CHAPTER 5

Tropospheric Processes:
Observations and Interpretation

Authors:

I.S.A. Isaksen	J.A. Fuglestvedt
Y.-P. Lee	C. Johnson
R. Atkinson	J. Lelieveld
H. Sidebottom	A. Thompson

Additional Contributors:

W. Brune	M. Oppenheimer ·
J. Kaye	T. Berntsen

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Contents

SCIENTIFIC SUMMARY

- **Calculated O_3 changes:** Models predict increasing tropospheric ozone in the Northern Hemisphere in response to increasing emissions of NO_x, CO, CH_4, and NMHC that vary markedly with latitude, altitude, and season. These variations have to be taken into account if indirect climate effects are to be estimated.

  Model differences in the calculated ozone increase from NO_x emissions are large (~factor of 3). In addition the spatial and temporal variations are particularly large, and the model results are highly sensitive to the adopted background concentrations. All this precludes a quantitative assessment at the present time. NO_x emitted from aircrafts produces ozone much more efficiently than ground-based emission (by > a factor 10).

  Model differences and spatial variations in the O_3 increase in response to CH_4 emissions are moderate (both within 50 percent). The sensitivity to background assumptions is also moderate. Calculations of ozone changes can be done with reasonable accuracy.

- **Calculated OH changes:** Increases in CH_4, CO and HC emissions lead to reduced OH values, while increased NO_x emissions lead to enhanced OH levels. As a result of these opposing effects the sign of future OH changes cannot be predicted. The indirect effect of CH_4 emission on the CH_4 distribution, through its effect on OH, is estimated to be ~35 percent.

- **Indirect effects on global warming potential (GWP):** The indirect effects from CH_4 emissions on O_3 and CH_4 concentrations can be estimated with moderate accuracy. At present no estimates can be made of the indirect effects of NO_x surface emissions, as uncertainties in the calculations are too large. Furthermore, the impact on O_3 and CH_4 from NO_x emissions is in opposing directions.

- **Tropospheric chemistry of hydrochlorofluorocarbons (HCFCs) and hydrofluorocarbons (HFCs):** Experimental studies show that the breakdown of the HCFCs and HFCs is generally as expected from analogy with the C_1 haloalkanes, and alkanes. However, several of the intermediate oxidation products (COFCl, COF_2, CF_3COF, CCl_3COF, and the halogenated peroxyacyl nitrates) may have long lifetimes in the upper troposphere, and transport to the stratosphere could occur. This could influence the stratospheric ozone chemistry and radiation. Although future changes in OH, which cannot yet be estimated, will affect the breakdown of HCFCs and HFCs, these compounds will not have an effect on OH and the tropospheric O_3 chemistry.

Impact of increased emission on climate gases (+ gives increases in global averages, – gives decreases):

Incr. emission	OH	O_3	τ (CH_4, HCFC, HCF)
CH_4	–	+	+
NO_x	+	+	–
CO	–	+	+
HC	–	+	+

5.1—INTRODUCTION

In the present chapter three aspects of tropospheric chemical processes imposed by man-made emission of source gases will be discussed. First, we will look at the implications for the OH distribution and thereby for the lifetime of source gases which are controlled by reactions with OH in the troposphere (e.g., CH_4 and HCFC). This is of importance for stratospheric ozone and for climate. Second, we will study the impact of source gas emission on tropospheric ozone and discuss the possibility to estimate indirect climate effects from the changes in ozone and other climate gases. Finally, the degradation of HFC and HCFCs is discussed.

Recent observations of ozone indicate substantial increases in the free tropospheric distribution over the last 1 to 2 decades (see Chapter 2 on measured trends in Ozone and Temperature). Ozone sonde observations over central Europe show that the increase occurs at least up to heights of approximately 10 km. Unfortunately, free tropospheric ozone changes are less well documented over other areas. Nevertheless, the observed ozone increases point to a fundamental change in the oxidation processes in the troposphere as ozone is a key player in tropospheric chemical processes.

Changes in the OH distribution in the troposphere could be of particular importance as OH provides the main sink for a large number of gases. It controls the distribution of CO and CH_4 (Weinstock, 1969) which are significant for tropospheric chemistry and also for gases affecting stratospheric ozone like HCFCs and HFCs (see the discussion later in this chapter and WMO, 1990). Changes in OH may also have a significant impact on climate change through the same loss reactions (IPCC, 1990). For instance, reduced OH enhances CH_4 concentrations and those of other radiatively active gases which are controlled by OH.

This chapter will be an update and extension of previous reviews of the tropospheric O_3 and OH chemistry (WMO, 1989; WMO, 1990). Recent studies have highlighted the importance of tropospheric chemical changes (e.g., changes in O_3 and OH) for the stratospheric ozone and climate issues. We are particularly interested in assessing our capability to predict changes in O_3 and OH resulting from changed emission of source gases (CH_4 and

other hydrocarbons, CO and NO_x), in order to predict their contribution to climate and stratospheric chemical changes. The emphasis will be on model estimates of such changes.

## 5.2 PROCESSES CONTROLLING TROPOSPHERIC O_3 AND OH

The chemistry of the troposphere is primarily driven by ultraviolet (UV) radiation with wavelengths shorter than about 320 nm. The OH radicals are formed by photodissociation of O_3 in the presence of water vapor:

$$O_3 + h\nu \ (\lambda \leq 320 \ nm) \rightarrow O(^1D) + O_2 \qquad R1$$

$$O(^1D) + H_2O \rightarrow 2OH \qquad R2$$
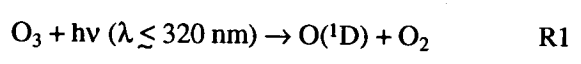
Tropospheric ozone may be produced by in situ chemistry (Crutzen, 1973; Chameides and Walker, 1973; Fishman and Crutzen, 1978) or by transfer from the stratosphere, where O_3 is generated by the photodissociation of molecular oxygen at altitudes above 25 km, followed by combination of the ground state oxygen atoms with O_2:

$$O_2 + h\nu \ (\lambda < 242 \ nm) \rightarrow 2O(^3P) \qquad R3$$

$$O(^3P) + O_2 + M \rightarrow O_3 + M \qquad R4$$
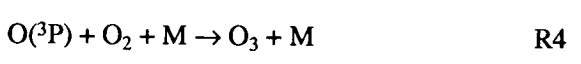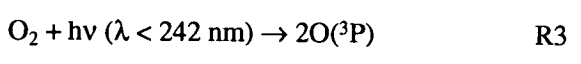
The in situ source of tropospheric ozone is the reaction of HO_2 with NO followed by the photodissociation of the nitrogen dioxide produced and the $O(^3P) + O_2$ reaction (R4).

$$HO_2 + NO \rightarrow NO_2 + OH \qquad R5$$

$$NO_2 + h\nu \ (\lambda < 400 \ nm) \rightarrow O(^3P) + NO \qquad R6$$
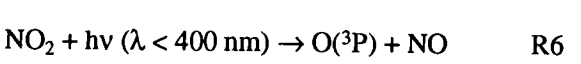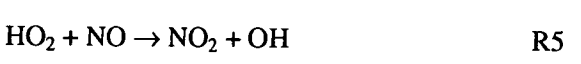
Although NO and NO_2 concentrations are very low throughout most of the troposphere, the effect of this reaction sequence can provide a significant O_3 source. Ozone may also be produced by reaction sequences where organic peroxy radicals are involved instead of HO_2.

Reaction R1 followed by reaction R2 is of significance for the ozone distribution in the troposphere, as it provides a major sink for ozone.

There is also an *in situ* loss of ozone through reaction with NO_2 (to give NO_3), HO_2, and unsaturated hydrocarbons. The most important of these reactions is the one with HO_2

$$HO_2 + O_3 \rightarrow OH + 2O_2 \qquad (R7)$$
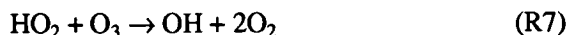
Although tropospheric O_3 only makes up about 10 percent of all ozone in the atmosphere, its amount is clearly central to the problem of the oxidizing efficiency of the troposphere, since O_3 photolysis is the primary source of OH radicals as well as being an oxidizing species itself. Through the formation of OH it determines the cleansing efficiency of the troposphere. Therefore, ozone ultimately maintains the chemical composition of the troposphere. Because of the central role of OH, the chemistry of many species, notably of CO, CH_4 and NO_x is strongly intertwined. In the background troposphere, remote from most of the direct effects of human activities, probably as much as 70 percent of the OH radicals react with CO, and a substantial part of the rest with CH_4. It follows that the future trends of oxidizing capacity will be tied to the future tropospheric burdens of CO, CH_4, nonmethane hydrocarbons, and other organics, as well as nitrogen oxides.

An understanding of tropospheric chemistry and estimating of the impacts of human activities require detailed knowledge of the photochemical reactions affecting CH_4, CO and O_3. Catalytic reactions with nitrogen oxides strongly affect photochemical processes. NO_x has natural and strong anthropogenic sources, most importantly the combustion of fossil fuels. Atmospheric environments are called NO_x-rich when NO volume-mixing ratios exceed those of O_3 by much more than the ratio of the rate coefficients between the ozone destruction reaction R7 and the ozone production reaction R5.

This ratio of k_{R7}/k_{R5} is about 2.5×10^{-4}. Since the O_3 mixing ratio near the earth's surface in the background atmosphere is roughly 20 ppbv, O_3 can be produced at NO mixing ratios exceeding $\approx$ 5 pptv, approximately equivalent to 15 to 20 pptv NO_x. Because of ozone loss by reactions R1 and R2, however, net ozone production takes place at larger NO_x volume-mixing ratios, depending on latitude and season. Especially in warm humid air, reaction R2 becomes so important that net production of O_3

requires quantities of NO_x that are several times larger. Over large parts of the Northern Hemisphere, where NO_x emissions are considerably enhanced by anthropogenic activities, net photochemical O_3 production is commonplace. In more pristine oceanic environments, in much of the Southern Hemisphere, where observations show low NO_x values (Ehhalt *et al.*, 1991; WMO, 1990), and in the middle troposphere, ozone destruction becomes more important.

Although OH radicals react with CH_4 and CO, these reactions do not always lead to a net loss of OH. They are merely the starting points for various, often lengthy reaction chains, which may partly compensate or even overcompensate, the initial removal of OH. For instance, in the presence of a sufficiently large amount of NO_x, the oxidation of CH_4 initiates reactions that lead to the formation of ozone without net loss of OH and NO_x. In NO_x-rich environments the dominant pathway to the first stable oxidation product, formaldehyde (CH_2O) yields NO_2 and HO_2. The hydroperoxyl radical (HO_2) reacts with NO, forms NO_2 and regenerates OH (reaction R5). UV radiation photodissociates the NO_2 molecules and produces O_3 (reaction R4). Further breakdown of CH_2O (which has a lifetime of less than a day) yields more HO_2 radicals, which, through the catalytic action of NO_x, also generate O_3 and OH. In the presence of sufficient NO_x, oxidation of one molecule of CH_4 yields more than one molecule of O_3, whereas further conversion of CO into CO_2 leads to additional O_3 production (Crutzen, 1988).

In NO_x-poor environments, on the other hand, alternative oxidation pathways to CH_2O become important, proceeding over the intermediate CH_3O_2H; no ozone is formed. Further breakdown of CH_2O again yields HO_2 radicals. In the absence of NO to react with, these radicals destroy O_3 (reaction R7). The net effect of the entire reaction sequence is loss of both O_3 and OH. Since anthropogenic emissions from the industrialized continents constitute the dominant source of NO_x, and because NO_x has a lifetime in the atmosphere of only a few days (during which it can travel at most a few thousand kilometers), we believe that a large part of the troposphere is in a NO_x-poor state. This is supported by NO_x measurements over the Pacific Ocean (McFarland *et al.*, 1979; Ridley *et al.*, 1987). Note, however, that in the upper troposphere

downward transport of NO_x derived from N_2O oxidation in the stratosphere and production from lightning can become important. Nevertheless, a substantial fraction of the background troposphere contains so little NO_x that there is little or no ozone produced. Under these circumstances we may also expect that OH radicals are lost by the oxidation of CO and CH_4. An increase in CH_4 and CO emissions can thus, via reduction of OH, amplify the growth of these species, an important positive feedback. It is therefore clear that understanding the distribution of NO_x in the troposphere is crucial for our ability to predict chemical changes in the troposphere.

5.3 COMPLEXITIES IN O_3 AND OH PREDICTIONS

The large variations in regional NO_x distributions have important implications for our understanding of the location of NO_x sources relative to their importance in ozone production. First of all, because water occupies such a large fraction of the earth's surface, more than 90 percent of the volume of the troposphere is contained in the region that we classify as the remote free troposphere. Second, because of the nonlinearity in the ozone production, a NO_x molecule in the remote free troposphere is much more effective in producing ozone than if such a molecule is introduced in more industrialized regions (Liu et al., 1987). This nonlinearity is illustrated in Figure 5-1. Here, the ozone production efficiency, which is defined as the amount of ozone produced for the amount of NO_x released, is plotted as a function of the NO_x mixing ratio. Values in this figure were calculated for summer conditions at 40°N. However, the values are not expected to be significantly different at other latitudes. It should be noted that, depending on the assumption made concerning heterogeneous and nighttime chemistry of NO_x, these values are rather uncertain and may depend on meteorology and season. Nevertheless, from the figure, one can see that a molecule of NO_x released in areas with 10 pptv of NO_x mixing ratio (e.g. remote oceanic areas) will produce about 10 times as much ozone as an NO_x molecule released in areas with more than 10 ppbv of NO_x (e.g., an urban center). In other words, for a constant NO_x source strength, NO_x entering or being transported to the remote atmosphere is more efficient in producing ozone than
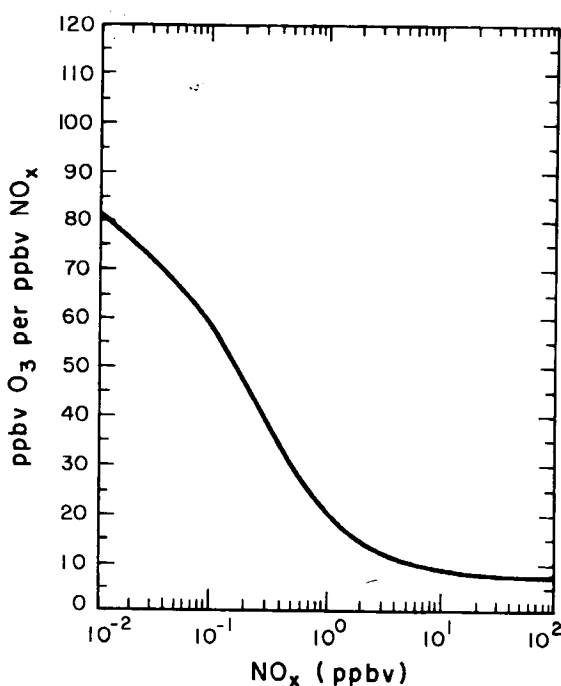

Figure 5-1 Ozone increases per NO_x molecule as a function of NO_x levels.

if it were introduced into the atmosphere in an industrialized region and oxidized there.

5.4 RECENT DEVELOPMENTS IN PROCESSES AFFECTING O_3 AND OH

5.4.1 CH_4 and CH_3CCl_3 Chemistry: Implications for OH

Chemical destruction of CH_4 in the atmosphere is about 97 percent accounted for by reaction with OH radicals, of which 90 percent occurs in the troposphere. An additional small, but still significant biological CH_4 sink is microbial oxidation in soil surface layers. Various compilations of methane sources and sinks have been developed; a frequently quoted study is that by Cicerone and Oremland (1988), in which a global CH_4 sink by OH of 400 to 600 Tg yr^{-1} is presented. However, recently, the rate coefficient of the reaction between CH_4 and OH has been revised, reducing it by about 20 percent (Vaghjiani and Ravishankara, 1991). This implies that

the CH_4 sink through OH is most likely in the lower part of the above range.

The accuracy of the CH_4 lifetime is largely determined by our ability to reproduce realistic OH distributions with global-scale chemistry-transport models, which in turn are tested against measurements of methylchloroform (CH_3CCl_3). This compound is emitted in relatively well known quantities ($\pm$ 20 percent) by the chemical industry. Until now, it has been generally assumed that CH_3CCl_3 is destroyed only by reactions with OH radicals, so that agreement between measured and modeled CH_3CCl_3 concentrations has been interpreted as validation of the model predicted OH distributions. However, Wine and Chameides (1990) have suggested that the oceans constitute an additional sink of CH_3CCl_3, so that global average OH abundances may have been overestimated by up to several tens of percent. Also, for the reaction rate coefficient for CH_3CCl_3 + OH, only a few measurements are available, so that it cannot be ruled out that this reaction will be revised in the future (see also the discussion in Chapter 1).

5.4.2 Changes in Global OH

The importance of knowing OH distributions accurately is underscored by considering that hydrogen containing halocarbon (HCFC, HFC) concentrations in the atmosphere are determined by OH abundances. HCFCs and HFCs are the likely replacements of the long-lived CFCs that will be phased out by the turn of the century, because of the ability of CFCs to reach the stratosphere, where they contribute to ozone depletion. In fact, one compound, F-21, is already in widespread use and its concentration is measured to be approximately 100 pptv (1987) and increasing rapidly (WMO, 1990). Since the hydrogen atom in HCFCs and HFCs can be abstracted by OH, the chemical lifetimes of some of these compounds are short enough to prevent large amounts from being transported into the stratosphere. However, several of these compounds have still large enough lifetimes to be of importance for the chlorine loading of the stratosphere.

Significant changes in the global distribution of OH may have occurred over the last two centuries as the composition of the troposphere is documented to have evolved dramatically. Current changes in key compounds like CH_4 and CO which are observed to

increase (see Chapter 1) and NO_x are expected to affect the OH abundances. Future change in global OH abundance would critically affect predictions of future trends in CH_4, CH_3CCl_3 and the HCFCs (Chapter 8).

Direct measurements of OH in the troposphere giving global distribution is difficult due to short lifetime ($<$ 1 s) and low concentrations. One method of deriving an average global distribution is to use a tropospheric photochemical model for an appropriate range of global conditions (*e.g.*, Logan *et al.*, 1981; Isaksen and Hov, 1987; Thompson *et al.*, 1989). Such calculations require observations or calculations of sunlight as well as a large number of key species involved in the tropospheric OH chemistry (O_3, NO_x, H_2O, CO, CH_4, ...). The OH global fields thus derived have considerable uncertainties (Prather and Spivakovsky, 1990; Spivakovsky *et al.*, 1990a, 1990b), probably of the order of 30 percent to 50 percent (see discussion in WMO, 1990).

A second approach is to adopt a set of calculated OH distributions and to recalibrate or scale them with global tracer model experiments using species with known sources and with chemical losses proportional to OH. This approach has been applied successfully to ^{14}CO and ^{12}CO in a global two-dimensional tracer model (Volz *et al.*, 1981; Derwent and Volz-Thomas, 1990). This work has been followed up by a three-dimensional chemical tracer model study using the global distribution of CH_3CCl_3 to recalibrate the OH fields. Any such recalibration of the OH fields is highly sensitive to the underlying model: errors in the formulation, numerics, circulation, or spatial averaging of the model are usually unspecified or unknown, and they are difficult to propagate to the derived OH fields.

The Atmospheric Lifetime Experiment/Global Atmospheric Gases Experiment (ALE/GAGE) analysis of CH_3CCl_3 (Prinn *et al.*, 1987, 1992) presents a derivation of the overall atmospheric lifetime for CH_3CCl_3. By assuming that the loss is due solely to tropospheric OH (with a small, 10 percent correction for stratospheric losses), they infer a global mean OH concentration. Due to the coarse spatial resolution used in this study, the concept of a global mean value is not very meaningful nor well defined without specifying the spatial dependence of the rate coefficient and the tracer distribution. Nevertheless, the globally averaged loss of CH_3CCl_3

attributed to reaction with OH can be scaled to other reactions such as CH_4 and the HCFCs with similar distributions and rate coefficients to a high degree of accuracy. Therefore, the derivation of a CH_3CCl_3 atmospheric residence time from the ALE/GAGE analysis places a strong single constraint on the integrated tropospheric OH distribution. Unfortunately, stratospheric losses and other sinks such as oceanic uptake (Wine and Chameides, 1990) complicate the interpretation of the ALE/GAGE results. Prinn et al. (1992) deduce a trend in global OH from the ALE/GAGE CH_3CCl_3 record of + 1.0 percent ± 1.2 percent per year over the past decade. Their result may depend on the choice of a simple tropospheric box model. For example the shift in CH_3CCl_3 use over the past decade from the United States to Japan and the Far East is predicted (using a three-dimensional chemical transport model, Prather, 1991) to have caused a geographical redistribution of the CH_3CCl_3 which reduce the inferred global burden, and thereby leading to an assumed increase in the tropospheric loss comparable to that derived.

Given the complexities in determining a global OH concentration today and difficulties in interpreting the past record of trace gas change empirically-derived values for OH will be model dependent and have large uncertainties connected to errors in kinetics, trace gas concentrations, etc.

5.4.3 Other Processes Affecting Tropospheric Ozone

A. Heterogeneous chemistry

As discussed above, the possibility exists that global chemistry-transport models validated indirectly through CH_3CCl_3 analysis overpredict OH concentrations. The same might be true for model-derived OH distribution where only gas phase chemistry is considered. For example, it has been shown by Lelieveld and Crutzen (1990) that chemical reactions in clouds reduce photochemical production of O_3, due to separation of the insoluble NO from the soluble HO_2 between gas and aqueous phase, thus hampering reaction R5. Further, aqueous phase destruction of O_3 is significant, via

$$O_3(aq) + O_2^- \overset{H_2O}{\longrightarrow} OH + 2O_2 + OH^- \qquad (R8)$$
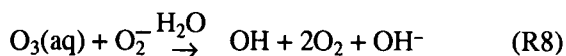
Another important reaction in the aqueous phase is that between dissolved, hydrolyzed formaldehyde and OH. This reaction yields HO_2 that, after dissociation to O_2^-, contributes to O_3 destruction via reaction R8. Thus, a catalytic cycle is set up, in which O_3 and CH_2O are destroyed through aqueous phase OH and O_2^- regeneration. As a consequence of this cloud-induced O_3 reduction and that of CH_2O (being a source of HO_2) the oxidizing capacity of the troposphere is decreased. Furthermore, during the night N_2O_5 is formed via the reactions

$$NO_2 + O_3 \rightarrow NO_3 + O_2 \qquad (R9)$$

$$NO_3 + NO_2 \overset{M}{\rightarrow} N_2O_5 \qquad (R10)$$
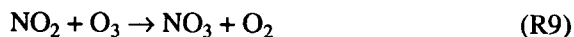
(during daytime NO_3 is rapidly photolyzed). If the N_2O_5 comes into a cloud, HNO_3 is formed almost instantaneously. HNO_3 has a long chemical lifetime and, due to its high solubility, is efficiently removed by deposition processes, so that HNO_3 formation is a sink for NO_x. Reduction of NO_x through N_2O_5 scavenging in clouds additionally decreases O_3 production via reactions R5 and R6, whereas OH regeneration by reaction R5 is decreased.

B. Hydrocarbons and PAN

Another aspect that has received increased attention recently, is the role of higher hydrocarbons in global scale tropospheric chemistry (e.g., Kanakidou et al., 1991). It has long been recognized that these compounds are precursors of peroxyacetyl-nitrate (PAN), which can act as a globally important reservoir species of NO_x (Crutzen, 1979). PAN is thermally instable, and rapidly broken up at high temperatures. But after upward transport to higher, colder air layers its lifetime can increase up to several months, during which long-range transport can take place. Recent measurements show that the PAN levels can exceed NO_x by a factor of 2 to 6 in the free troposphere, with typical values of 100 to 200 pptv, and could thus contribute significantly to the redistribution of active nitrogen compounds in the free troposphere.

Very reactive natural hydrocarbons, such as isoprene and terpenes, which are emitted in large quantities by terrestrial ecosystems, can also contribute significantly to the formation of ozone and

PAN (Liu *et al.*, 1987; Chameides *et al.*, 1988). Blake *et al.* (1991) measured enhanced ozone levels (>90 ppbv) in the planetary boundary layer over the Eastern United States extending into the free troposphere, during a period with high isoprene levels. Isoprene was found to dominate the OH and ozone chemistry in the area. A main question to be answered is to what extent such natural production of hydrocarbons contributes significantly to free tropospheric ozone formation.

C. Radiative effects on ozone

Recent developments with respect to the influence of sulfate particles on climate change processes have indicated that, by enhancing backscattering of solar shortwave radiation, anthropogenic sulfur emissions may have counteracted climate warming by the increased emissions of greenhouse gases (Wigley, 1991). Since about 90 percent of the anthropogenic sulfur releases to the atmosphere occur in the Northern Hemisphere, and because SO_2 and sulfate have lifetimes of less than a week, the process is limited to the Northern Hemisphere. Charlson *et al.* (1991) have shown that anthropogenic sulfate enhances the hemispherically reflected solar radiation to such an extent, that the current warming by growth of CO_2 may be strongly reduced on a hemispheric scale. Although this estimate is still uncertain, based on incomplete scientific understanding, it seems possible that the decreased shortwave radiative flux in the Northern Hemisphere also reduces OH formation, and thus affects the oxidizing capacity of the troposphere.

The large reductions in lower stratospheric ozone observed over the last decade, could, according to the observations by Schnell *et al.* (1991) be significant for tropospheric O_3 and OH formation. Shortwave UV radiation could be strongly enhanced and increase OH production (R1) with varying effect on O_3 formation (Liu and Trainer, 1988).

In regions already high in NO_x, hydrocarbons and O_3, higher levels of UV imply higher rates of O_3 formation, assuming no other radiative changes are occurring. This is because photodissociation leading to OH and HO_2 increases the processes R5 and R6, leading to O_3 formation. In hydrocarbon and NO_x-poor environments the additional UV implies net O_3 loss through the reactions R1, R2, and R7. Indeed,

tropospheric O_3 loss caused by perturbed UV during recent years of Antarctic ozone hole may have been observed at the South Pole, a NO_x-poor environment (Schnell *et al.*, 1991; Thompson, 1991). In either case; the effect on tropospheric OH resulting from stratospheric ozone depletion is to give higher levels through reactions R1 and R2.

A further consideration to be taken into account when future O_3 and OH levels are to be estimated is the possible effect of a global warming. This could affect moisture levels, cloud amount and distribution, precipitation, and dynamics on different scales. It is difficult to predict the consequences for O_3 and OH formation as a number of processes are likely to be affected, some leading to increases in O_3 or OH and some leading to decreases (Thompson *et al.*, 1989).

5.5 MODELING TROPOSPHERIC OZONE CHANGES

Ozone sonde measurements reported in chapter 10 of this assessment indicate that ozone has increased by 1 to 1.5 percent per year in the free troposphere over Europe during the last 20 to 25 years. This is likely an increase due to increased emissions of the ozone precursors NO_x, CO, CH_4, and other hydrocarbons during this time period.

In order to quantify the potential for tropospheric ozone formation by these gases, several model studies have been performed in which the emissions of the source gases were changed one by one. The impact on the tropospheric OH distribution, and thereby on methane, as a major greenhouse gas, has also been studied.

The following perturbation calculations have been carried out by several model groups:

- Doubled NO_x surface emission.
- Doubled CH_4 surface mixing ratio or surface fluxes.
- Increase of 0.5 Tg N/yr NO_x emission from airplanes.
- Doubled CO surface emission.
- Doubled NMHC surface emission.

5.5.1 Source Gases

The calculated changes in tropospheric ozone and in OH will be determined by the changes in

source strength and distribution of the source gases. A thorough discussion of methane, the nonmethane hydrocarbons, and carbon monoxide is given in Chapter 1, and these species will be mentioned only briefly in this Chapter.

• **Methane:** The long chemical lifetime of methane makes it a well mixed gas in the troposphere, with hemispheric differences less than 10 percent. Its impact on the ozone chemistry is therefore not very sensitive to the source distribution, but rather to the total methane emission, which is best determined indirectly by the global methane distribution (mean global concentration is at present 1.72 ppmv in the troposphere) and the loss through the OH reaction. The limiting factor is the accuracy with which we can estimate the tropospheric OH distribution (see the discussion above). Changes in methane emission are therefore expected to have a global effect on the ozone chemistry. Observed methane increase has been 0.7 to 0.8 percent per year during the last years (Table 1-1 in Chapter 1).

• **Nonmethane hydrocarbons:** These source gases are, first of all, expected to affect the ozone and OH chemistry in polluted regions where the anthropogenic emission is large. Due to the wide range of reactivity of NMHC their impact on the chemistry outside polluted regions depends strongly on the partitioning between the individual hydrocarbons. Such considerations are taken into account in model calculations of the impact of these sources on tropospheric chemistry. All the anthropogenically released NMHC have lifetimes short enough to show strong latitudinal and seasonal variations in concentrations, in most cases reflecting enhanced Northern Hemispheric mid-latitude emissions.

Outside the more polluted regional areas natural biogenic sources like isoprene could be the dominant ozone precursors as demonstrated by Blake *et al.* (1991). Although these compounds are very reactive and therefore predominantly are oxidized in the atmospheric boundary layer, they could contribute to free tropospheric ozone formation through ozone transport. However, estimates of their contribution to the free tropospheric ozone formation and OH changes are to be made, and require realistic descriptions of the transport of gases between the boundary layer and the free troposphere.

Anthropogenic emissions of NMHC are estimated to be 100 to 120 Tg/yr. Natural emissions are highly uncertain, but probably substantially larger than the anthropogenic emissions.

• **CO:** This is a major compound in tropospheric ozone chemistry, providing the main loss reaction for OH as well as enhancing the ozone formation by reaction R7 through the regeneration of HO_2:

$$OH + CO \rightarrow H + CO_2 \qquad (R11)$$

$$H + O_2 + M \rightarrow HO_2 + M \qquad (R12)$$
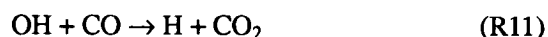
Observations of CO (see, Cicerone, 1988) show that Northern Hemispheric CO distribution is strongly influenced by large anthropogenic emissions (see Table 1-4 in Chapter 1), while Southern Hemispheric distribution is dominated by the production from methane oxidation, with additional production at low latitudes from natural sources (oxidation of natural hydrocarbons) as well as anthropogenic biomass burning which are not well quantified. Since the lifetime of CO is only a few months, large latitudinal variations in concentrations are found, reflecting the variation in the source distribution. Typical mixing ratios of 150 to 200 ppbv are observed in the Northern Hemisphere. In the Southern Hemisphere its mixing ratios are in the range 50 to 70 ppbv.

• **NO_x compounds.** The tropospheric lifetime of NO_x is very short (days or less) compared to the other gases we have discussed. The concentrations therefore vary strongly in space and in time, depending on the strengths and distribution of the sources. It is thus not very meaningful to define an average global or hemispheric distribution. From a modeling point of view it is important to have a good representation of the source distribution as ozone and OH distributions depend critically on the NO_x levels.

Several sources contribute to the formation of tropospheric NO_x as shown below.

The emission estimates of the natural sources (biogenic emission from soils, lightning) are connected with large uncertainties. Emission from soil has large temporal and spatial variations (Sanhueza *et al.*, 1990). This source may grow due to increased use of N-fertilizers. Production from lightning (and from airplanes) is of particular

importance as the NO_x is emitted directly into the free troposphere.

Table 5-1 Estimated emission of NO_x (Tg N/yr) (Sanhueza, 1991).

A. Natural
  —Soils   10–20
  —Lightning   2–8
  —Transport from stratosphere 1

B. Anthropogenic
  —Fossil fuel combustion 21
  —Biomass burning   2.5–8.5
  —Tropospheric aircraft <u>0.6</u>
          37.1–59.1

The following source strengths are used in the reference calculations:

Fossil fuel combustion	21	Tg N/yr
Biomass burning/Soils	16	"
Lightning	6	"
Trsp. from stratosphere	0.6	"
Airplanes	0.7	"

Figure 5-2 shows a comparison between a measured NO profile at northern mid-latitudes (Ehhalt *et al.*,
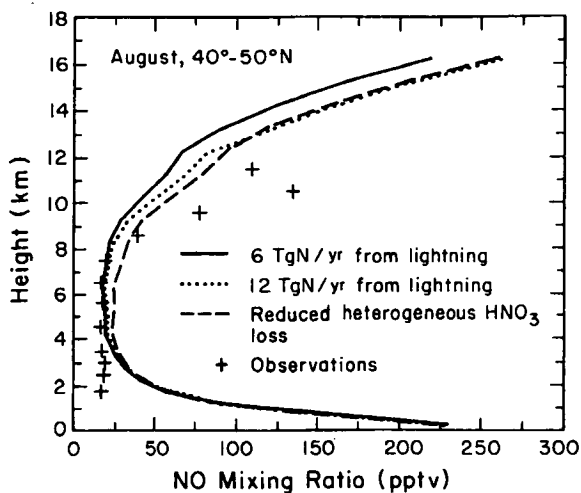

Figure 5-2 Height profile for the NO distribution at 40-50°N, with observed NO profiles from the same latitudes.

1991) and calculated height distribution at the same latitudes. Although we should expect large variations in NO, making it difficult to compare model results with observations, some common features emerge. NO has a minimum in the middle troposphere (4 to 8 km) where mixing ratios are sufficiently low to expect *in situ* ozone loss. There is a marked increase above these heights which is assumed to be a result of NO_x production from lightning, airplanes and from transport from the stratosphere.

The results are seen to be sensitive to the strength of the lightning source and the the removal efficiency of HNO_3 in the middle and upper troposphere. The results indicate that calculations underestimate NO_x levels at these heights. Drummond *et al.* (1988) and Ehhalt *et al.* (1991) suggest that fast convective transport from the surface could contribute significantly to NO_x at these heights. It should be mentioned that transport by convective processes could be an effective pump of NO_x, CO, and other insoluble gases from the boundary layer to the upper troposphere (Dickerson *et al.*, 1987; Pickering *et al.*, 1991). These types of processes are not included in the calculations, and the given profile could therefore represent an underestimate of NO_x.

5.5.2 Calculated Ozone Perturbations

Figure 5-3 gives the global and yearly average height profiles of ozone changes due to increased emissions of NO_x from surface sources, increased emission of CH_4, and increased NO_x emission from aircraft. With the exception of airplane emission all model perturbations give smallest increases in the upper troposphere. Ozone changes show the fastest drop with height in the case of increased surface NO_x emissions.

There are substantial differences in the calculated ozone production from the different models. The "multiregion one-dimensional model" (National Aeronautics and Space Administration/Goddard Space Flight Center) seems to give somewhat larger ozone increases than the two-dimensional models (Harwell, Oslo), but there are also pronounced differences between the two-dimensional models in the cases of increased NO_x emissions, particularly in the upper troposphere. Calculated ozone changes due to increased CH_4 show more consistency between the models.

Ozone changes will, since it has a relatively short lifetime, depend on the distribution of the precursor

gas emissions. Anthropogenic influences are strongest in the Northern Hemisphere, hence ozone changes are most pronounced in this hemisphere. Figure 5-4 shows height profiles for ozone changes at 40°N latitude and 40°S latitude for NO_x increases and CH_4 increases. The hemispheric, seasonal and height

differences in ozone increases are particularly strong in the case of increased NO_x emissions. Any impact on climate from tropospheric ozone changes will therefore be highly variable.

In these perturbation studies the source strength of the different gases emitted is highly different. In order to make comparisons of the efficiencies in producing ozone, all increases are given relative to emission of one mass unit and normalized to the
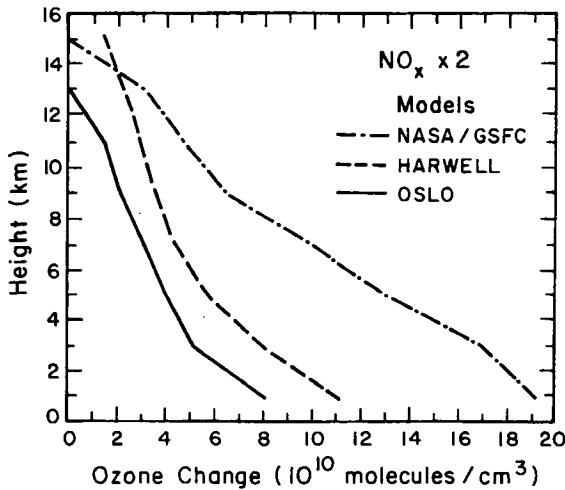

Figure 5-3a Global average height profiles of O_3 increases for doubled NO_x surface emission.

Table 5-2 Calculated average global changes in tropospheric ozone (percent) due to the increased emission of ozone precursors given in Table 5-1.

Model	NASA/GSFC	HARWELL	OSLO
2 x NO_x	13.8	6.6	3.7*(5.0)
2 x CH_4	15.2	11.3**	10.4**
2 x AIRPL.		3.4	0.8*
2 x CO			8.9*
2 x NMHC			6.8*

*Refers to calculations where surface fluxes of methane are kept constant.

**Refers to doubling in surface fluxes. All other calculations have a fixed methane mixing ratio at the lower boundary. (In the case of doubled CH_4, surface methane concentrations are twice the current values).
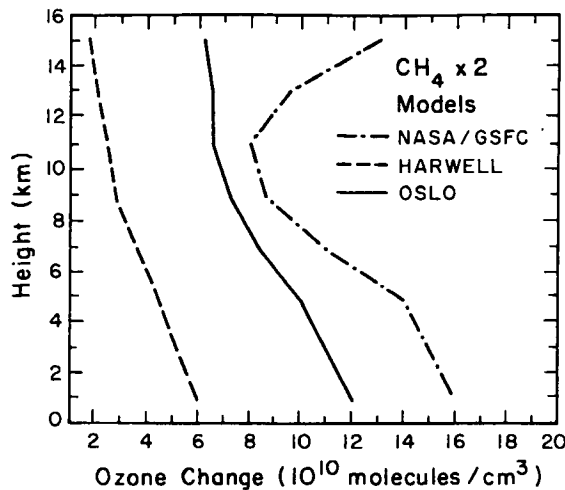

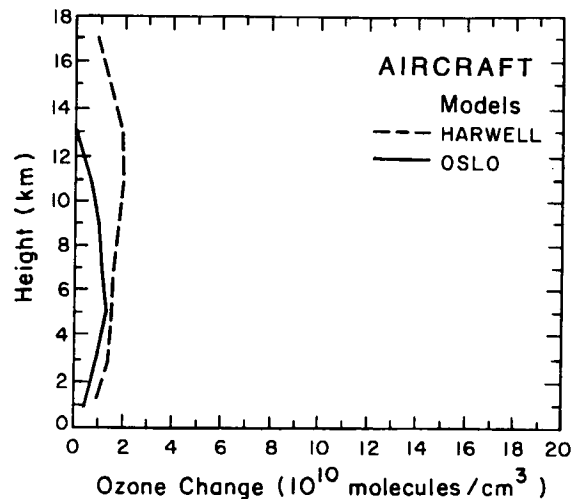**Figure 5-3b** Global average height profiles of O_3 increases for doubled CH_4 emission.

Figure 5-3c Global average height profiles of O_3 increases for increased emission from airplanes.

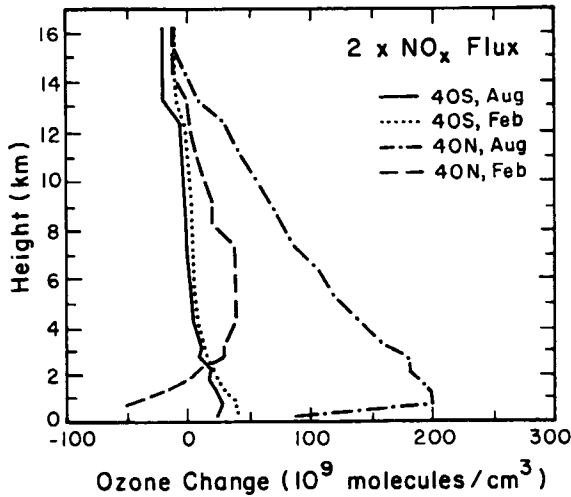impact from methane. The results are given in Table 5-3.

Figure 5-4a Height profiles for ozone increases at 40°N latitude and 40°S latitude for February and August for doubled NO$_x$ surface emission.
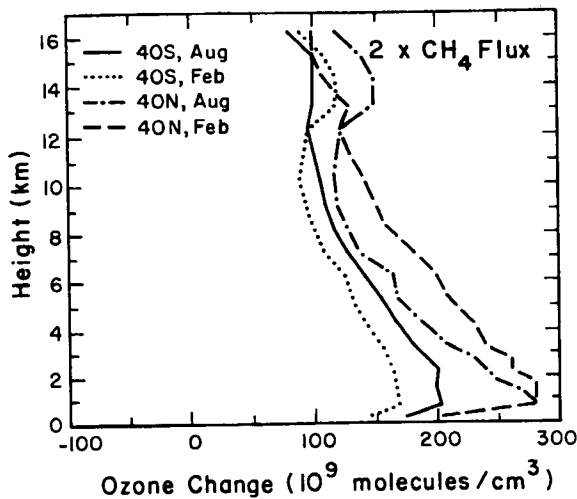

Figure 5-4b. Height profiles for ozone increases at 40°N latitude and 40°S latitude for February and August for doubled CH$_4$ emission.

Table 5-3 Efficiencies of the source gas emissions in producing tropospheric ozone. The numbers are given relative to the efficiency of methane emission. (Calculated with the Oslo model.)

	2 x NO$_x$	2x AIRPL	2 x CH$_4$	2 x CO	2 x NMHC
Rel.eff	3.0	50	1	0.2	0.5

It is clear that NO$_x$ emitted from airplanes in the upper troposphere is much more efficient in enhancing ozone than ground based emissions of NO$_x$ (a factor of 17 in these calculations). We should notice that we are here looking at the tropospheric average production. In the context of climate impact, upper tropospheric O$_3$ changes are more important than changes in the lower troposphere (Wang *et al.*, 1980; Lacis *et al.*, 1990). NO$_x$ emissions from airplanes are therefore even more important than ground based releases as changes occur predominantly in the upper troposphere (see Figure 5-3). Both CO and NMHC are less efficient ozone producers than methane.

5.5.3 Changes in OH and in the Oxidation Potential of the Troposphere

Changes in the ozone distribution are accompanied by changes in OH and in source gases that are controlled by OH. From a climate point of view we are especially interested in the impact of OH changes on methane, we therefore concentrate our discussion on the interaction of chemical changes with methane through the reaction:

$$OH + CH_4 \rightarrow CH_3 + H_2O \qquad (R13)$$
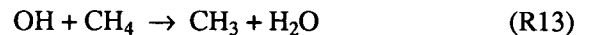
This reaction is of importance because it provides the dominating loss mechanism for methane in the atmosphere as well as being an important loss reaction for OH.

We should remember that changes in OH also have impact on the abundances of other greenhouse gases like the HCFCs and the HFCs.

Table 5-4 gives calculated changes in the globally averaged OH concentrations in the model cases studied.

Table 5-4 OH changes (percent)

	NASA/GSFC	HARWELL	OSLO
2 x NO$_x$	17.4	15.2	15.4*(14.3)
2 x CH$_4$	-17.7	-10.2	-16.9*(-10.8)
2 x AIRPL		2.6	2.0*
2 x CO			-21.3*
2 x NMHC			-5.5*

*Refers to fluxes as lower-boundary values, otherwise the lower-boundary concentrations are fixed.

There is a consistent picture emerging from the calculations showing that increased NO$_x$ emissions lead to enhanced OH and thereby increased oxidation in the troposphere, while increases in the emissions of the other source gases lead to reduced OH values.

A substantial part of the increase in methane concentrations could result from the positive feedback imposed by increasing methane on OH through reaction R13 (Chameides *et al.*, 1977; Sze, 1977; Isaksen, 1988). The magnitude of this feedback depends on how important reaction R13 is for the OH loss. The effect of the feedback increases with increasing methane levels as methane becomes more important for the OH loss at higher methane values. This is illustrated in Figure 5-5 where the relation between increased fluxes and

increased mixing ratios of CH$_4$ in the atmosphere is given. The feedback is given by the expression

$$f = [(c-c1)/c1]/[(F-F1)/F1] -1 \qquad (R14)$$

where c1 and F1 are present day concentrations and fluxes respectively, and c and F are perturbed levels.

At present day methane levels the feedback amounts to about 35 percent. This feedback accounts for an indirect effect that adds to the GWP of methane. In a similar way the feedback will affect the concentrations when emissions are reduced, but it will become less significant at lower concentrations.

5.5.4 Sensitivity Tests

As previously pointed out, there might be large nonlinear effects connected to formation of ozone in the atmosphere (see Figure 5-1) due to the large spatial and temporal variations of NO$_x$ and the interaction with methane. Two sets of sensitivity tests have been performed. Calculations of the efficiency of ozone formation for: a) 10 percent increases in NO$_x$ and CH$_4$ emissions instead of a doubling, and b) double NO$_x$ and CH$_4$ emissions with a background production of 12 Tg N/yr from lightning (instead of 6 Tg N/yr). The results of these comparisons are shown in Table 5-5.
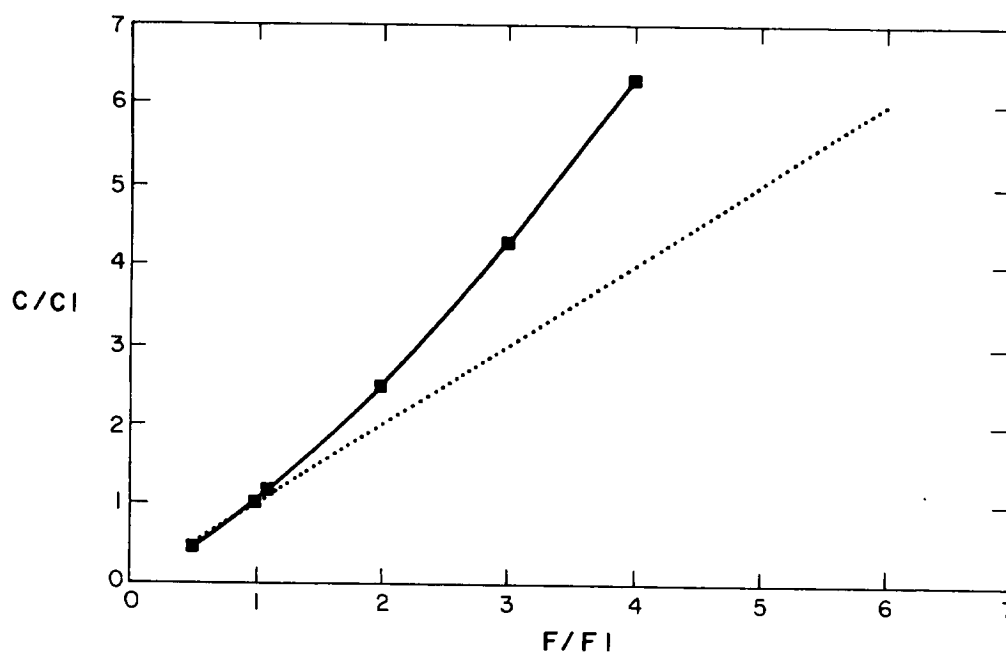

Figure 5-5 Calculated changes in average global mean concentration of CH$_4$ as a function of changes in fluxes. The straight line represents no feedback between OH and CH$_4$.

TROPOSPHERIC PROCESSES

Table 5-5 Calculation of the efficiency of ozone formation from increased emissions of NO$_x$ and CH$_4$. All numbers in (a) and (b) are compared to the efficiency of doubling CH$_4$ fluxes with a lightning production of 6 Tg N/yr. The numbers should therefore be compared with the numbers given in Table 5-3.

(a)	10 percent NO$_x$ incr.	4.1
	10 percent CH$_4$ incr.	1.2
(b)	2 x NO$_x$	1.6
	2 x CH$_4$	1.07
	2 x AIRPL	24.8

When NO$_x$ emissions from lightning are increased from 6 to 12 Tg N/yr in the model calculations and the CH$_4$ surface mixing rations are kept at fixed levels, the CH$_4$ emissions increase by 11 percent showing that the OH concentrations have increased.

Table 5-5 shows that tropospheric ozone production from NO$_x$ increases is sensitive to the levels of NO$_x$ in the atmosphere as well as the increase in the emissions. Small increases in emissions lead, as we could expect, to more efficient ozone production. When NO$_x$ fluxes are increased by 10 percent, ozone production increases by approximately 40 percent, compared to the production when NO$_x$ fluxes are

doubled. Higher background levels of NO$_x$ reduce the efficiency of ozone production from increased NO$_x$ fluxes markedly. The sensitivity of methane induced ozone production to the adapted background levels of NO$_x$ and to changes in fluxes is moderate. It is seen that CH$_4$ produces ozone slightly more efficiently at higher NO$_x$ background levels, and the efficiency varies little with changes in the surface fluxes.

Tests of the response of ozone changes to changes in emissions of pollutants reveal that efficiencies are sensitive to the region where emission takes place (*e.g.*, NO$_x$ emitted in polluted regions, gives different ozone production efficiency than NO$_x$ emitted in less polluted regions).

5.5.5 Recent Changes in Tropospheric O$_3$ and OH

It has been pointed out that tropospheric OH could have decreased substantially over the past several decades due to suppression by increasing CH$_4$ and CO (Levine *et al.*, 1985; Thompson and Cicerone, 1986). On the other hand, increasing O$_3$ and NO$_x$ since pre-industrial times may have caused OH to increase in certain parts of the troposphere (Isaksen and Hov, 1987; Crutzen and Zimmermann, 1991), making predictions of present trends difficult to make. Simulations of eight scenarios with varying rates of
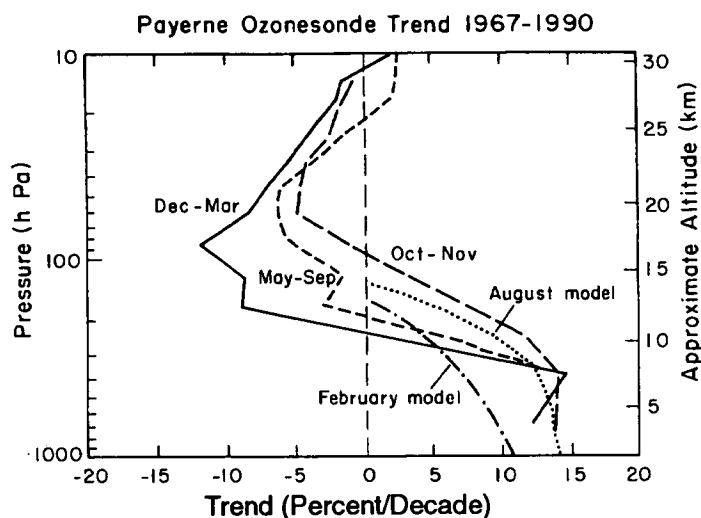

Figure 5-6 Height profile for the calculated and observed decadel ozone increases over the last 20 years at northern mid-latitudes (40–50°). Observations are from Payerne, Switzerland.

5.14

CH_4, CO, and NO emissions performed for a 1990 U.S. Assessment (USEPA, 1990) showed a small increase in global OH over the next 50 years (Isaksen et al., 1989) whereas two other models (Prather, 1989; Thompson et al., 1990) projected moderate losses over that period.

Ozone is probably increasing due to enhanced emissions of hydrocarbons, CO, and NO.

A model simulation of the chemical development of the troposphere over the last 20 years, assuming a doubling of anthropogenic emission of NO_x in this period, whereas emissions of CO and CH_4 have been increased by 0.8 and 1.0 percent per year respectively, and similar increases in anthropogenic NMHC, give global average ozone increases of 9.4 percent and a negligible change in OH (~1 percent). The mid-latitudinal height profile of the O_3 increase is shown in Figure 5-6, and is compared with Payerne, Switzerland, ozone sonde observations. The strong decadel ozone increase observed in the free troposphere up to approximately 10 km is also reflected in the model calculations.

Table 5-6 shows globally-averaged long-term future O_3 growth rates from several recent model studies that assume roughly current CH_4 and CO growth levels. Tropospheric O_3 increases are predicted to continue in the 0.2–1.5 percent/year range. Rates are different depending on how the models treat regional inhomogenities.

**Table 5-6 Model ozone predictions with "business-as-usual" increases in CH_4, CO, and NO, 1985–2040.**

Model	%Annual Increase, Global Mean
2D-Hough & Derwent (1990	0.2–0.4
2D-Law & Pyle (1991)	1–1.5
2D-Valentin (1990)	>0.2
USEPA (1990): 2D-Isaksen	0.1
USEPA (1990): M-1D-Thompson	0.3
USEPA (1990): OD-Prather AMAC	0.3

5.6 TROPOSPHERIC DEGRADATIONS OF HFCs AND HCFCs

The dominant loss process for the HFCs and HCFCs in the atmosphere is through reaction with the OH radical in the troposphere. Photolysis and reaction with the $O(^1D)$ atom in the stratosphere will also contribute a minor additional loss process. The rate constants for the OH radical reactions with the HFCs and HCFCs are now reasonably well known (DeMore et al., 1990; IUPAC, 1991). The calculated tropospheric lifetimes are inversely proportional to the OH radical reaction rate constants at ~270 K, and are tabulated elsewhere in this report. Since these lifetimes are predominantly determined by the tropospheric OH radical concentration, any change in tropospheric OH will directly impact the fraction transported into the stratosphere (see discussion above for future tropospheric OH trends).

These OH radical reactions proceed by H-atom abstraction to form a haloalkyl radical (taking the compound CX_3CHYZ as an example, where X, Y and Z are H, Cl, Br and/or F)

$$OH + CX_3CHYZ \rightarrow H_2O + CX_3CYZ \qquad (R15)$$
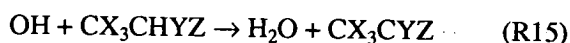
The reactions subsequent to this initial H-atom abstraction have not been completely elucidated to date, and our present knowledge of the tropospheric degradations of the HFCs and HCFCs is in part based on analogy with the reasonably well understood reactions of the alkanes and the C_1 haloalkanes (WMO, 1990). A generalized reaction scheme is shown in Figure 5-7, leading to the first-generation products. If the carbonyl $CX_3C(O)Y$ is an aldehyde (Y = H), then a further reaction sequence can occur, as shown in Figure 5-8, and the CX_3 radical produced in these reactions then undergoes an analogous series of reactions as outlined for the CX_3CYZ radical in Figure 5-7.

Recent available experimental data obtained for the C_1 and C_2 HFCs and HCFCs are consistent with this general degradation scheme. The various steps in this degradation scheme are discussed briefly below, with an emphasis on the potential for transport of chlorine- and bromine-containing intermediate product species into the stratosphere.

• **Reaction of the Haloalkyl Radical, CX_3CYZ:**
The sole reaction under tropospheric conditions is with O_2 to form the peroxy radical, CX_3CYZOO (WMO, 1990).

• **Reactions of the Peroxy Radical, CX_3CYZOO:**
The peroxy radicals may react with NO, NO_2, and HO_2 radicals under tropospheric conditions. Given
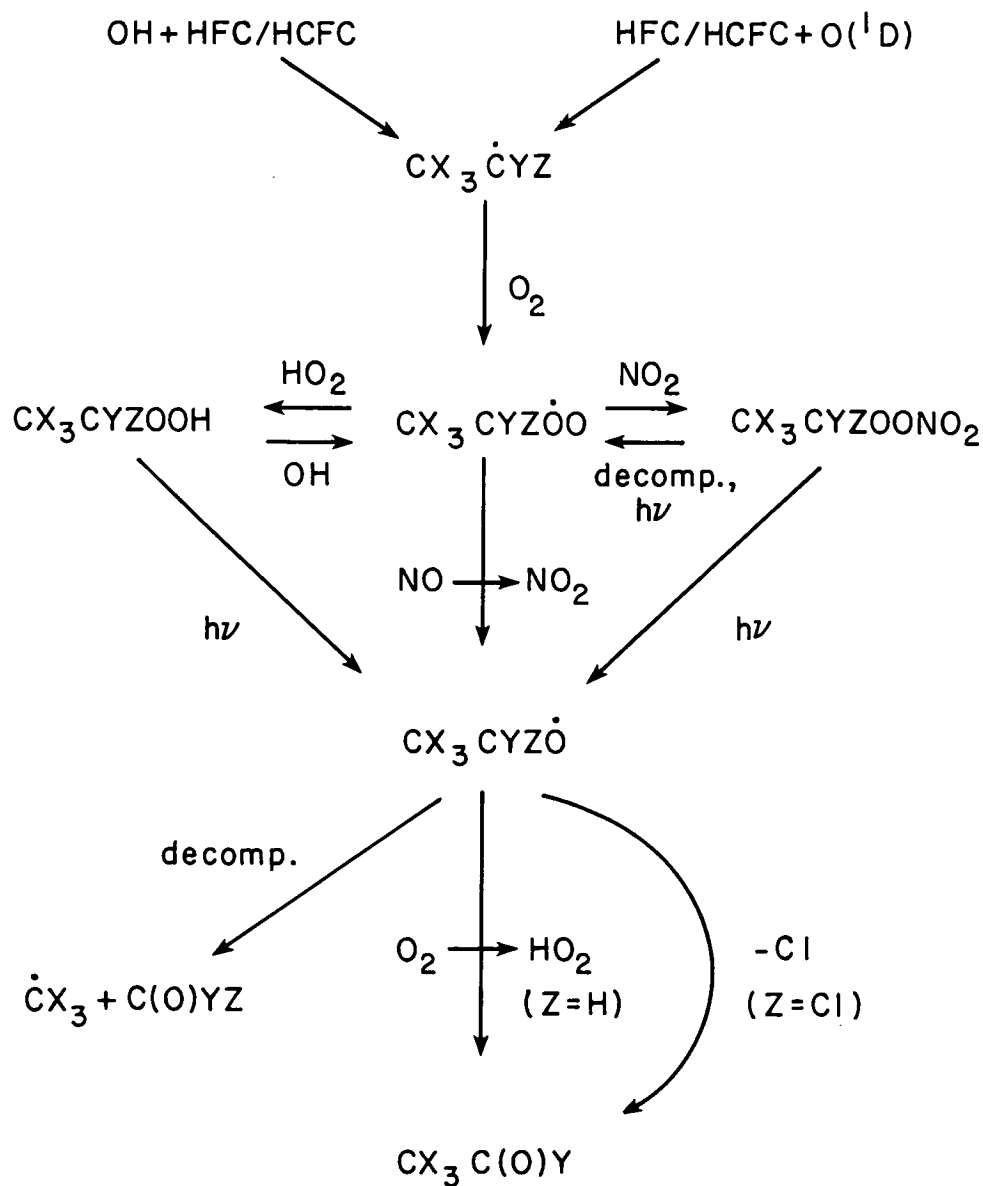
$$OH + HFC/HCFC \qquad\qquad HFC/HCFC + O(^1D)$$

$$\searrow \qquad \swarrow$$

$$CX_3\dot{C}YZ$$

$$\downarrow O_2$$

$$CX_3CYZOOH \quad \underset{OH}{\overset{HO_2}{\rightleftarrows}} \quad CX_3CYZ\dot{O}O \quad \underset{\substack{decomp.,\\h\nu}}{\overset{NO_2}{\rightleftarrows}} \quad CX_3CYZOONO_2$$

$$h\nu \searrow \qquad\qquad NO \longrightarrow NO_2 \qquad\qquad \swarrow h\nu$$

$$\downarrow$$

$$CX_3CYZ\dot{O}$$

$$decomp. \swarrow \qquad\qquad \downarrow \qquad\qquad -Cl$$

$$\dot{C}X_3 + C(O)YZ \qquad O_2 \longrightarrow HO_2 \qquad (Z=Cl)$$
$$(Z=H)$$

$$CX_3C(O)Y$$

Figure 5-7 Degradation scheme for HFC/HCFC initiated by the reactions with OH and O(1D).

5.16

$$CX_3CHO \xrightarrow{h\nu} \overset{\bullet}{C}X_3 + HCO$$

$$\downarrow OH$$

$$CX_3\overset{\bullet}{C}O \xrightarrow[\text{decomp.}]{} \overset{\bullet}{C}X_3 + CO$$

$$\downarrow O_2$$

products, including CX_3COOH, $CX_3C(O)OOH$ $\xleftarrow[RO_2^{\bullet}]{HO_2}$ $CX_3C(O)O\overset{\bullet}{O}$ $\underset{\substack{\text{decomp.,} \\ h\nu}}{\overset{NO_2}{\rightleftarrows}}$ $CX_3C(O)OONO_2$

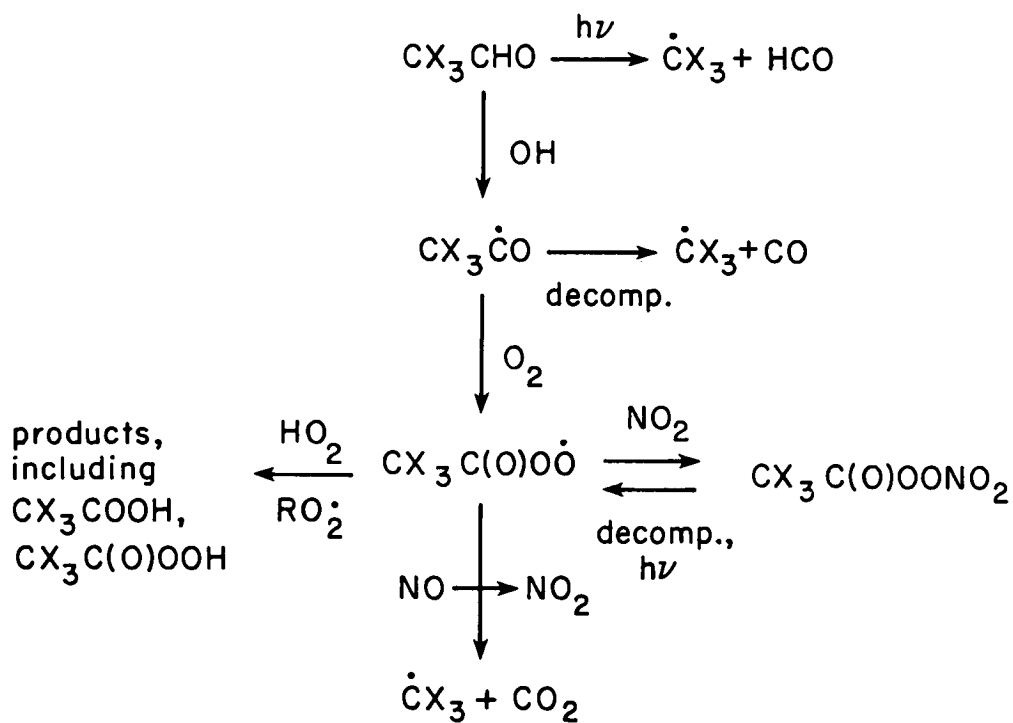$$NO \longrightarrow NO_2$$

$$\downarrow$$

$$\overset{\bullet}{C}X_3 + CO_2$$

Figure 5-8 Example of oxidation scheme for HFC/HCFC oxidation products (aldehydes).
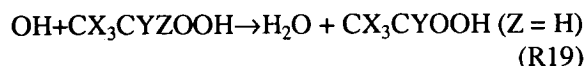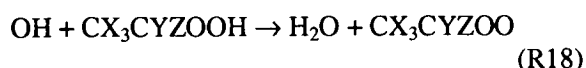
the relative magnitudes of the rate constants for reactions of peroxy radicals with these species and their atmospheric concentrations, the major loss process for CX_3CYZOO radicals in the atmosphere will be with NO (WMO, 1990; Hayman *et al.*, 1991). While the reaction with NO is expected to form mainly the alkoxy radical, CX_3CYZO, formation of the organic nitrate, $CX_3CYZONO_2$, from the pathway

$$CX_3CYZOO + NO \xrightarrow{M} CX_3CYZONO_2 \qquad (R16)$$

may also occur to a minor extent. Formation of ethyl nitrate from the reaction of NO with the ethyl peroxy radical accounts for approximately 1 percent of the overall reaction at 298°K and atmospheric pressure (Atkinson *et al.*, 1982). The products and quantum yields of photolysis of alkyl nitrates have not been extensively studied, although the lack of structure in the absorption spectra of these compounds suggests that the quantum yield for decomposition is close to unity. The available evidence indicates that the major reaction channel involves breaking of the $O-NO_2$ bond generating the alkoxy radical (Roberts, 1990). Thus, it is unlikely that halogenated nitrates will have significant atmospheric lifetimes but will photolyze to give the corresponding alkoxy radical.

The reactions of the peroxy radical with HO_2 and NO_2 lead to the formation of hydroperoxides and peroxynitrates, respectively (Figure 5-7).

• **Hydroperoxides**: The hydroperoxides are expected to undergo photolysis and reaction with the OH radical.

$$CX_3CYZOOH + hv \rightarrow CX_3CYZO + OH \qquad (R17)$$

$$OH + CX_3CYZOOH \rightarrow H_2O + CX_3CYZOO \qquad (R18)$$

$$OH + CX_3CYZOOH \rightarrow H_2O + CX_3CYOOH \ (Z = H) \qquad (R19)$$

$$CX_3CYOOH \rightarrow CX_3C(O)Y + OH \qquad (R20)$$

To date, kinetic and photolysis data are available only for CH_3OOH and these data indicate lifetimes of ~5 days for each of these processes, with an overall lifetime due to photolysis and OH radical reaction of ~2 to 3 days. In addition, wet deposition of the hydroperoxides is expected to be efficient, and dry deposition may also be rapid (*WMO*, 1990). The tropospheric residence times of the halogenated hydroperoxides are then expected to be short, of the order of a few days or less, and the potential for transport of chlorine into the stratosphere through the intermediacy of the hydroperoxides is very low.

• **Haloalkyl Peroxynitrates**: The haloalkyl peroxynitrates, $ROONO_2$, thermally decompose back to the peroxy radical and NO_2

$$CX_3CYZOONO_2 \rightleftarrows CX_3CYZOO + NO_2 \qquad (R21)$$

The lifetimes of methyl and ethyl peroxynitrate due to this thermal decomposition range from ~1 sec at the earth's surface (288 K) to ~10^6 sec (10 days) in the upper troposphere (Zabel *et al.*, 1989; IUPAC, 1989, 1991; WMO, 1990). For the haloalkyl peroxynitrates $ROONO_2$, where $R = CF_2Cl$, $CFCl_2$, and CCl_3, the thermal decomposition rates are slower, and the lifetimes due to thermal decomposition range from 5-20 sec at 298 K to 0.1 to 1 year in the upper troposphere (Köppenkastrop and Zabel, 1991). The thermal decomposition rates for $CF_2ClCH_2OONO_2$ and $CFCl_2CH_2OONO_2$ have been measured (Kirchner *et al.*, 1991) and the data indicate a lifetime due to thermal decomposition of ~2 days in the upper troposphere (*i.e.*, less than those of $CF_2ClOONO_2$, $CFCl_2OONO_2$, and CCl_3OONO_2). This limited set of thermal decomposition data show that the haloalkyl peroxynitrates of structure $ROONO_2$, where $R = CF_2Cl$, $CFCl_2$ and CCl_3, are thermally stable over a time period of months to a few years in the upper troposphere, especially at high NO_2/NO concentration ratios, and suggest that this may also be the case for compounds of the structure RCX_2OONO_2, where $X = Cl$ and/or F.
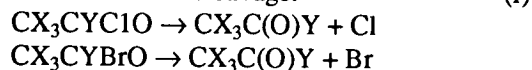
In addition to thermal decomposition, the peroxynitrates are expected to undergo photolysis, based on the limited data of Cox and Tyndall (1979), Morel *et al.* (1980) and Sander and Watson (1980) for CH_3OONO_2, $CFCl_2OONO_2$, and CCl_3OONO_2, with calculated lifetimes of ~5 days in the lower troposphere. These data indicate that the lifetimes of the peroxynitrates will be sufficiently short that significant transport to the stratosphere will not occur, except possibly at high latitudes during wintertime nighttime conditions for $CF_2ClOONO_2$, $CFCl_2OONO_2$, and CCl_3OONO_2 (and possibly other, as yet not studied, peroxynitrates).

• **Acyl Peroxynitrates:** For the halogen-containing acyl peroxynitrates, $RC(O)OONO_2$, the thermal decomposition lifetimes are expected, by analogy with those for peroxyacetyl and peroxypropionyl nitrates (PAN and PPN, respectively), to be much longer than those for the peroxynitrates $ROONO_2$. Rate data for the thermal decomposition of $CF_2ClC(O)O_2NO_2$ reported by Kirchner *et al.* (1991) support this conclusion. The results show that the thermal lifetime is extremely long, varying from ~3 hour at 298 K to ~5000 year in the upper troposphere (220 K) and its total lifetime in the upper troposphere will be limited by its photolysis rate. Thus, as for the alkyl peroxynitrates, halogenation appears to increase the thermal stability of acyl peroxynitrates. Since photolysis is also likely to be slow (by analogy with peroxyacetyl nitrate) (IUPAC, 1989, 1991), the lifetimes of the haloperoxyacyl nitrates due to chemical processes are likely to be long in the upper troposphere, and the potential for transport of chlorine to the stratosphere exists. This is possible for the peroxyacyl nitrates which may be formed in the tropospheric degradation reactions of HCFC-141b and 142b.
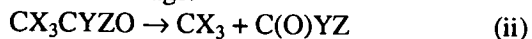
• **Acids and Acyl Hydroperoxides:** By analogy with the reactions of the $CH_3C(O)OO$ radical, haloacyl peroxy radicals, $CX_3C(O)OO$, may react with HO_2 and also with CH_3O_2 in the lower troposphere (WMO, 1990). The products of these reactions are expected to be acids, $CX_3C(O)OOH$. Reaction with the OH radical is likely to be slow, and the most probable fate of these species is via wet deposition and rain out.

• **Reactions of Haloalkoxy Radicals:** There are a number of potential reaction pathways for the atmospheric degradation of haloalkoxy radicals.
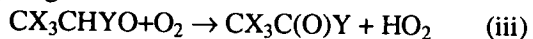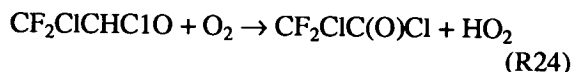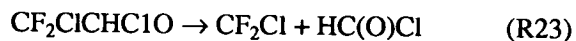
C-Cl or C-Br bond cleavage: (i)
$$CX_3CYClO \rightarrow CX_3C(O)Y + Cl$$
$$CX_3CYBrO \rightarrow CX_3C(O)Y + Br$$

C-C bond cleavage:
$$CX_3CYZO \rightarrow CX_3 + C(O)YZ \qquad (ii)$$

Hydrogen abstraction:
$$CX_3CHYO + O_2 \rightarrow CX_3C(O)Y + HO_2 \qquad (iii)$$

For example, for the $CF_2ClCHClO$ radical formed from HCFC-132b

$$CF_2ClCHClO \rightarrow CF_2ClCHO + Cl \qquad (R22)$$

$$CF_2ClCHClO \rightarrow CF_2Cl + HC(O)Cl \qquad (R23)$$

$$CF_2ClCHClO + O_2 \rightarrow CF_2ClC(O)Cl + HO_2 \qquad (R24)$$

The majority of the experimental data concerning the reactions of haloalkoxy radicals has come from chlorine atom-initiated oxidation of halogenated alkanes and alkenes. Most of this work has been carried out at 298 K and atmospheric pressure in air. It is assumed that the removal processes for these radicals determined in chlorine-rich systems are applicable to atmospheric conditions. A number of general conclusions concerning the relative importance of the available reaction pathways may be drawn from the available experimental data (Bertrand *et al.*, 1971; Sanhueza *et al.*, 1976; Carr *et al.*, 1986; Lesclaux *et al.*, 1987; WMO, 1990; Nelson *et al.*, 1990; Edney *et al.*, 1991; Hayman *et al.*, 1991; Jemi-Alade *et al.*, 1991; Libuda *et al.*, 1991; Meller *et al.*, 1991; Scollard *et al.*, 1991; Tuazon and Atkinson, 1991; Zellner *et al.*, 1991).

(i) CX_2ClO radicals (X = H, Cl or F) eliminate a Cl atom, except for CH_2ClO where reaction with O_2 is the dominant reaction. The reactions for the CH_2BrO and $CHBr_2O$ radicals are totally analogous to those for the corresponding chlorine-containing radicals.

(ii) CF_3O radicals are believed to be the product of the reaction of CF_3O_2 with NO under atmospheric conditions. However, the mechanism for oxidation of the CF_3O radical is uncertain. Fluorine atom loss and reaction with O_2 are improbable since both reactions are appreciably endothermic. It is generally assumed that the final product of the tropospheric degradation of CF_3O radicals will be $C(O)F_2$, although the formation of other products cannot be discounted.

(iii) CX_3CH_2O radicals (X = H, Cl or F) react either with O_2 to form the aldehyde and an HO_2 radical, or undergo C-C bond cleavage.

(iv) CX_3CCl_2O and CX_3CFClO radicals decompose by Cl atom elimination rather than by C-C bond fission. From the available data this type of reaction occurs whatever the substituent X.

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(v) CX_3CF_2O radicals underdo C-C bond cleavage.

(vi) CX_3CHYO radicals (Y = Cl or F) have two important reaction channels. The relative importance of the C-C bond breaking process and reaction with O_2 appears to be a function of both the nature of X and Y and is expected to be temperature dependent. Recent results for the CF_3CHFO radical show that at 298 K and one atmosphere of air C-C bond fission is the dominant reaction channel (~75 percent) (Meller et al., 1991; Tuazon and Atkinson, 1991; Zellner et al., 1991). For atmospheric modeling purposes both the effect of O_2 pressure and temperature on the relative importance of the two pathways is required.

• **Carbonyl Compounds:**

Aldehydes. The absorption spectra of HC(O)Cl and HC(O)Br extend beyond 290 nm (Libuda et al., 1990, 1991) and lead to calculated photolysis lifetimes in the troposphere of 50 days and ~4 days, respectively, assuming unit photodissociation quantum yields. HC(O)F will not photolyze in the troposphere (Libuda et al., 1991). Only for HC(O)Cl has the OH radical reaction been studied (Libuda et al., 1990), with an upper limit to the rate constant of $<3.2 \times 10^{-13} cm^3 molecule^{-1}s^{-1}$ at 298°K being reported. These OH radical and absorption cross-section data indicate that HC(O)Cl and HC(O)Br will have short lifetimes in the troposphere. HC(O)F is, however, expected to have a much longer lifetime with respect to OH radical reaction and photolysis.

The tropospheric lifetimes of the halogenated acetaldehydes due to reaction with OH radicals are calculated to range from about four days for CH_2ClCHO to around 20 days for CF_3CHO (Dóbé et al., 1989; Nelson et al., 1990; Starcke et al., 1990; Balestra-Garcia et al., 1991; Scollard et al., 1991). The absorption cross sections have been measured for several Cl and Br-containing acetaldehydes (Starcke et al., 1990; Libuda et al., 1991; Rattigan et al., 1991). Photolysis lifetimes in the troposphere are about 1 to 7 hours, based on unit photodissociation quantum yields. Assuming the halogenated acetaldehydes have similar quantum yields to acetaldehyde, their photolysis lifetimes may be several days. These available OH rate constant and photolysis data for halogenated acetaldehydes indicate that they will rapidly degrade in the troposphere, and not be important reservoirs for halogen atoms.

Carbonyl halides. Reaction of the OH radical with $C(O)Cl_2$ has been shown to be slow, with an upper limit to the rate constant of $<1 \times 10^{-15} cm^3$ molecule $^{-1} s^{-1}$ having been determined at 298 K (Nelson et al., 1990), and the analogous reactions with C(O)FCl and $C(O)F_2$ are expected to be similarly slow. The absorption cross sections of the carbonyl halides have been measured (CODATA, 1982; Libuda et al., 1991; Meller et al., 1991). The absorption spectrum of $C(O)Br_2$ extends beyond 290 nm, and leads to a calculated photolysis lifetimes in the troposphere of less than one week (Libuda et al. 1991). The absorption spectrum of $C(O)Cl_2$ extends to 290 nm (Meller et al., 1991), with the longwavelength limits of C(O)FCl and $C(O)F_2$ being 250 nm and 230 nm, respectively (Meller et al., 1991). The calculated lower tropospheric lifetime of $C(O)Cl_2$ due to photolysis is approximately 50 days, assuming a unit quantum yield. For C(O)FCl and $C(O)F_2$, photolysis will not occur in the troposphere. Thus these carbonyl halides are expected to have long tropospheric lifetimes due to chemical loss processes. Uptake into water droplets and oceans with subsequent hydrolysis could be a possible removal process in competition with transport to the stratosphere. It has generally been assumed that removal in cloud-water and the oceans is relatively efficient, leading to a low flux of these species into the stratosphere (WMO, 1990). However, Worsnop et al. (1991) have only been able to obtain upper limits for the uptake coefficients for $C(O)F_2$ and $C(O)Cl_2$ into aqueous droplets of less than 10^{-3}. Furthermore, the calculated washout ratio W of W = 4.1 for $C(O)Cl_2$ at 278 K reported by Dana et al. (1985) is consistent with only slow or very slow rain-out of $C(O)Cl_2$ (compare with W = 5-6 for CH_3CCl_3 at 298 K and with washout ratios of 10^4 to 10^6 for very efficiently rained-out chemicals (Dana et al., 1985)). These results indicate that if indeed wet deposition is important, removal into the oceans may dominate over cloudwater uptake. Further studies of the uptake of these compounds to water droplets is urgently needed.

Acetyl halides. As for the carbonyl halides, the fully halogenated acetyl halides, $CX_3C(O)Y$, are not expected to react with the OH radical at significant rates. Moreover, those acetyl halides containing H atoms, such as $CH_3C(O)Cl$, are expected to react only slowly with the OH radical, as observed for $CH_3C(O)Cl$ (Nelson et al., 1990). Hence the major

tropospheric loss processes for the acetyl halides will be photolysis and/or wet deposition. Absorption cross sections have been measured for several acetyl halides ($CF_3C(O)Cl$, $CF_3C(O)F$, $CH_3C(O)F$, $CH_3C(O)Cl$, $CH_2ClC(O)Cl$, $CHCl_2C(O)Cl$ and $CCl_3C(O)Cl$) (Libuda et al., 1991; Meller et al., 1991; Rattigan et al., 1991). Assuming unit quantum yields for photo-dissociation, the calculated tropospheric lifetimes are approximately: $CF_3C(O)Cl$, 85 days (Rattigan et al., 1991); $CF_3C(O)F$, 1700 years (Rattigan et al., 1991); $CH_3C(O)F$, 24 years (Rattigan et al., 1991); $CH_3C(O)Cl$, 75 days (Libuda et al., 1991); $CH_2ClC(O)Cl$, 30 days (Libuda et al., 1991); $CHCl_2C(O)Cl$, 9 days (Libuda et al., 1991); and $CCl_3C(O)Cl$, 6 days (Libuda et al., 1991).

These data indicate that photolysis of the acetyl chlorides, $CX_3C(O)Cl$, will be important in the troposphere, whereas the removal of the acetyl fluorides via photolysis is likely to be negligible. There is no evidence at the present time to indicate that photolysis of the acetyl halides leads to the formation of chlorofluorocarbons, as for example (Meller et al., 1991):

$$CF_3C(O)Cl + hv \rightarrow CF_3Cl + CO \qquad (R25)$$
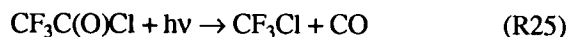
As for $C(O)Cl_2$ and $C(O)F_2$, (Worsnop et al., 1991) have found no evidence for uptake of $CF_3 C(O)Cl$ and $CCl_3C(O)Cl$ into water droplets, leading to uptake coefficients of less than 10^{-3}. Direct measurements of wet deposition rates are of vital importance in order to assess the possibility of transport of these species to the stratosphere.

5.7 CONCLUSIONS

Increases in emissions of pollutants like NO_x, CH_4, NMHC and CO can all lead to increases in tropospheric ozone, and could explain the observed ozone increases registered over northern hemispheric latitudes. The efficiencies of these source-gases vary markedly, depending on where the emissions take place, particularly for NO_x emissions. Furthermore, estimates of ozone production resulting from NO_x emission seem to be model-dependent, setting limitations on the use of such calculations. Calculations of ozone changes from methane increases are more uniform, and thus easier to perform.

Taking into account the strong variability of tropospheric NO_x, the limited sets of NO_x observations that are available, and the key role NO_x plays in tropospheric ozone chemistry, high priority should be given to observations of NO_x compounds.

Only limited observations of free tropospheric ozone increases exist. A better coverage of free tropospheric ozone variations and trends is essential in order to understand and predict ozone changes resulting from changes in source gas emissions.

It seems to be difficult to predict how tropospheric OH is going to change with the present accuracy of our models. While increased emission of CH_4, NMHC and CO tend to suppress tropospheric OH, increased emission of NO_x has the opposite effect. Predictions of how future combined changes in emissions may affect OH are therefore difficult to make.

On the other hand, increased emissions of CH_4 are likely to have a marked positive feedback effect on its concentrations through the reaction with OH, leading to an enhanced climate effect.

The impact (+ gives increases in global averages, – gives decreases) of anthropogenic emissions on OH, O_3 and the lifetime τ of climate gases which are controlled by OH in the troposphere are summarized in the table below.

Incr. emission	OH	O_3	τ (CH_4, HCFC, HCF)
CH_4	–	+	+
NO_x	+	+	–
CO	–	+	+
HC	–	+	+

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