recirculation requires more energy than gas transport through a biofilter. The reliability of operation of bioscrubbers is smaller relative to the other biological methods as a consequence of the possible washing away of the active microorganisms. Also, the filter materials usually used in biofilters such as peat have a high buffering capacity which diminishes the sensitivity of the biofilter to different kinds of fluctuations such as water content and pH. A disadvantage of the biofilter is that it requires a longer filtration time so the volume of the filter bed must be relatively large compared to other removal methods. Multilayer filter beds can overcome this problem although the installation and maintenance costs will be higher.

The cost of a biofilter process is low compared to conventional physical and chemical processes. The cost depends on the total volume of the waste gas to be treated, on the concentration and the nature of the pollutants to be removed and on the cost of servicing the filter system with dust filters, heat exchangers, humidifiers etc.. Biofilters are commonly used for both industrial and agricultural applications whereas biotrickling filters are primarily used in non-industrial situations (compost production, agricultural and sewage treatment); bioscrubbers on the other hand are favoured in industrial situations [3].

Although the development of biofiltration techniques had the primary aim of eliminating odorous components in gas effluents, recent investigations have shown biofiltration to be applicable on a much broader scale in the prevention of air contamination with undesired compounds [5] Current research focuses on the biodegradation of xenobiotic compounds which biological organisms in the biosphere have not been exposed to in evolution.

The biodegradability of organic compounds generally reflects their source: they can be categorised as biogenic (of natural origin) or anthropogenic (man-made). Anthropogenic compounds can be divided into two groups - synthetic compounds and the xenobiotic compounds. Xenobiotic compounds are further sub-divided into weak, recalcitrant or persistent depending on the ease of biodegradability. Weak xenobiotics resemble biogenic compounds in that they are easily degraded whereas recalcitrant and persistent xenobiotics contain unnatural structures resulting in the biodegradability being very low (i.e. recalcitrant xenobiotics) or zero (i.e. persistent xenobiotics).

The removal and oxidation rates of VOCs depends on the biodegradability and reactivity of the gases. Table 3.2 lists the relative biodegradability of some VOCs.

Halogenated hydrocarbons are generally considered as "slow" or "very slow" degraders; however, during the 1980's much time and effort has been spent in developing new strains of microorganisms that are capable of degrading halogenated compounds Microorganisms have shown a tremendous ability to adapt themselves to new substrates, new metabolic pathways may be developed by mutations and the exchange of heritable properties; such natural hereditary changes may lead to the development of enzymes which are capable of degrading xenobiotic compounds. One such group of enzymes are the dehalogenases which are capable of hydrolysing chlorinated and brominated compounds (e g. dichloromethane, chloroethane and 1,2-dichloroethane). For halogenated chemicals in the environment the need is to reduce their recalcitrance; thus it is

Rapidly Degradable VOCs	Slowly Degradable VOCs	Very Slow Degradable VOCs
Alcohols Aldehydes Ketones Ethers Esters Organic acids Amines Thiols Other molecules containing O, N or S functional groups	Hydrocarbons (aliphatics degrade faster than aromatic compounds) Phenols Dichloromethane	Halogenated hydrocarbons e.g. trichloroethane, carbon tetrachloride and pentachlorophenol. Polyaromatic hydrocarbons

Table 3.2: The degradability of some VOCs [2].

now necessary to further develop biological systems that will degrade and detoxify these environmental pollutants.

Since the 1970's, Ireland has become a popular location for many manufacturing industries; as a result, statutory controls in the form of license requirements have had to be developed and implemented for emissions of liquid and gaseous pollutants. As a result, the use of biofilters in the industrial work place has a lot of potential as a method of waste control. However, this technology is still in its infancy In order to determine whether a biofiltration system is suitable for specific industrial applications, test systems in the form of laboratory column biofilters, pilot-plant scale biofilters and test rigs have to be set up and monitored. Bord na Mona established a research centre located in Newbridge, County Kildare in 1990 to develop peat based biofilters for treating liquid and gaseous waste. One of their aims was to carry out more research into the biodegradation of chlorinated organics.

Dichloromethane (DCM) is one of the most commonly used chlorinated organic solvents in production processes in the pharmaceutical industry i.e. it is used as a solvent, for purification purposes and in formulation steps. DCM is also highly volatile and has a relatively long atmospheric lifetime (calculated as 296 - 427 days, Chapter 2 Section 3 of this work); because it contains two chlorine atoms, it can be considered a potential threat to the ozone layer if sufficient quantities were emitted into the atmosphere. As there are no immediate replacements for DCM it is still used in many industries and the problem of disposal arises. In the past, DCM was disposed of by traditional methods i.e. incineration, adsorption of waste gas containing low concentrations of DCM by activated carbon and distillation of DCM contaminated waste water. These methods however only remove DCM as opposed to destroying it.

For the past ten years or so it has been realised that DCM is capable of being biologically degraded [6]. Several strains of microorganisms from the Hyphomicrobium family have been isolated for the biodegradation of dichloromethane (DCM) from various sources including activated sludge [5, 7]. These organisms contain the dehalogenase enzyme which catalyses the addidion of DCM to a reduced protein (glutathion). Following this process DCM is hydrolysed to HCl and formaldehyde; the formaldehyde is either oxidised to CO_2 or used for the build up of biomass [6].

One of the main problems in the biodegradation of DCM is the build up of HCl; this serves to decrease the pH of the system which affects the microbial population to an extent that if the pH falls to 4.0, biological activity stops [4].

Biological systems including biofilters have been set up to study the degradation of DCM. Elimination capacities of 60 g DCM $hr^{-1}m^{-3}$ of liquid in a bioscrubber filled with a suspension of 30 g dm^{-3} of active carbon innoculated with Hyphomicrobium DM2 has been reported [7]; also degradation of DCM contained in a gas containing a mixture of organic compounds using a multistage biofilter system have been reported [8, 9] where the third stage was innoculated with Hyphomicrobium. Stucki [6] monitored the performance of a compost biofilter innoculated with Hyphomicrobium in degrading a gas stream containing only DCM and reported a 50 - 70% efficiency of removal; the relatively slow removal efficiency was attributed to the difficulty in controlling the pH of the system which fell very rapidly after start up. Stucki concluded that the biofiltration technique was only suitable for removing very low DCM concentrations where very little HCl was produced. Both Stucki [6] and Wolf [10] found that biowashers and trickling filters were more suited to the degradation of DCM in off-gas streams as the pH of the systems was more easily controlled and also the bioscrubber was less sensitive to fluctuations in high component concentrations in the waste gas and also large concentration fluctuations [10].

This work was concerned with determining the ability of a laboratory scale peat fibre biofilter innoculated with Hyphomicrobium sp to degrade an artificial gas stream containing < 40 g m^{-3} dichloromethane (DCM) with the ultimate aim of scaling up the system to an industrial size unit.

3.2 DESIGN AND OPERATING PRINCIPLES OF A BIOFILTER

A biofilter for the control of gaseous pollutants consists of one or more filter beds of biologically active material. Filter beds are typically one metre in height and they can operate as open or closed systems. Figure 3.1 illustrates a schematic diagram of a biofilter apparatus. The basic design of the biofilter includes a biofilter unit, a gas pretreatment section for preconditioning the waste gas and its transport to and distribution in the filter bed. Heat exchangers to cool hot off-gases

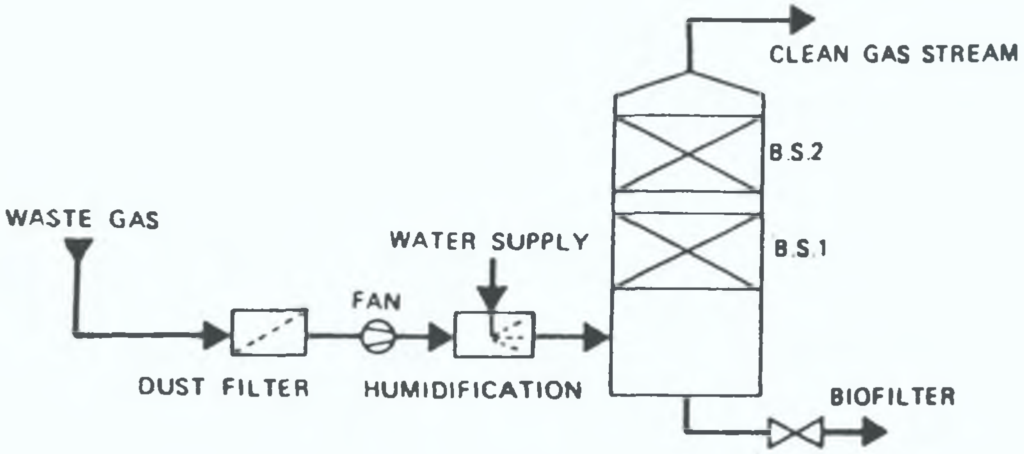

Figure 3.1: A schematic diagram of a biofilter apparatus.

or filters for the removal of particulates may be required for certain types of emissions. Radial blowers are generally used to over come the back pressure caused by the filter. A gas humidifier is also used in most applications to saturate the waste gas stream as drying of the filter material results especially when high flow rates are used; other problems such as the death of the organisms and loss of treatment efficiency can also result from drying of the filter material. Sprinkler systems are generally used to maintain the required moisture content in the filter bed. The contaminated off-gas is vented through the biofilter from the emitting source.

Given a sufficient residence time, the air contaminants will diffuse into the biofilm which surrounds the filter particles and will be aerobically degraded by the microorganisms present in the filter material.

The proper design and operation of a biofilter requires the consideration of a number of technical issues which are considered in the following sections:

Filter Construction and Sizing

The type of construction and installation of a biofilter for a given application i.e. open single-bed, enclosed multiple-bed or roof top installation will depend on the availability of space relative to the required filter volume. For different waste gases the filter volume required for the desired removal efficiency depends primarily on the rate of pollutant loading relative to the filter's degradation capacity and on the pollutant's concentration in the raw gas. The filter's large mass often provides sufficient buffer capacity to prevent breakthrough during peak loadings and thus allows sizing based on hourly average rather than instantaneous peak loads.

The waste gas flow rates affect the filter size, with surface loads of up to 300 m^3 h^{-1} of gas per m^3 of filter being permissible without creating high back pressures. For compact filter materials, high surface loads sometimes required for dilute gas streams result in the pressure drop in the filter becoming a size determining parameter.

Filter Material

For efficient operation of a biofilter, the packing material must meet several requirements: it must provide optimum environmental conditions for the resident microbial population in order to achieve and maintain high degradation rates; the filter particle size and distribution and pore structure should provide large reactive surfaces and low pressure drops; compaction should be kept to a minimum which reduces the need for maintenance and replacement of the filter material. The filter material should also have good buffering capabilities, good water retention abilities, a low rate of decomposition and a negligible specific odour.

Soil and composts are favoured filter materials in biofilter systems as they are porous which allows the gas stream to flow through while simultaneously adsorbing the VOCs. Soils have porosities of 40 - 50% and surface areas ranging from 1-100 m^2 g^{-1} [2] while compost has a 50 - 80% porosity with a similar surface area to soil. Compost also contains 50 - 80% (by mass) of partially humified organic matter [2]. These porosities and surface areas are similar to synthetic sorbents; however, the major distinction is that soil and composts contain a large microbial population (bacteria and fungi) which are capable of oxidising organic compounds to CO_2. Another distinction is that moisture in the waste gas stream is beneficial for microbial oxidation whereas moisture in synthetic sorbents reduces the sorption capacity of these materials.

Pores are smaller and less permeable in soil than in compost, therefore larger filter beds are required in soil filters; this problem can be overcome by using multistage filters, but the moisture content of the bed becomes more difficult to control. Compost is more suited to large air flows containing easily biodegradable VOCs and odorous compounds [2] due to its high permeability. Compost beds also require shaking periodically to prevent caking of the material and the formation of anaerobic zones within the filter. An other disadvantage of compost is that metabolic by products from halogenated VOCs such as HCl must be washed out of the system otherwise the drop in pH will be detrimental to the microorganisms in the compost, with soil however, mixing with $CaCO_3$ increases the neutralisation capacity. Compost can also be mixed with $CaCO_3$ but this causes compaction of the filter bed. $CaCO_3$ itself does not have an inhibitory effect on the microorganisms, however, the reaction product $CaCl_2$ becomes inhibitory at concentrations of 50-60 mol m^{-3} due to the Ca^{2+} ion [5];

therefore removal of buffer salts is also necessary to maintain good treatment efficiencies [6] Compost is also hydrophobic when dry and rewetting is tedious and labour intensive, whereas soil is hydrophilic so that dry soil beds are easily rewetted.

Peat fibre has also been shown to be a suitable choice of filter material in biofilter applications. The main constituent of peat fibre is the root remains of the common cotton grass (Eriophorum Angustifolium). It is very resistant to decay as evidenced by its presence in a relatively undecomposed state in the bog ecosystem. Due to its resistance to decay it is probable that this material is composed mainly of lignin Peat fibre used for biofiltration purposes is present in very small amounts and must be extracted from raw milled peat.

Peat's suitability arises from its ability to sustain large microbial populations, it has a high buffering capacity, a high pore volume and a large surface area. Other materials such as porous clay or polystyrene spheres can be added to the filter material to increase the reactive surface and the durability of the biofilter and in cases where emissions are intermittent, activated carbon can also be mixed with the packing material to increase its buffer capacity

Moisture Control

Maintaining the optimum moisture content in the filter material is the major operational requirement in a biofilter Without providing additional moisture the raw waste gas would dry out the filter bed. Moisture is essential for the survival and metabolism of the organisms and also it contributes to the filter's buffering capacity. Non-optimum moisture content of the filter bed results in compaction of the bed, breakthrough of incompletely treated raw gas and the formation of anaerobic zones which emit odorous compounds. An optimum moisture content is considered to be between 50 - 70% by weight [11]. The structure of the filter material is negatively influenced by the addition of large quantities of water. As an added precaution, humidification of the waste gas is recommended with greater than 95% saturation being desirable for water soluble compounds. Moisture content in a filter used for eliminating gases containing water insoluble components (e.g. toluene) must be rigorously controlled.

The drying out process of the filter material is a consequence of the biological process which is endothermic and an unsaturated gas stream. As drying out is maximun at the gas inlet area of the biofilter then ideally the inlet gas stream should be located at the region where humidification occurs [12].

Excess drainage from the filter bed is the only potential source of waste water discharge from the biofilter; the drain water may contain some of the less biodegradable off-gas constituents that have been flushed out of the filter bed. In cases where acidic degradation products are formed (e.g. HCl is formed in the degradation of chlorinated organic compounds) the drainage water will be characterised by a low pH.

pH Control

Since most microorganisms prefer a specific pH range, pH changes in the filter material will strongly affect their activity. Depending on the type of microorganisms that are present, large drops in pH can restrict the growth or destroy the microbial population and reduce if not eliminate the filter's degradation capacity. Acidification of the filter bed is one of the major problems in the degradation of chlorinated xenobitics. Ottengraf [4] measured the elimination capacity of a biotrickling filter as a function of pH in the removal of DCM and found that when the pH value reached 4.0 the microbiological activity stopped. It is generally accepted that the optimum pH range for biofilters is 4.5 - 8.5.

Degradative Organisms

The organisms responsible for the oxidation of VOCs to CO_2 and water are the same heterotrophic bacteria and fungi that degrade organic wastes in nature, in waste water treatment plants and land fills. Heterotrophic organisms utilise organic compounds for energy and convert them to CO_2 and water. Bacteria degrade small organic molecules that are easily ingested into their cells; some bacteria can adapt to break down large organic molecules. Soils and composts contain roughly 1 x 10^6 bacteria per gram [2]. Fungi tend to degrade more complicated molecules and they can excrete extracellular enzymes that break down polymers. The fungal population in soils and compost is usually 1 x 10^5 fungi per gram [2] and fluctuates with the type of organic input. The growth and activity of the microorganisms depends on the physical and chemical conditions in the filter bed such as water, oxygen, mineral and organic matter content, the pH and the temperature.

The diversity of the active microbial flora depends on the composition of the waste gas treated. Waste gases from specialised industrial plants which contain a limited number of chemical compounds result in the microflora being restricted to a few species whereas odorous air discharged from sewage works and agricultural sources result in a much more diverse population. For xenobiotic VOCs such as chlorinated hydrocarbons the biofilter must be innoculated with specific microorganisms which are developed in the laboratory from soil cultures that are better adapted to degrading specific compounds. The introduction of the innoculum into the filter bed upon start up will generally shift the distribution of existing microbial populations towards strains that metabolise the target pollutants. For easily biodegradable compounds acclimatisation usually lasts about ten days [13]. Innoculation of the filter material can result in a reduced acclimatisation period. The innoculation of the filter material usually increases degradation rates but these increases are usually short lived as the microbes in the innoculum have to compete with the native microorganisms already adapted to the field conditions.

Temperature

An important parameter influencing microbiological activity is the temperature at which the process is carried out. A temperature increase of 7% has been shown to increase the elimination capacity of a styrene-eliminating biofilter by a factor of approximately 2 [4]. The optimum temperature range for microbial activity is accepted to be within the 5 - 40 ^{o}C band, although limited activity is possible over a broader temperature range.

Maintenance of the Biofilter

The routine and periodic maintenance of biofilters primarily involves a regular check of the operating parameters such as the waste gas temperature and humidity, the filter's temperature and back pressure; all of these parameters may be monitored automatically. In open biofilter systems it can be difficult to control the moisture content and the pH of the system so periodic sampling of the filter material is required. The major maintenance requirements of open filters are turning the filter material regularly and replacing it after several years. Fully enclosed systems are designed to have little maintenance requirements since access to and visual inspection of the material is restricted. This is accomplished by automatic moisture control and selecting filter materials that compact slowly.

Monitoring the Biofilter Performance

The parameters to consider when monitoring the performance of a biofilter are the inlet and outlet gas concentrations. In cases of closed biofilter systems, the outlet gas concentrations are measured from the exit of the filter whereas in an open system a sampling plan has to be devised to ensure that representative samples are obtained; quite often monitoring hoods are used to cover a defined filter area which is typically 1 m^3 [13] and allows determination of the exit gas concentration per filter area. Gas chromatography incorporating a flame ionisation detector (FID) or a photoionisation detector (PID) is the most common method for monitoring gas concentrations across a biofilter system. In the cases of multi-component off-gases it is recommended that response factors for the detector systems are calculated [13]. Other important parameters include the pH of the filter packing and the moisture content.

Potential System Failures

An accurate knowledge of the waste gas composition is necessary as insufficient treatment of the gas can result if the filter has been under sized. The presence of compounds in the off-gas that are toxic to the resident microorganisms i.e. SO_2 and particulates in the waste gas can result in sludge formation Other problems leading to inefficiency include insufficient humidification, compaction of inappropriate filter material and fluctuations in pH due to the production of acids in the degradation process Given proper design and operation of a biofilter these failures can be avoided and their effects minimised.

The performance of a continually operating biofilter system is the result of a complex interaction between physical and microbiological phenomena often denoted as the macrokinetics of the process Research into the macrokinetics of the degradation process has only been carried out on monocultures, therefore it is necessary to make several assumptions when applying the model to biofilters containing hetergeneous cultures. Theoretical descriptions of the process involved in the operation of a biofilter have been outlined by Ottengraf [3, 5, 11, 14] where the macrokinetics of the degrading process of a large number of VOCs have been studied. The main conclusions drawn from this work are:

(a) the macrokinetics of the elimination process in a biological filter bed can be modelled as an absorption process in a wet biolayer surrounding the packing material and is accompanied by a biological degradation reaction;

(b) the elimination of these compounds within the bed follows zero order reaction kinetics down to very low substrate concentrations i.e. the degradation rate is independent of the substrate concentration;
(c) at low gas phase concentrations or water solubilities of the compound under investigation, the elimination rate of the filter bed may become diffusion controlled in the biolayer;
(d) the zero order kinetics of the elimination process means that any biodegradable compound may be removed completely during a finite residence time of the gas phase in the filter bed.

In the description of the elimination of carbon sources by a biofilter, Ottengraf [5] has shown the existence of two concentration domains: (a) where the biolayer is fully active and the conversion rate is controlled by the reaction rate of the component and the microorganisms; this situation is defined as the reaction limitation and (b) where the biolayer is not fully active e.g. the depth of penetration of the component is smaller than the layer thickness. In this case the conversion rate is controlled by the rate of diffusion of the component between the gas phase and the liquid phase of the biolayer. This situation is called the diffusion limitation. The diffusion limitation is controlled by the concentration gradient in the biolayer and therefore by the concentration level at the gas/liquid interface; this situation occurs at low gas concentrations. The implementation of the diffusion limitation process results in the decrease in the elimination capacity of the biofilter and occurs at a specific gas-phase concentration e.g. 0.2 g m^{-3} for butylacetate, and ethyl acetate and 3 g m^{-3} for toluene [11].

The parameter of interest in determining the biofilter performance is the elimination capacity (EC) of the biofilter expressed in grams of component or organic carbon eliminated per m^3 of packing material per hour [g m^{-3} h^{-1}]. It is a function of the gas inlet concentration and a constant gas flow rate and is defined as:

$$EC = \omega/H\,[C_i - C_o] \qquad 3\ 1$$

where ω is the gas flow rate ($dm^3\ h^{-1}$), H is the volume occupied by the filter material (dm^3) and C_i and C_o are the inlet and outlet gas concentrations respectively ($g\ m^{-3}$).

Other parameters calculated in this work were the percentage removal of DCM from the waste gas stream, the pH of the peat fibre used as the packing material and the pH of the drain water The results are presented in section 3.3.2.

3.3 EXPERIMENTAL RESULTS FROM BIOFILTER

3.3.1 General Description of Experimental Setup

Experimental studies of the biodegradation of DCM were conducted using a laboratory size biofilter which is illustrated in Figure 3.2. The filter unit consisted of a length of Wavin pipe (0.61 m length and 0.07 m diameter) which was fitted with two air tight lids (top and bottom) Plug holes were inserted in both lids - for drainage purposes at the bottom and humidification of the filter material at the top. The holes were stoppered with rubber bungs. Swagelok fittings were inserted in both lids to allow the gas to enter and exit the biofilter unit. A perforated sieve plate was inserted in the bottom of the unit to allow the drain water to collect and to prevent the build up of exit gas. Table 3 3 lists the design parameters for the biofilter system used in this work.

An artificial gas stream was generated by bubbling a slow air stream through a glass tube containing DCM; this air flow was diluted by a fast air stream flowing at 24 ± 0 75 $dm^3\ h^{-1}$. The combined air flow then passed onto the top of the biofilter unit. No other nutrients were supplied to the filter bed. The exit gas stream was vented through a window. Teflon tubing (4 mm i d.) was used to connect the air cylinder (obtained from Irish Industrial gases) to the biofilter. A "T" piece was inserted at the entrance of the biofilter for sampling purposes. The biofilter was drained daily and the pH of the drain water checked frequently using a Corning 240 pH meter The humidification of the peat bed was carried out on a daily basis by spraying the top of the filter bed with 200 cm^3 of tap water of pH 7 8, after week 30 no additional water was added to the biofilter.

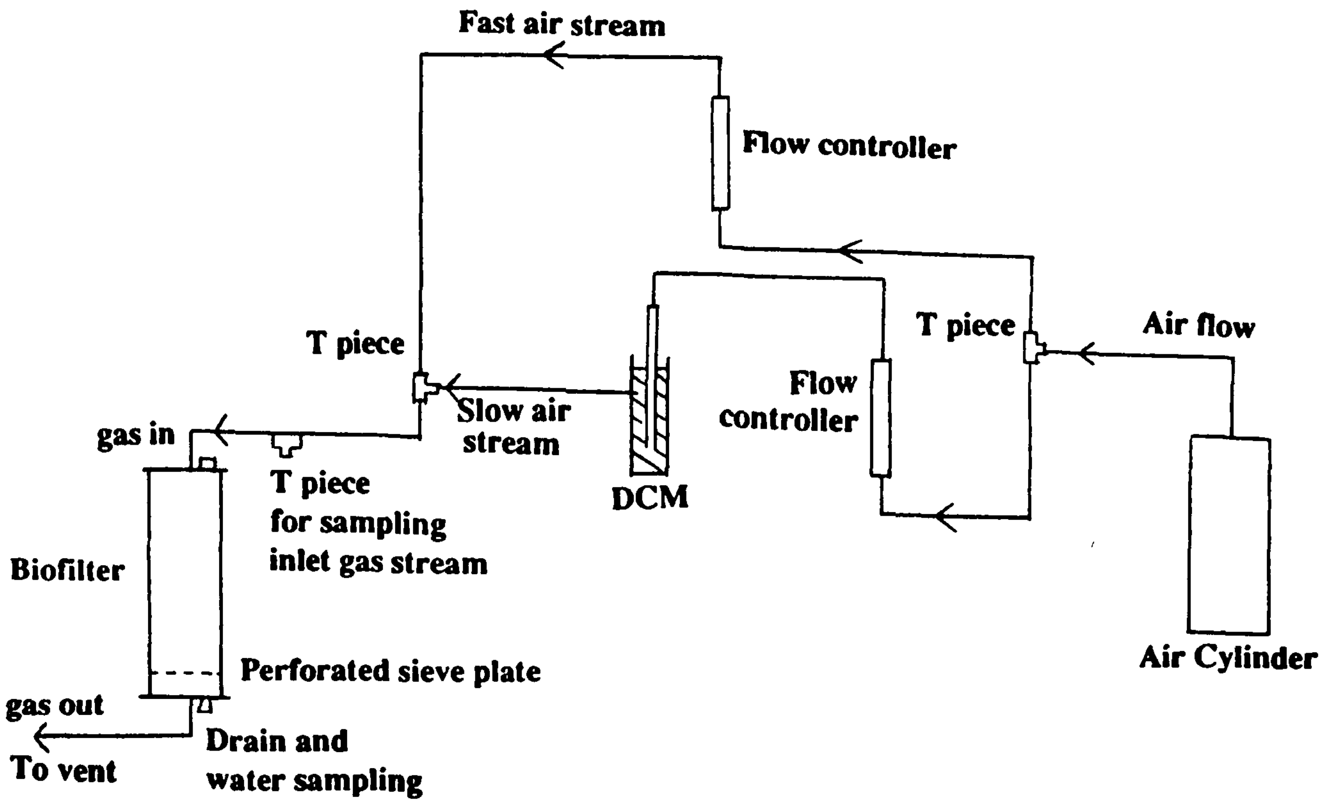

Figure 3.2: A schematic representation of the laboratory scale biofilter used in the elimination of DCM from an artifical gas stream.

Height of biofilter unit	0.61 m
Height of filter bed	0.57 m
Diameter of biofilter unit	0.17 m
Vol. of biofilter unit	0.014 m^3
Vol. of biofilter unit - false floor	0.013m^3
Dry weight of filter material used	1.25 kg
Density of packing material	96.2 kg m^{-3}
Loading of filter material	0.21 kg m
Water content of peat prior to use	33%
pH of peat fibre used in filter	4.4
Gas flow through biofilter	24 dm^3 h^{-1}
Gas loading	1.8 m^3 h^{-1} m^3
Inlet gas concentration	3 - 12 x 10^3 ppm 10 - 41 g m^{-3}
Operation temperature	298 ± 2 K

Table 3.3: Biofilter design parameters.

Samples of the inlet and outlet gas streams were taken using a Hamilton gas tight syringe. 250 µl samples were analysed using a PU4550 Gas Chromatograph incorporating a Flame Ionisation Detector (FID). The column used was 10% PEG on Chromosorb W AW (100-120 µl) at an oven temperature of 393 K, injector temperature 473 K and a detector temperature of 523 K. The carrier gas used was nitrogen (Irish Industrial gases) and was maintained at a flow rate of 45 ± 1 cm^3 min^{-1} through the duration of the study The fuel gases used were Air

(Irish Industrial gases) and Hydrogen (Irish Industrial gases). A Hewlett Packard Integrator (3390A) was used to record the chromatograms of the samples. Standard curves in the range 10 to 41 g m^3 DCM were set up periodically to calculate the response factor for the detector and also to determine the inlet and outlet gas concentrations. The standard curves were analysed by a least squares method, in all cases the slopes of lines agreed within ± 0.01% and had correlation coefficients > 0.99.

3.3.2 Experimental Results

Prior to the start up of the biofilter the miosture content, the pH and the bacteria and fungal counts of the peat fibre used as the packing material in the biofilter were determined. The pH of the filter material was measured at the top and bottom of the biofilter again at weeks 3, 5, 10 and 30 by measuring the pH of a solution that contained 10 g of peat immersed in 100 mls of distilled water for sixty minutes. The peat fibre was removed prior to carrying out the pH measurement. The moisture content of peat samples also taken from the top and bottom of the bed were calculated at weeks 1, 5 and 30 by placing 10 g of peat fibre in a muffle furnace at 100 ^{o}C for five hours and calculating the water content by the weight difference. These results are presented in Tables 3.3 and 3.4 respectively.

Bacteria and fungal counts were carried out at weeks 1 and 30 of operation by placing 1 gram (dry weight) in a sterilised saline solution which was mashed for 1 minute. 1 cm^3 of the resulting solution was then placed in 9 cm^3 of sterilised saline solution and from this serial dilutions to 10^{-8} were performed under aeseptic conditions. Samples from each dilution were plated on malt extract agar and left at 30^{o}C for 3 days after which the number of colony forming units were counted. These results are listed in Tables 3.5.

Verification that biodegradation of DCM to form HCl was occurring during the operation of the biofilter was carried out by calculating the chloride concentration in the drain water from the biofilter. A background chloride concentration was measured from a sample of the tap water used to wet the packing material Chloride measurements were carried out using a chloride Ion Selective Electrode (Orion, Model 94175c. reference electrode Orion, Model 900200). The electrode response was standardised according to the manufacturer's specification. A standard curve in the range 10^{-1} to 10^{-5} M chloride was set up (refer to Figure 3.4), from this the chloride concentrations of the tap water and the drain water were calculated to be 24 and 30 ppm respectively.

pH					
	WEEK 1	WEEK 3	WEEK 5	WEEK 10	WEEK 30
TOP	4.3	4.8	4.8	5.0	4.6
BOTTOM	4.8	4.5	4.4	4.3	6.5

Table 3.4: pH of peat fibre samples taken at various stages of biofilter operation.

MOISTURE CONTENT (%)			
	WEEK 1	WEEK 5	WEEK 30
	33.0		
TOP		70.0	70.6
BOTTOM		75.0	71.0

Table 3.5: Moisture content of peat fibre calculated at weeks 1, 5 and 30.

MICROBIAL POPULATIONS (colony forming units (cfu) per g dry weight of peat fibre)		
	WEEK 1	WEEK 30
BACTERIA	1.21 x 10^7	6.0 x 10^5
FUNGI	1.01 x 10^6	2.3 x 10^5

Table 3.6: The microbial populations in cfu per g of dry peat fibre used for the filter material (week 1) and after 20 weeks of operation having been innoculated at week 10 (i e. week 30).

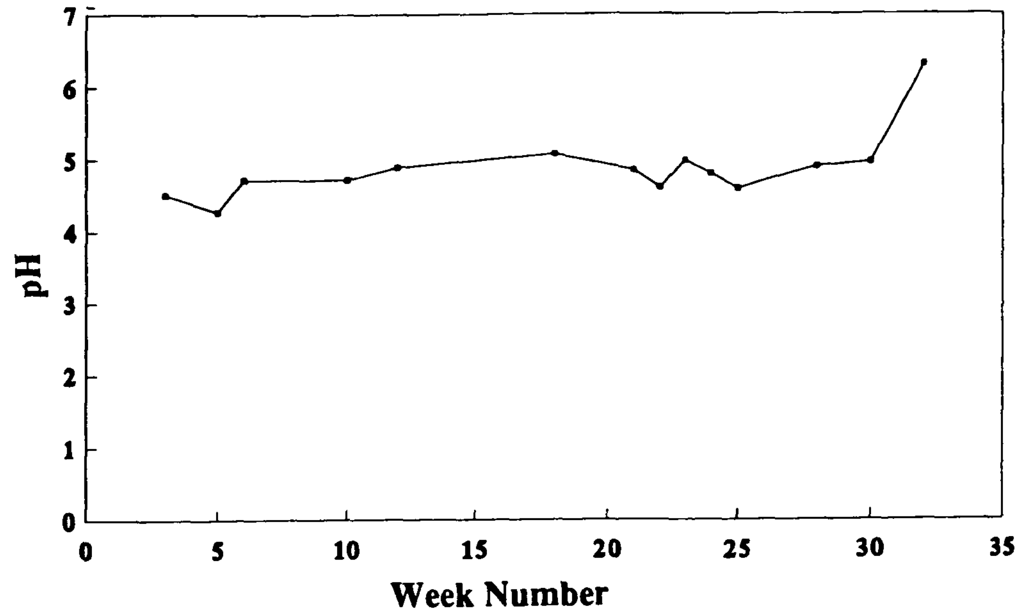

Figure 3.3: pH of the drain water taken from the biofilter from week 1 to week 32.

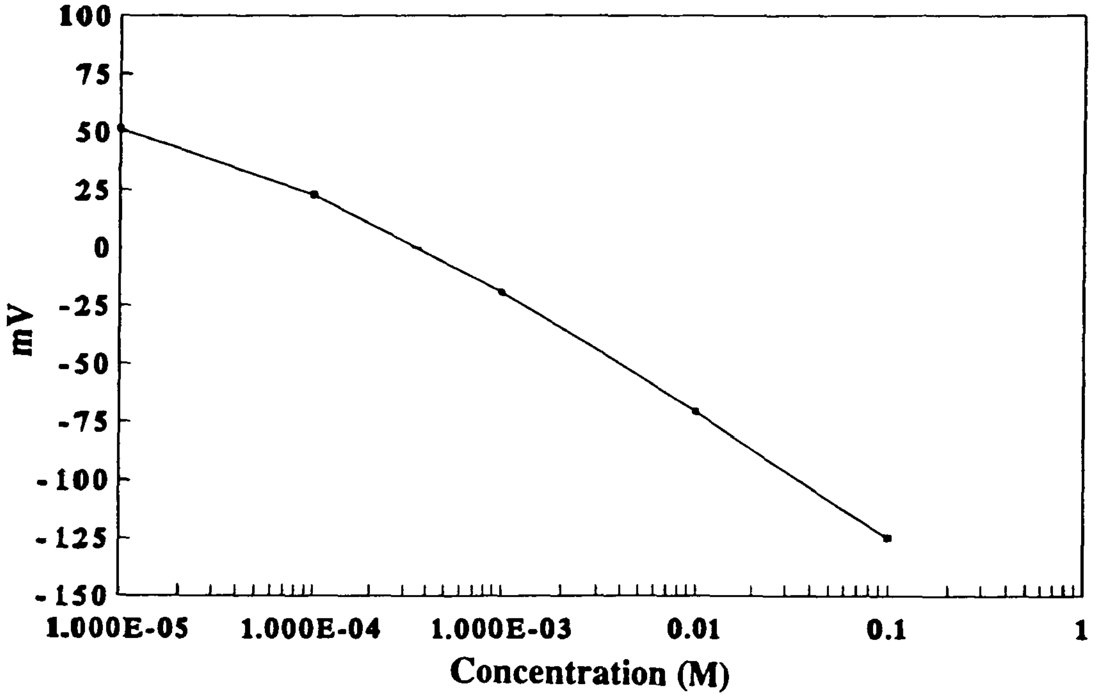

Figure 3.4: Standard curve used to calculate the chloride concentrations in the drain water from the biofilter using a chloride Ion Selective Electrode

For the first 10 weeks of operation of the biofilter the gas stream was allowed to flow through the biofilter and no innoculum was used. In week 10, the peat was innoculated with Hyphomicrobium sp obtained from Bord na Mona. The performance of the biofilter was monitored continuously for the 32 week duration of the project. Table 3 7 lists the inlet and outlet gas concentrations expressed in units of g m^{-3} calculated for each sample taken. The 59 samples taken were spread over a 32 week period and the first 26 samples being taken within weeks 1 to 6. After this period the frequency of sampling was reduced until one sample per week was taken.

The gas inlet and outlet concentrations (in g m^{-3}) versus the day they were taken were plotted and is illustrated in Figure 3 5. As the inlet gas concentrations in the gas stream varied, a maximum and minimum concentration each day was calculated from a series of four sample injections. The outlet gas sample concentrations were found to be reproducible and the average value from three sample injections was used From these results the percentage removal was calculated and plotted as a function of the day and is shown in Figure 3.6.

The elimination capacity which is expressed as the number of g of DCM removed per m^3 of filter material per hour of operation was calculated for each maximum gas inlet concentration; the elimination capacity was then plotted versus the gas inlet concentration (Figure 3.7) to determine whether the maximum elimination capacity of the biofilter had been reached and also whether the elimination of DCM increased with increasing inlet gas concentrations.

DAY	C_i^a		C_o^b	n^c	DAY	C_i^a		C_o^b	n^c	DAY	C_i^a		C_o^b	n^c
	MAX	MIN				MAX	MIN				MAX	MIN		
1	12.8	8.8	2.7	1	**22**	23.1	18.7	4.0	2	**43**	34.8	20.4	10.6	1
2	20.4	8.4	1.9	2	**23**	34.7	28.7	13.1	2	**44**	34.3	22.1	11.8	1
3	12.2	7.4	4.6	4	**24**	22.7	15.4	6.5	2	**45**	25.2	21.5	12.0	1
4	12.6	6.9	3.3	2	**25**	27.6	19.2	7.1	2	**46**	19.1	16.2	7.8	1
5	8.1	4.4	2.5	3	**26**	11.3	6.2	0.8	2	**47**	38.3	25.1	5.1	1
6	24.0	18.2	13.2	2	**27**	7.3	2.3	0.3	2	**48**	36.2	30.3	4.7	1
7	27.5	21.7	12.2	2	**28**	5.4	2.0	0.5	1	**49**	26.0	20.7	8.4	1
8	14.0	8.7	5.5	1	**29**	20.4	15.4	8.22	1	**50**	15.0	10.4	1.8	1
9	12.8	10.5	5.4	2	**30**	15.7	12.8	8.9	1	**51**	27.7	20.8	4.1	1
10	17.1	8.6	6.1	1	**31**	17.2	6.6	1.6	1	**52**	13.8	8.5	0.6	1
11	6.3	5.3	4.0	2	**32**	13.7	7.3	2.2	1	**53**	7.3	5.4	2.6	1
12	25.3	19.4	9.9	1	**33**	7.9	4.4	0.6	1	**54**	13.1	10.6	6.2	1
13	27.5	16.9	10.0	1	**34**	22.2	14.3	6.3	1	**55**	5.8	4.5	2.6	1
14	7.3	2.6	1.6	2	**35**	13.4	10.3	6.1	1	**56**	34.7	26.7	12.2	1
15	4.0	2.8	0.6	1	**36**	18.5	13.2	6.4	1	**57**	19.5	16.8	8.0	1
16	27.9	22.5	14.4	1	**37**	13.6	11.5	6.9	1	**58**	39.4	37.6	13.0	1
17	26.5	12.3	3.4	2	**38**	14.8	11.5	9.6	1	**59**	11.9	5.7	2.2	1
18	8.7	4.6	3.0	2	**39**	15.1	12.3	7.6	1					
19	18.4	14.7	2.7	2	**40**	14.8	12.1	5.1	1					
20	16.4	11.8	2.7	2	**41**	23.1	20.0	6.1	1					
21	14.1	8.4	3.2	2	**42**	13.9	11.3	7.6	1					

a inlet conc. (g m^{-3})

b outlet conc. (g m^{-3}).

c number of samples taken on the day.

Table 3.7: Maximum and minimum gas inlet concentrations and outlet concentrations (g m^{-3}) calculated for 59 samples taken over a 32 week period.

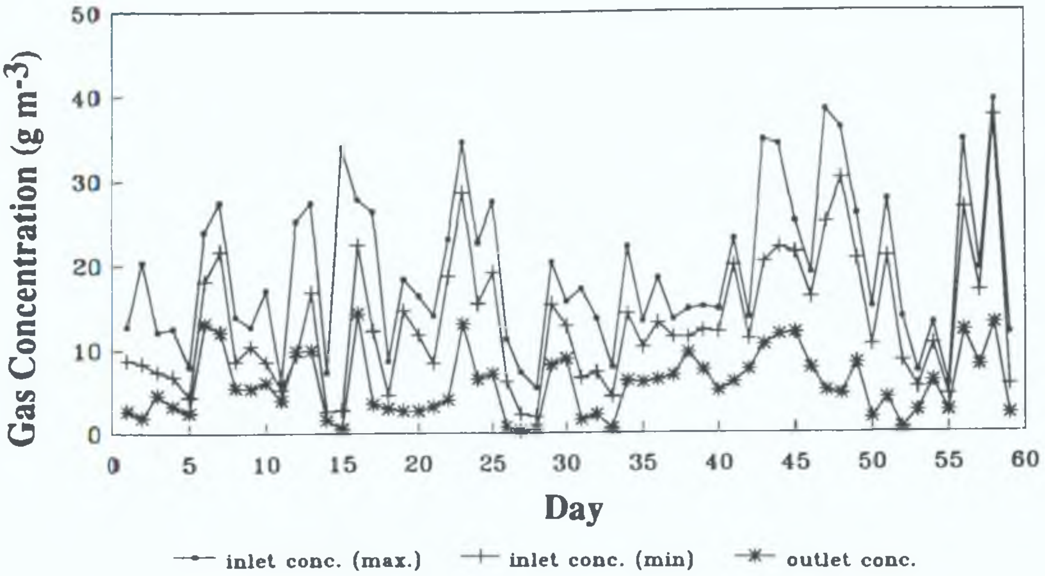

Figure 3.5: A plot of gas concentration (max. and min. inlet concentrations and outlet concentration in g m^{-3}) versus the day on which the sample was taken.

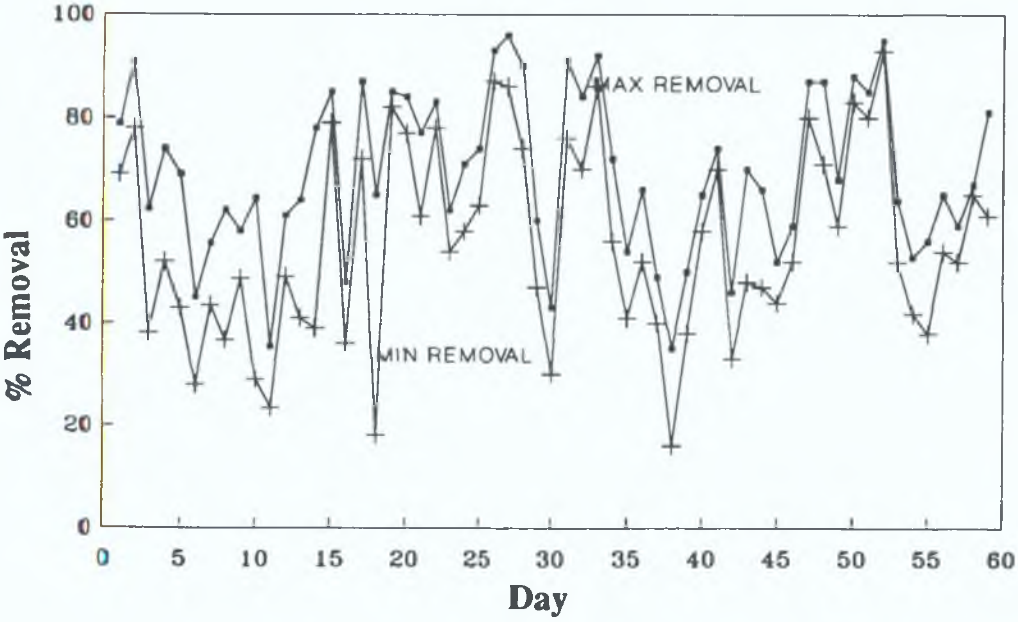

Figure 3.6: Percentage removal of DCM from the artificial waste gas stream by the biofilter; calculated from the inlet - outlet gas concentration over a period of 32 weeks.

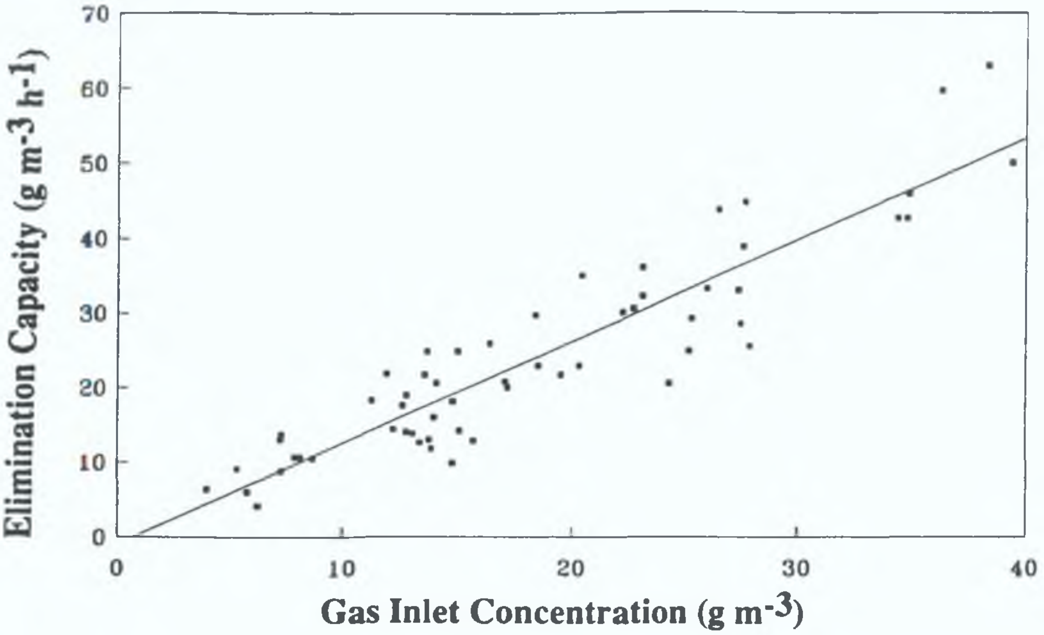

Figure3.7: Elimination capacity (g $m^{-3}h^{-1}$) versus gas inlet concentration for the removal of DCM from an artificial gas stream over a period of 32 weeks.

3.4 DISCUSSION

Both the pH and the water content of the peat fibre used as the filter packing material were quite low (measured as 4.4 and 33% respectively), which is characteristic of undisturbed raw peat taken directly from the source; however the microbial counts produced a relatively high number of colony forming units per gram of material which would indicate that the peat was handled significantly between being taken from the place of origin (i.e. the bog) and placed in the biofilter. This could have occurred during the milling process used to extract the peat fibre from the raw peat. Table 3.4 shows the pH of the peat at both the top and the bottom of the biofilter at weeks 1, 3, 5, 10 and 30. From weeks 1 to 10 there is a noticable increase in the pH at the top of the biofilter while the converse is true for the peat at the filter bottom. This could be explained by the fact that from week 1 of operation removal of DCM from the gas stream was observed; this could be due to adsorption by the peat or by biodegradation of DCM by the organisms naturally present in the peat. If adsorption by the peat occurred then the pH of the peat would be expected to remain constant during operation as there would be no production of HCl, however as the pH gradient reverses during weeks 1 to 10 this indicates that acid production is occurring. The fact that the biofilter was sprayed with tap water on a daily basis should also be considered as the water would wash the acid down the column and from the peat, this would account for the low pH of the drain water collected from the biofilter. The pH of the peat fibre at week 30 however was quite different in that the pH at the top of the column was significantly lower than at the bottom. As peat samples were not taken between weeks 10 and week 30 it is difficult to say whether a trend in the change in the pH would have been observed over this time period; the change in pH is possibly due to the water washing any acid produced as a result of biological activity from the system.

The variation in the pH of the drain water is illustrated in Figure 3.3 and was observed to vary between pH 4.0 and 5.0 for weeks 1 to 30; the pH of the water added to the biofilter was measured to be 7.8, this decrease in the pH value of the samples taken would indicate the presence of acids. However, at week 32 the pH value of the drain water increased to 6.2. As there was no additional water added to the biofilter after week 30, the only source of drain water is that which comes from the peat fibre; this increase in pH would suggest that either acid production has decreased drammatically since humidification of the biofilter was stopped or that the water draining from the bed was not washing the acids from the peat. Since DCM is only sparingly soluble in water, this conclusion is reasonable.

The water content of the peat located at the top and bottom of the biofilter was measured at weeks 5 and 30 (refer to Table 3.5) and was found to be at the maximum recommended value [11]. Although the values obtained may be considered to be too high it was felt that it was necessary to add water to the biofilter on a regular basis to prevent a drop in pH due to the production of HCl. However, after week 30 no additional water was added to the biofilter to determine whether the percentage removal of DCM would be noticably affected. After week 30 two additional inlet and outlet gas samples were taken (corresponding to sample number 58 (week 31) and 59 (week 32) in Figures 3.5 and 3.6); the percentage removal calculated for these samples was not noticeably different relative to the other measurements taken during the 30 week period of operation. Further measurements of the percentage removal would have to be made over several weeks and also the moisture content of the peat calculated to determine conclusively whether a reduced water content in the peat affected the percentage removal of DCM.

To establish whether biodegradation of DCM was actually occurring in the biofilter as opposed to adsorption by the peat or that the DCM was being washed out by the water added in the humidification process, chloride concentrations were determined in samples of the tap water used to wet the peat and a sample of the drain water taken in week 32; concentrations of 24 ppm and 30 ppm Cl^- were calculated respectively from the standard curve plotted in Figure 3.4. As DCM is only "slightly" soluble in water [15] the excess chloride ions would probably result from the presence of HCl indicating that biological activity might be responsible for the removal of DCM.

Bacteria and fungal counts were carried out at weeks 1 and 30 of operation and are given in Table 3 6. It is apparent that the number of bacteria and fungi per gram dry weight of peat have decreased since the start of operation even though the biofiloter was innoculated at week 10. As DCM was the only nutrient source added to the biofilter the only organisms that will remain alive and grow are those that are capable of degrading DCM. The fungal population of the peat was not as adversely affected in their survival as the bacteria, however this is more than likely due to the low pH values as opposed to their degradative abilities.

Table 3.7 lists the inlet and outlet gas concentrations measured during the 32 week period of the study. Due to the nature of the artificial gas stream, fluctuations in the inlet gas concentrations were observed; as a result a range of inlet concentrations from a series of four samples were calculated as opposed to an absolute value. The outlet gas concentrations however, were generally reproducible and an average value was calculated from a series of three samples. The first 26 samples taken were spread over a period of 6 weeks; an average of two samples per day were taken from the inlet and outlet gas stream which were then averaged to give a daily inlet and outlet DCM concentration; after week 6 one sample per day was taken and the frequency of sampling each week was reduced to one representative sample per week.

The fluctuations in the inlet concentrations and the outlet concentration are illustrated in Figure 3.5. The variation in the maximum and minimum inlet gas concentrations tend to mirror each other i.e. a large increase in the maximum inlet concentration is accompanied by a large minimum inlet concentration; however, the difference between these concentrations was never constant with the largest difference being approximately 16 g m^{-3} (day 2) and the smallest difference was calculated to be 1 g m^{-3} (day 11).

The outlet concentrations remained quite constant with approximately 78% of these values being less than 10 g m^{-3}. The outlet concentration increased above 10 g m^{-3} when the maximum inlet concentrations were greater than 25 g m^{-3} with the largest outlet concentration being measured on day 6 as 13.2 g m^{-3}.

Figure 3.6 illustrates the percentage removal of DCM from the gas stream also calculated on a daily basis for the duration of the project. As the inlet concentration of DCM was difficult to control a maximum and a minimum percentage removal was calculated. A comparison between Figures 3.5 and 3.6 was made to try and establish any trends between the inlet concentrations (maximum and minimum) and the percentage removal; however, no observable patterns were noticeable from the data. Innoculation of the biofilter occurred on day 34; from Figure 3.5 it is observed that the outlet concentrations of DCM increased and reached a high on day 45 before decreasing. This could be attributed to the microorganisms in the innoculum becoming acclimatised to the physicochemical conditions existing in the biofilter. After day 45 the outlet concentrations decreased however they did not reach a steady level. The largest percentage removal occurred in the 40 - 80 % region with 8% of the samples being less than 40% and 31% of the samples being greater than 80%.

The elimination capacity for the biofilter was calculated for all the samples taken and plotted against the gas inlet concentration (refer to Figure 3.7). From the graph it is apparent that the elimination capacity is a function of the gas inlet concentration and that elimination of DCM is occurring in the diffusion controlled region [3, 4, 5, 11]. As the graph does not form a plateau the maximum elimination capacity for this biofilter cannot be calculated however the elimination capacity for the concentrations used in this work was measured to be approximately 53 g DCM m^{-3} hr^{-1}. This value is quite high however, the elimination capacity is a function of the gas load (1.8 $m^3hr^{-1}m^{-3}$) which is very low.

For industrial applications, a biofilter would have to be capable of dealing with large volumes of waste gas thus the gas loading would be much higher than that used in this work. As a result the residence time of the gas in the biofilter unit would be much shorter which would result in a decrease in the elimination capacity of the biofilter.

3.5 CONCLUSION

The biofilter's performance and physical characteristics were monitored over a period of 32 weeks. The pH values of the peat were observed to be quite low however biological activity remained and partial degradation of DCM was observed. Acid formation was confirmed by measuring the chloride content of the drain water from the biofilter which indicated that biodegradation was probably occurring. The moisture content of the peat was high at around 70% but this was necessary to ensure that acids produced as part of the degradation process were washed out of the system. Both the bacteria and fungi counts were lower than in the original peat used in the biofilter, this was attributed to the fact that DCM was the only nutrient source added to the biofilter and also that the pH of the system was low. The elimination capacity of the biofilter was calculated to be 53 g m^{-3} hr^{-1} at a gas loading of 1.8 $m^{-3}hr^{-1}m^{-3}$ and was observed to increase with increasing DCM concentrations.

This work was concerned with determining whether a biofilter was capable of removing and degrading DCM from an artificial gas stream with the ultimate aim of using peat fibre biofilters in industrial applications. From the results obtained it is apparent that the biofiltration technique is suitable for removing large concentrations of DCM at low gas loads; however, it would be necessary to scale up the size of the biofilter unit to enable the process to handle larger volumes of gas typical of industrial processes. In this case further studies on the effects of the larger gas loads on the elimination capacity would have to be undertaken.

Studies on factors affecting the removal of DCM such as a lower moisture content, different filter materials, internal control of pH by the addition of buffers to the filter material (e.g. $CaCO_3$) and different strains of microorganisms should also be carried out in an attempt to optimise the removal of DCM.

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4.0

APPENDIX

4.1 PUBLICATIONS

"Rate Constants and Atmospheric Lifetimes For The Reactions of OH Radicals and Cl atoms With A Series Of Haloalkanes", T.Donaghy, I Shanahan, M Hande, S Fitzpatrick, *Int J Chem Kinet*; 25(4), 273 - 284 (1993).