REVIEW OF POLLUTANT TRANSFORMATION PROCESSES RELEVANT TO THE ALBERTA OIL SANDS AREA

by

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ABSTRACT

Chemical transformation processes in polluted atmospheres are described, with particular reference to the oil sands area in northeastern Alberta. The relevant atmospheric chemistry is discussed under four headings: clean air chemistry, oxidant chemistry, SO_2 chemistry, and aerosol chemistry. It is concluded that high ozone concentrations and the formation of PAN-type oxidants would probably take place, especially during the summer when the ambient concentrations of naturally-occurring reactive hydrocarbons from the wooded surroundings and other evaporated hydrocarbons at the site of the oil sand extraction plants might be sufficient to fuel the oxidant chemistry. Since the major polluting species in the oil sands area is expected to be SO_2, the atmospheric chemistry of SO_2 is reviewed in detail. Homogeneous gas phase reactions via interaction with oxidative processes is indicated to be a probable prime transformation route for the conversion of SO_2 to sulphate during the summer, while aqueous phase reactions will be of importance all year round. Purely heterogeneous reaction routes are expected to be of minor importance. In reviewing the published literature, emphasis was given to recent studies, up to December, 1976, resulting in a list of 428 references.

Those studies having direct relevance to the climatic and geographic conditions of northeastern Alberta are described in a separate chapter. In this regard, the effects of low winter temperatures and the large difference in the amount and spectral distribution of available sunlight between summer and winter are indicated and compared with results from a few other unrelated studies which can be extrapolated to northeastern Alberta, in order to make a prognosis on how these factors might influence the chemical evolution of polluted atmospheres.

Atmospheric chemical transformation processes for which mechanistic or experimental data are lacking, are identified and some research projects which would lead to a better understanding and prediction of the chemistry of polluted air are outlined, with special emphasis on the particular problems which may arise in the vicinity of the oil sand extraction plants.

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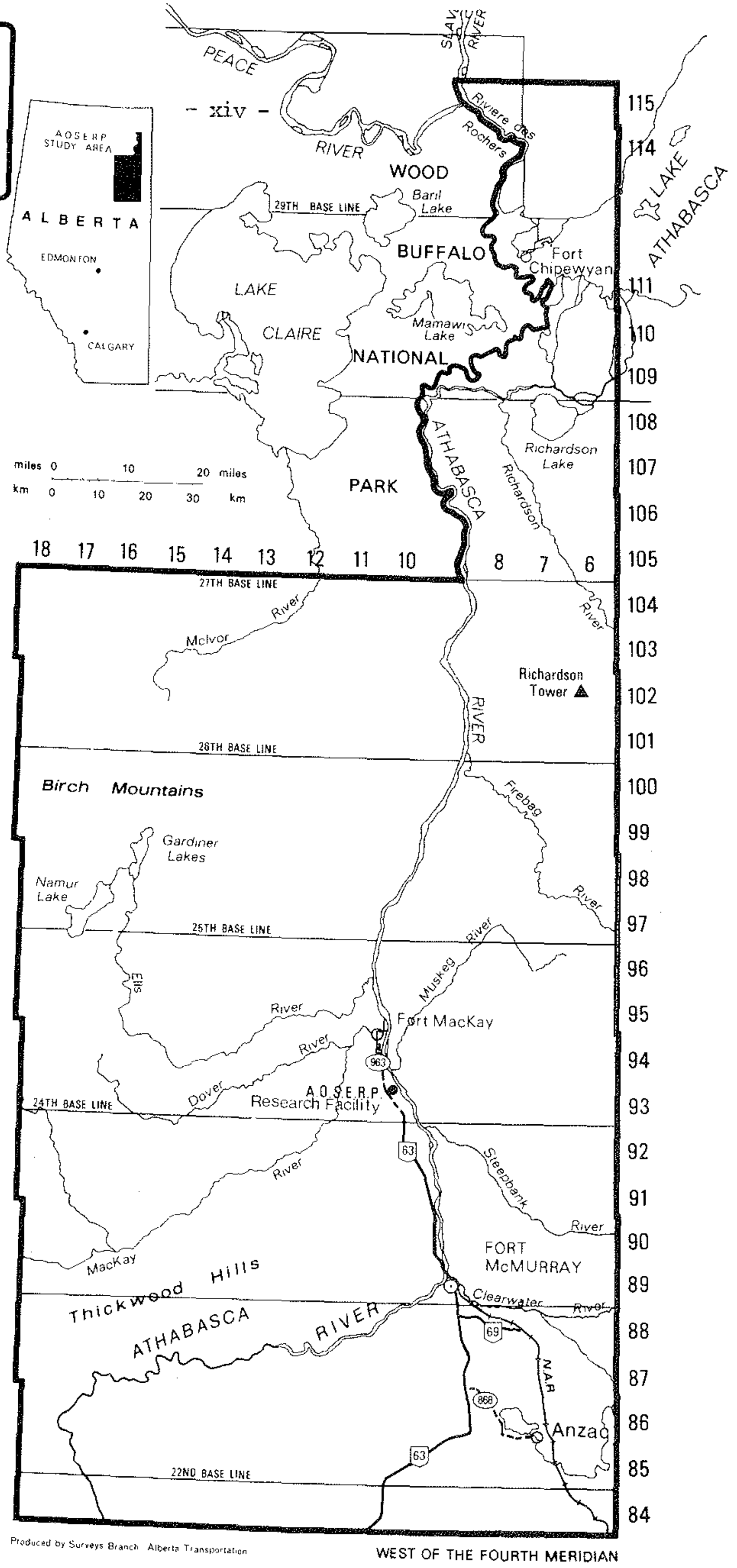

Figure 1. Location of the AOSERP Study Area.

1. INTRODUCTION

This report will review the published literature on possible chemical pollutant transformation processes that might occur in the atmosphere as a result of the operation of the oil sand plants in the neighborhood of Fort McMurray, Alberta, and will indicate some major areas of research activities which will be required in order to improve our understanding in this regard. In writing this report the authors have concentrated on the chemical processes occurring and several aspects of atmospheric transformations related to meteorological parameters will only be briefly mentioned. It cannot be emphasized enough that the study of air pollution is a multidisciplinary subject, and cooperation between scientists educated in many different branches of the physical sciences is required in order to obtain at least a reasonable description of the phenomena which characterize air pollution. The air pollution problems that can be anticipated from the oil sand complex are in some ways unique, due to the geographical location of the site. Existing, and most likely future plants, are in a rural, heavily wooded area where essentially unpolluted, clean air was present. Major cities (the only town of any size in the neighborhood is Fort McMurray with a projected population of the order of 20,000) or other industrial complexes are several hundred miles away. Because the broad pollutant plume from the oil sand complex will mix with very clean air, this constitutes an ideal system to study the atmospheric chemistry of primary pollutants in situ. Most systems studied to date are probably influenced by background air which in itself cannot be considered clean (e.g., Husar et al., 1976).

Another facet of the uniqueness of the oil sand complex is its northerly inland location. Special effects on the chemical transformations should therefore be anticipated from the large difference in the wavelength distribution and duration of sunlight during summer and winter. The other parameter in this regard is the ambient temperature. Although summer temperatures are quite comparable to those experienced in most industrialized areas, winter temperatures are much lower.

There is nowadays a growing awareness that the local emission of pollutants in the atmosphere might have a profound effect on the air quality over a very large range. A prime example is the pollution problem experienced in Sweden, which to a considerable extent can be ascribed to pollutant transport from the industrial complexes in central Europe and Britain (e.g., Brosset, 1976). It is not our intention here to suggest that serious air pollution problems from the oil sand operations will definitely occur in the more populated areas of southern and central Alberta, but merely to make the reader aware of the fact that transport of locally emitted pollutants undoubtedly will occur, and that their effects should be observed over a much larger area than in the direct vicinity of the plants. For instance, future emission standards will have to consider the (un)desirability of increased acidity of rain water over large areas. The simple law "what goes up has to come down" applies here as well. Recent studies have indicated that the amount of sulphate formed in the atmosphere does not depend on the concentration of SO_2, but on the total amount emitted. Another facet of the long range transport of pollutants is the current belief that high ozone concentrations in essentially rural areas are due to transport from urban/industrial complexes.

The main part of this report is concerned with a review of the literature in order to delineate the chemical transformations that might be expected. In chapter 2 we shall review the current state of knowledge of air pollution caused by urban-industrial complexes. To be able to properly assess such problems we first describe the current theories on the gas phase chemistry of the clean air. Recent studies in this regard indicate that the clean atmosphere constitutes a much more reactive chemical system than was previously believed. The presence of small, highly reactive radical species is of special importance, in view of the crucial role that they are now believed to play in polluted atmospheres. We will discuss only briefly the aerosol component of the clean atmosphere, since this is not thought to play an important role in this respect (some recent cloud models suggesting the contrary will be discussed in a later chapter.

Next we review the basic concepts of the oxidant chemistry. This type of pollution has been intensively studied because of its wide occurrence in most urban areas due to automobile traffic. However the basic ingredients for this type of pollution, i.e. oxides of nitrogen and hydrocarbons, should be expected to be emitted into the air from the oil sand operations as well.

Considerable attention is given to the possible transformation mechanisms of SO_2, in part because this gas is considered to be the prime component of the emitted pollution mixture. We have added a section to this chapter on actual plume measurement studies, since such studies are concerned with actual atmospheric measurements. It seems however that most studies in this field are of questionable validity for one reason or another.

The last part of chapter 2 describes the current status of aerosol chemistry. Although some major developments in the physical description of aerosols have taken place over the last few years, it appears that knowledge of the chemical composition and reaction mechanisms that lead to aerosols is still embryonic.

Chapter 3 of this report is devoted to a survey of studies that have a direct impact on the unique location of the oil sand plants. Not too surprisingly the amount of relevant studies published in the literature is very small indeed. Nevertheless, results from unrelated work are discussed insofar as they have a bearing on the oil sand area. It is remarkable that studies on air pollution in subarctic areas are found in nonchemical journals.

Finally in chapter 4 we will suggest some major areas of research that could help in obtaining a better oversight of the air pollution chemistry of the atmosphere of northeastern Alberta. We are of the opinion that immediate initiation of such projects is warranted. However a detailed cost/benefit analysis of such projects is outside the scope of this report. We suggest devoting a special report on some of the major projects we outline because of their long term aspects and the necessary increase in personnel and equipment.

Atmospheric measurements in the Fort McMurray area are slowly becoming available, but the amount of data is still limited. Most extensive to date are monitoring data on SO_2. We decided therefore to limit ourselves mainly to a general description of chemical transformations that might play a role in the Fort McMurray atmosphere. In this regard the assumption that the broad pollution plume from the oil sand plants will contain SO_2, hydrocarbons and oxides of nitrogen, appears valid.

It might be noticed that we have placed emphasis on the very recent literature rather than elaborate on early work which has been proven obsolete. We feel that this is important in view of the rapid progress that has been made during the last few years in the elucidation of the ongoing chemistry of a polluted atmosphere. In fact while this report was written, several new and significant publications appeared and we have as far as possible included such work in our review. It seems likely that some of the major general uncertainties will be brought to a clearer understanding in the next few years. It is our hope and intention to be able to make contributions to this matter.

2. LITERATURE REVIEW OF ATMOSPHERIC TRANSFORMATION PROCESSES

2.1 CHEMISTRY OF THE CLEAN ATMOSPHERE

One of the basic prerequisites for a proper estimation of the impact of future polluting emissions into the atmosphere is a sound knowledge of the chemistry and composition of the unpolluted atmosphere. The atmosphere of the earth is by no means chemically inert. Most of the substances that are injected into the "clean" air by so-called polluting processes (industrial activities, heating, traffic, etc.) are already present via the normal processes of nature. Although this fact seems rather obvious, its consequences do not always seem to have been taken into account. Thus, naturally-occurring O_3 levels are very variable, seasonably dependent, and are now believed to range from 0.01 to 0.05 ppm. The higher limit makes a statutory limit on ozone concentrations of 0.08 ppm under certain conditions very difficult to realize. A more important factor, which only recently has received some attention, is the amount of photochemistry which takes place in unpolluted atmospheres, whereby some background levels for highly reactive radical species that play such a critical role in the chemistry of NO_x-hydrocarbons polluted atmospheres are established. In this section we will give a brief review of the chemistry of the unpolluted atmosphere, thereby setting the stage for a discussion of the effects of introduction of pollutants in this environment. An extensive review has recently appeared on this subject (Levy II, 1974).

2.1.1 Chemical Composition of the Atmosphere

We will not discuss the variation of concentration of chemical components with the height of the atmosphere, but merely focus our attention on the biosphere, i.e. the atmosphere directly above ground level where human activities take place, and only where necessary take altitude effects into account. In Table 1 we have listed the chemical molecules which are of interest to us, and their concentrations in the clean atmosphere. The ambient concentrations of the trace compounds are believed to be kept in more or less constant concentration through certain naturally occurring balancing mechanisms, i.e. nature provides self-balancing source and loss mechanisms so that the indicated concentrations are established. Some of the major mechanisms in this regard are: biological processes (e.g. CO_2 respiration, bacteriological formation of H_2S); diffusion to and from higher atmospheric layers (e.g. N_2O loss, freon-loss to, and O_3 diffusion from the stratosphere); rainout, washout and dry deposition of particulates and aerosols (e.g. deposition of $SO_4^=$ aerosols); and chemical transformation. The determination of these balancing mechanisms is still an active part of geophysical research, and the currently existing theories are by no means considered to be complete, nor proven to be correct.

An important aspect in the balancing mechanisms is the chemical transformations that can take place. As stated before, small radical species are believed to play a major role in this regard. However, almost no atmospheric measurements have been performed to establish the ambient concentrations of these radicals. The major source of most of this chemistry is believed to be the photochemical reaction of ozone to form $O(^1D)$ atoms, followed by reaction with water to produce HO radicals. The presence of HO radicals in quantities that had been predicted on basis of theoretical calculations in the atmosphere has very recently been established experimentally (Wang et al., 1975; Davis et al., 1976; Perner et al., 1976), thus giving a major boost to the credibility of large parts of the models. To better understand the importance of this observation, and at the same time get an idea of the complex chemical system in which pollutants will participate, the next section will describe the chemistry of the unpolluted atmosphere.

2.1.2 Summary of the Chemical Reactions in the Unpolluted Atmosphere

2.1.2.1 Sulphur chemistry

i. SO_2

A complete description of the reactions in which SO_2 participates will be given later in this report. Suffice to say here that in an unpolluted atmosphere the major reactions will be oxidation to ultimately form $SO_4^=$, wherein the following reactions are deemed to be important:

(a) photooxidation:

$$SO_2 + O_2 + h\nu \rightarrow SO_3 + O$$

Table 1

Gaseous Chemical composition of "clean" air*)

(from: Levy, 1974)

N_2 : 78.1%

O_2 : 20.9%

Ar : 0.9%

H_2O : rel. humidity 50%, T = 15°C: 8410 ppm
rel. humidity 50%, T = -15°C: 945 ppm

O_3 : 0.01 - 0.05 ppm

SO_2 : 0.2 ppb

H_2S : 0.2 ppb

$(CH_3)_2S$: ?

N_2O : 0.25 ppm

NO : 2 ppb

NO_2 : 4 ppb

HNO_3 : 30 ppb

NH_3 : 6 ppb

CO_2 : 320 ppm

CO : 0.1 - 0.15 ppm

CH_4 : 1.4 ppm

CH_2O : < 1 ppb

terpenes : ? (locally high, > 1 ppm)

H_2 : 0.4 - 0.6 ppm

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*) All concentrations are in volume mixing ratios; ppm = part per million, ppb = part per billion.

(b) radical reactions:

$$SO_2 + RO \rightarrow ROSO_2 \rightarrow \rightarrow H_2SO_4$$

$$SO_2 + RO_2 \rightarrow SO_3 + RO$$

where R = H, alkyl, acyl.

(c) cloud reactions:

$$SO_2 + H_2O \rightarrow \rightarrow SO_3^{=} \xrightarrow[\text{Metal ion, } NH_4^+]{O_2, O_3} SO_4^{=}$$

ii. H_2S

It is now believed that H_2S will be oxidized in the atmosphere to SO_2 almost entirely via the sequence:

$$H_2S + HO \rightarrow H_2O + HS$$

$$HS + O_2 \rightarrow \rightarrow SO_2$$

The rate of the first reaction is fast (Perry et al., 1976). The exact mechanism of the ensuing reactions of HS to ultimately form SO_2 is not known, although it has been postulated to involve HSO and HSO_2 intermediates (Becker et al., 1975).

iii. $(CH_3)_2S$

Although no definite data have been reported, the ultimate fate of $(CH_3)_2S$ is probably similar to that of H_2S, i.e. rapid conversion into SO_2 via initial HO attack. The mechanistic route along which this will occur is probably different, however, since the reactivity of $(CH_3)_2S$ seems to parallel that of olefins undoubtedly becauase of the presence of the methyl-groups (Cox and Sandalls, 1974).

iv. SO_3

Any SO_3 formed from SO_2 oxidation will very rapidly form H_2SO_4. The reaction might involve a heterogeneous dissolution of SO_3 into H_2O, although it has recently been shown that the homogeneous bimolecular reaction

$$SO_3 + H_2O \rightarrow H_2SO_4$$

is very fast as well (Castleman et al., 1975).

v. H_2SO_4 and sulphate aerosol

These chemicals are not expected to participate directly in chemical reactions, except for sulphate formation in solution between

H_2SO_4 and metal ions. They will be removed from the atmosphere by dry deposition, rainout or washout.

2.1.2.2 Oxygen chemistry

i. O_2, $O_2(^1\Sigma_g^-)$, $O_2(^1\Delta_g)$

O_2 will absorb sunlight to form metastable molecular oxygen species:

$$O_2 + h\nu\ (\lambda \sim 7600\ \text{Å}) \qquad O_2(^1\Sigma_g^-)$$

$$+\ h\nu(\lambda \sim 11000\ \text{Å}) \qquad O_2(^1\Delta_g)$$

$O_2(^1\Sigma_g^-)$ will probably be collisionally deactivated to the more metastable $O_2(^1\Delta_g)$ molecule, or to ground state $O_2(^3\Sigma_g^-)$. Since spin forbidden transitions are involved, only very low concentrations are to be expected of metastable O_2. In fact, the major reactions leading to the formation of $O_2(^1\Delta_g)$ seem to be the quenching of photoexcited NO_2 molecules (Frankicwicz and Berry, 1972):

$$NO_2^* + O_2 \rightarrow NO_2 + O_2(^1\Delta_g)$$

and the photolysis of O_3 (Kummler and Bortner, 1970):

$$O_3 + h\nu(\lambda < 3100) \rightarrow O(^1D) + O_2(^1\Delta_g)$$

However, $O_2(^1\Delta_g)$ is not very reactive, and the only consequence of its presence seems its effect on biological processes. It does not participate in atmospheric chemistry.

ii. (O^3P)

$O(^3P)$ is formed photolytically:

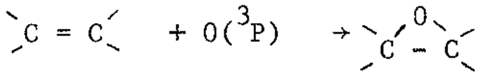
$$O_3 + h\nu(\sim 3100 < \lambda < 11800\ \text{Å}) \rightarrow O(^3P) + O_2^*$$

and $$NO_2 + h\nu(\lambda \lesssim 4000\ \text{Å}) \rightarrow O(^3P) + NO$$

The only significant reaction of $O(^3P)$ in the clean atmosphere is recombination with O_2 to form O_3:

$$O(^3P) + O_2 + M \rightarrow O_3 + M$$

If terpenes are present, a very small fraction of the $O(^3P)$ atoms could react with the olefinic bond, leading to the very carcinogenic epoxides:



$$>C=C< \ + O(^3P) \rightarrow >C\overset{O}{-}C<$$

iii. $O(^1D)$

The sole mode of formation of $O(^1D)$ in the atmosphere is the photolysis of O_3:

$$O_3 + h\nu(\lambda \lesssim 3150\ \mathring{A}) \rightarrow O(^1D) + O_2(^1\Delta_g)$$

The reaction only occurs in the high energy region of the solar spectrum. The efficiency of $O(^1D)$ formation is therefore highly dependent on the solar altitude (the higher the sun rises from the horizon, the more high energy radiation reaches the biosphere). It should thus be expected that $O(^1D)$ formation is very seasonally dependent at higher latitudes, as in northeastern Alberta (Bottenheim et al., 1976c).

The major reactions occurring in the atmosphere are:

$$O(^1D) + M(N_2,O_2) \rightarrow O(^3P) + M$$

$$O(^1D) + H_2O \rightarrow 2HO$$

Of these reactions, collisional deactivation is the major one. Reaction with H_2O, even though it occurs in only small amounts, is of crucial importance, since it is the only major primary source of HO radicals in the unpolluted atmosphere.

iv. O_3

The presence of O_3 in the lower atmosphere is of importance, since its photolysis yields $O(^1D)$ atoms, precursors of HO radicals. At present there are two conflicting theories as to the source of O_3: injection from the stratosphere, and chemical formation via HO and HO_2 chain reactions (Crutzen, 1974; Chameides and Walker, 1973, 1976). In the latter case the formation of O_3 depends on the concentration of nitrogen oxides and can be visualized by the scheme:

$$HO + CO \rightarrow H + CO_2$$

$$H + O_2 + M \rightarrow HO_2 + M$$

$$HO_2 + NO \rightarrow NO_2 + HO$$

$$NO_2 + h\nu(\lambda < 4000\ \mathring{A}) \rightarrow NO + O(^3P)$$

$$O(^3P) + O_2 + M \rightarrow O_3 + M$$

The main reactions of O_3 in the unpolluted atmosphere are, in addition to the often discussed photolysis (vide supra):

$$O_3 + NO \rightarrow NO_2 + O_2$$

$$NO_2 + O_3 \rightarrow NO_3 + O_2$$

$$O_3 + \text{olefin} \rightarrow \text{radical species}$$

The first reaction will not lead immediately to O_3 loss, because NO_2 photolyses to form $O(^3P)$. The second and third reactions will lead to O_3 loss, however.

2.1.2.3 Nitrogen chemistry

i. N_2O

This molecule is most likely inert in the lower troposphere. Its major source is denitrification of nitrate in soils and natural waters. The only known reactions that could occur are:

$$N_2O + O(^1D) \rightarrow N_2 + O_2$$

$$\rightarrow 2NO$$

$$N_2O + HO \rightarrow HO_2 + N_2$$

The first reaction is unimportant from concentration considerations, and the reaction with HO is very slow (Bierman et al., 1976; Atkinson et al., 1976b). Photolysis in the lower atmosphere does not occur (Stedman et al., 1976). It might be mentioned here that the apparent inertness of N_2O in the troposphere has recently led to concern that increasing use of fertilizers to aid food production might lead to detrimental effects on the ozone layer of the stratosphere similar to what has been predicted from supersonic transportation and the use of freons as aerosol propellants, since extensive fertilizer use could lead to increased release of N_2O in the atmosphere (Crutzen, 1976; Liu et al., 1976; McElroy et al., 1976; Pierotti and Rasmussen, 1976; Sze and Rice, 1976). However, very recently it was suggested that the soil itself might constitute a major sink for the evolved N_2O (Blackmer and Bremner, 1976).

ii. NH_3

NH_3 is not formed by atmospheric reactions. In the atmosphere it will react almost exclusively with HO radicals:

$$NH_3 + HO \rightarrow NH_2 + H_2O$$

This is a fast reaction (Stuhl, 1973; Zellner and Smith, 1974; Kurylo, 1973; Cox et al., 1975a; Perry et al., 1976). However, there is a disagreement on the fate of the NH_2 radical. Gesser (1955) suggested that NH_2 would be a source and sink for NO molecules via the reaction scheme:

$$NH_2 + O_2 \rightarrow NO + H_2O$$

$$NH_2 + NO \rightarrow N_2 + H_2O$$

thus leading to a steady state concentration of NO molecules. Recent tropospheric models (McConnel and McElroy, 1973; McConnel, 1973; Nicolet, 1974) have considered the first reaction as a probable source of NO_x in the unpolluted atmosphere. However, the experimental work of Cox et al., (1975a) and Lesclaux et al., (1975) has shown that the first reaction is several orders of magnitude slower than the second one, and Levine and Calvert (1977) have performed computer-simulation studies which indicate that only a very low steady state concentration of NO should be expected from these reactions. An entirely different and more elaborate reaction scheme as proposed by Jayanty et al., (1976) is considered unnecessary by Levine and Calvert. Other important reactions of NH_3 are its heterogeneous reactions with H_2SO_4 and HNO_3 to form salt particles. Moreover, NH_3 dissolves easily in water droplets, thus increasing the pH of the droplets and thereby increasing the rate of SO_2 oxidation in clouds.

iii. NO and NO_2 (NO_x)

These major nitrogen oxides are always coupled, since they reach a photostationary state very fast (Stedman and Jackson, 1975; Calvert, 1976a) the reactions:

$$NO + O_3 \rightarrow NO_2 + O_2$$

$$NO + HO_2 \rightarrow NO_2 + HO$$

$$NO_2 + h\nu(\lambda \lesssim 4000\ \mathring{A}) \rightarrow NO + O(^3P)$$

During the night the NO_2 concentration will be relatively large, whereas as soon as the sun rises, the equilibrium will be reestablished.

At present, the origin of the NO_x in the unpolluted atmosphere is not known with certainty, especially since the oxidation of NH_3 does not seem to result in significant NO formation (vide supra).

A biological source proposed by Robinson and Robbins (1970), has never been substantiated. Some of the difficulties in this respect have recently been discussed by McConnel (1973). Soil aspiration (Rasmussen et. al., 1975) and decomposition of organic material seem to be likely possibilities.

A loss mechanism is known; however,

$$HO + NO_2 + M \rightarrow HNO_3 + M$$

since the reformation of NO_x from HNO_3 via the reactions:

$$NO + HNO_3 \rightarrow H_2O + NO_3$$

$$HNO_3 + h\nu \rightarrow HO + NO_2$$

is very inefficient.

No NO_x molecules participate in many reactions that lead to other nitrogen-containing species which will be discussed below, and moreover are the source of high O_3 concentrations in at least one of the existing theories on the O_3 content in the troposphere (vide supra).

iv. NO_3 and N_2O_5

These two species play a minor role in the unpolluted atmosphere, since their formation rates are slow. They are usually taken into consideration, however since they influence the ambient NO_x concentrations. NO_3 will reform NO_x, through reaction with NO, and moreover it is the precursor of N_2O_5. NO_3 is potentially an oxidizing reagent but to date no major oxidation reactions have been found, certainly not in clean air.

N_2O_5 can react with H_2O to form HNO_3, thus leading to NO_x loss, but the reaction is very slow (Niki et al., 1973) and probably heterogeneous (Johnston and Graham, 1974). The pertinent reactions of NO_3 and N_2O_5 are:

$$NO_2 + O_3 \rightarrow NO_3 + O_2$$

$$NO_3 + NO \rightarrow 2NO_2$$

$$NO_3 + NO_2 \xrightarrow{M} N_2O_5$$

$$N_2O_5 \xrightarrow{M} NO_2 + NO_3$$

$$N_2O_5 + H_2O \rightarrow 2HNO_3$$

The loss of NO_3 and N_2O_5 through photolysis, although frequently invoked in tropospheric models, is probably too slow to be of any importance, as has recently been discussed by Daubendieck and Calvert (1975).

v. HNO_2

Nitrous acid is a temporary storage mode for NO_x during daytime. Its formation reactions are:

$$NO + NO_2 + H_2O \rightarrow 2HNO_2$$

$$NO + HO(+M) \rightarrow HNO_2(+M)$$

$$NO_2 + HO_2 \rightarrow HNO_2 + O_2$$

of which the first reaction is slow (Chan et al., 1976a), but the others are relatively fast (Overend et al., 1976; Simonaitis and Heicklen, 1976; Atkinson et al., 1976a; Sie et al., 1976; Cox et al., 1976a; and references therein).

The only major reaction of HNO_2 is photolysis:

$$HNO_2 + h\nu \rightarrow HO + NO$$

Incorporation in water droplets leading to nitrite salts is possible. This reaction is more important during nighttime, when HNO_2 is fairly stable.

vi. HNO_3

Nitric acid is essentially an end product of the atmospheric nitrogen cycle. It is formed in the reaction:

$$HO + NO_2 + M \rightarrow HNO_3 + M$$

Its chemical decomposition reactions,

$HNO_3 + h\nu \rightarrow HO + NO_2$ (Johnston and Graham, 1973; Johnston et al., 1974)

$HNO_3 + HO \rightarrow NO_3 + H_2O$ (Johnston, 1974; Smith and Zellner, 1975)

are very slow, and the major loss of HNO_3 is through rainout and particulate removal (formation of nitrate salts).

2.1.2.4 Carbon chemistry

i. CO_2

An important atmospheric reaction leading to CO_2 formation in the unpolluted atmosphere is the reaction:

$$HO + CO \rightarrow CO_2 + H$$

Although this reaction seems to control the CO concentration, it is only minor as far as total CO_2 concentration is concerned. In the lower atmosphere CO_2 does not participate in gas phase reactions. It is, however, responsible for the always slightly acid nature of rainwater through dissolution:

$$\begin{array}{ccccc} CO_2 + H_2O & \rightleftarrows & H_2O.CO_2 & \rightleftarrows & H^+ + HCO_3^- \\ & & & & \updownarrow \\ & & & & H^+ + CO_3^= \end{array}$$

(cf. Likens, 1976).

ii. CH_4

There are no important chemical modes of formation for methane in the atmosphere. The very uniform presence of CH_4 in the atmosphere is a source of the CH_3O_2 radical through the reaction (Cox et al., 1976b; Zellner and Steinert, 1976):

$$CH_4 + HO \rightarrow H_2O + CH_3 \xrightarrow{O_2,M} CH_3O_2$$

A host of other radical reactions will then lead to formaldehyde and eventually CO formation. We will discuss the radical reactions later.

iii. CH_2O

CH_2O is mainly formed from the reaction:

$$CH_3O + O_2 \rightarrow CH_2O + HO_2$$

The origin of the CH_3O radical will be discussed later. Other sources of CH_2O and higher analogue aldehydes are the destruction reactions of other hydrocarbons in the atmosphere, mainly through reaction with HO radicals and O_3:

$$\text{hydrocarbon} + HO/O_3 \rightarrow O_2 \rightarrow \text{aldehyde} + RO_2 \text{ radicals} + RO \text{ radicals}$$

However, possibly with the exception of the terpenes in areas of dense foliage, non-methane hydrocarbons are present in only very low concentration in the unpolluted atmosphere.

The important reactions of CH_2O in the atmosphere are:

$$CH_2O + h\nu \rightarrow H_2 + CO$$

$$\rightarrow H + HCO$$

$$CH_2O + HO \rightarrow HO_2 + HCO$$

and with exception of the first reaction are thus sources of HO_2 radicals, since H and HCO react almost exclusively as follows:

$$H + O_2 + M \rightarrow HO_2 + M \quad \text{(Davis, 1974a)}$$

$$HCO + O_2 \rightarrow HO_2 + CO \quad \text{(Washida et al., 1974)}$$

An alternative reaction path for the $HCO + O_2$ interaction is as follows:

$$HCO + O_2 + M \rightarrow HCOO_2 + M$$

Recently Niki et al., (1976a) and Osif and Heicklen (1976) presented evidence to the effect that the efficiencies of these $HCO + O_2$ interactions are almost equal.

iv. CO

The chemistry of CO has already been discussed above and

and can be summarized by the reactions:

$$H_2CO \xrightarrow{h\nu, HO} CO$$

$$HO + CO \rightarrow CO_2 + H$$

v. Terpenes

The only non-methane hydrocarbons that probably are present in important concentrations are terpenes. Their destruction will initially take place via reactions with O_3 and HO, at first with comparable overall rates. However, later on in the day, when HO concentrations have been built up under the influence of the sunlight, reactions with HO are probably dominant because of their very high rate constants (Westberg and Rasmussen, 1972; Grimsrud et al., 1975; Winer et al., 1976). These destruction reactions will involve several radical intermediates, the structures of which are not known. It is assumed that the blue haze in summer over wooded areas is due to aerosol formation from radical reactions that originate from the intermediates formed in the destruction of terpenes (Went, 1960).

2.1.2.5 H_2, peroxides

H_2 is formed in the atmosphere by photolysis of formaldehyde. Its only mode of destruction, which is slow, seems to be

$$H_2 + HO \rightarrow H_2O + H$$

Peroxides H_2O_2 and CH_3O_2H are intermediates in the radical-radical termination reactions that will be discussed next. They react with HO and probably participate in the photochemical reformation of radicals. Little is known about the CH_3O_2H molecule. Heterogeneous decomposition is another possibility (Hanst and Calvert, 1959) and rainout might occur. The reactions, (of minor importance) are:

$$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$$

$$CH_3O_2 + HO_2 \rightarrow CH_3O_2H + O_2$$

$$H_2O_2/CH_3O_2H + h\nu \rightarrow HO + HO/CH_3O$$

$$H_2O_2/CH_3O_2H + HO \rightarrow H_2O + HO_2/CH_3O_2$$

$$H_2O_2/CH_3O_2H \xrightarrow{\text{(heterogeneous)}} H_2O + O/CH_2O$$

2.1.2.6 Radical chemistry

From the foregoing discussion of the reactions in which the different molecules in the atmosphere participate, we have already seen that most of the major reactions involve small radicals. Although their concentration in the atmosphere is usually low, their high reactivity makes them the driving forces behind most of the atmospheric transformation reactions. It seems therefore appropriate to treat their reactions in a separate section.

The initiating step for radical reactions occurring in the unpolluted atmosphere is the photolysis of O_3 by high energy radiation of the sun, followed by interaction of the $O(^1D)$ atoms with water:

$$O_3 + h\nu(\lambda \lesssim 3150\ \mathring{A}) \rightarrow O(^1D) + O_2(^1\Delta_g)$$

$$O(^1D) + H_2O \rightarrow 2HO$$

Since this reaction depends on sunlight, we can anticipate that the radical reactions and consequently most of the other reactions discussed above will slow down considerably, and may even come to a complete standstill, during the night.

The major characteristic of the atmospheric radical chemistry is that as soon as some radicals are formed, they will start a host of other reactions wherein radicals are interconverted. This leads moreover to the formation of products that will regenerate radicals through interaction with sunlight. This is a characteristic of chain reactions, and thus the chemical transformation will continue until sunset when no photochemical reformation of radicals is possible, and eventually the radical concentrations drop to insignificant levels by mutual radical-radical termination reactions. Major photolytic sources of reformation of radicals are the photolysis of formaldehyde and nitrous acid,

$$H_2CO + h\nu \rightarrow HCO + H$$

followed by

$$HCO + O_2 \rightarrow HO_2 + CO$$

$$H + O_2(+M) \rightarrow HO_2(+M)$$

and

$$HNO_2 + h\nu \rightarrow HO + NO$$

Smaller contributions are to be expected from the reactions:

$$H_2O_2 + h\nu \rightarrow 2HO$$

$$CH_3O_2H + h\nu \rightarrow CH_3O + HO$$

In the presence of terpenes we can expect higher analogue aldehydes and ketones as products of the olefin-radical and olefin-ozone interactions. These will photolyse as well, resulting in the formation of RO_2 radicals, where R = H, alkyl or acyl.

We turn next to radical interconversion reactions. Reactions of the HO radical leading to the formation of HO_2 and RO_2 are the following:

$$HO + CO \rightarrow CO_2 + H \xrightarrow{O_2} HO_2$$

$$HO + CH_2O \rightarrow H_2O + HCO \xrightarrow{O_2} HO_2 + CO$$

$$HO + RCHO \rightarrow H_2O + RCO \xrightarrow{O_2} RCO_3$$

$$HO + H_2O_2 \rightarrow H_2O + HO_2$$

$$(HO + O_3 \rightarrow O_2 + HO_2)$$

$$HO + H_2 \rightarrow H_2O + H \xrightarrow{O_2} HO_2$$

$$HO + CH_4 \rightarrow H_2O + CH_3 \xrightarrow{O_2} CH_3O_2$$

$$HO + \text{hydrocarbon} \rightarrow H_2O + R. \xrightarrow{O_2} RO_2$$

HO_2 and CH_3O_2, the more important species produced, will react to regenerate new radicals through the following reactions:

$$HO_2/CH_3O_2 + NO \rightarrow NO_2 + HO/CH_3O$$

$$(HO_2 + O_3 \rightarrow 2O_2 + HO)$$

$$CH_3O_2 + CH_3O_2 \rightarrow 2CH_3O + O_2$$

The CH_3O radicals thus formed will react almost exclusively with O_2 in an unpolluted atmosphere to regenerate an HO_2 radical and another radical source, i.e. CH_2O:

$$CH_3O + O_2 \rightarrow HO_2 + CH_2O$$

It might be mentioned here that this reaction is rather slow (Wiebe and Heicklen, 1973; Glasson, 1975) and therefore other, fast reactions of

CH_3O may be occurring. Unfortunately the reactions of CH_3O have not been measured quantitatively, with the exception of the following:

$$CH_3O + NO_x \rightarrow CH_3ONO_x$$

(Wiebe et al., 1973; Glasson, 1975). Due to low NO_x concentrations, this reaction is of minor significance in the unpolluted atmosphere.

The next set of reactions seemingly lead to radical termination, but actually their products can regenerate radicals through photolysis:

$$HO + NO \rightarrow HNO_2 \xrightarrow{h\nu} HO + NO$$

$$HO_2 + HO_2 \rightarrow O_2 + H_2O_2 \xrightarrow{h\nu} 2HO$$

$$CH_3O_2 + CH_3O_2 \rightarrow O_2 + CH_3OH + CH_2O \xrightarrow{h\nu, O_2} 2HO_2 + CO$$

$$CH_3O_2 + HO_2 \rightarrow O_2 + CH_3O_2H \xrightarrow{h\nu} CH_3O + HO$$

It should be noted, though, that alternative reaction paths exist for H_2O_2, CH_2O and CH_3O_2H, i.e. reaction with HO radicals:

$$H_2O_2 + HO \rightarrow H_2O + HO_2$$

$$CH_2O + HO \xrightarrow{O_2} H_2O + HO_2 + CO$$

$$CH_3O_2H + HO \rightarrow H_2O + CH_3O_2$$

in which case a net loss of radicals takes place.

The remaining radical destruction reactions are:

$$HO + HO_2 \rightarrow H_2O + O_2$$

$$HO + NO_2(+M) \rightarrow HNO_3(+M)$$

The second reaction is not a complete termination since some photolysis of HNO_3 will take place in the atmosphere; however, the photolysis rate is very small under solar radiation (Johnson and Graham, 1973; Johnson et al., 1974). The radical reactions following the initial reactions with terpenes should be essentially the same as described for CH_3O and CH_3O_2, where now high analogue alkyl groups are involved. The alkyl groups will degrade in several steps during which higher analogue aldehydes are formed in conjunction with HO, HO_2 and CH_3O_2 radicals. These aldehydes will then again photolyze or react with HO radicals, resulting in the formation of HO_2, and RO_2 and RCO_3 peroxy radicals. The only additional reactions we have to consider in this case are those from the acylperoxy radicals, which can lead to organic (per) acid formation, cf:

$$RCO_3 + HO_2 \rightarrow RCO_3H + O_2$$

$$\begin{tikzcd} RCO_3 + NO \arrow[r] & RCO_2 + NO \arrow[dr, "O_2"] & \\ & & RO_2 + CO_2 \end{tikzcd}$$

2.1.3 Unpolluted Atmosphere Modelling

The chemical reactions, described in section B, form as a whole an exceedingly complex reaction system, which can be modelled through a set of differential equations to test its validity. The following input parameters have to be taken into account in such mathematical exercises:

- ambient concentrations of some of the major molecular constituents that do not originate from chemical transformation in the atmosphere.
- rate constants of all indicated chemical reactions.

The second set of input parameters is quite problematic, since many of the reactions involving free radicals are very difficult to determine in the laboratory. Since many rate constants are therefore not experimentally known, estimates have to be made. A list of all the known reactions thought to be of importance in the chemistry of a clean atmosphere, together with their measured or estimated rate constants, is compiled in the Appendix. The rates of photochemical reactions constituted a special class. The intensity-wavelength distribution of sunlight is dependent on several factors, such as solar altitude, molecular scattering, reflection from surfaces (albedo) and intricate models have been developed (Leighton, 1961; Peterson, 1976). An additional problem is the generally incomplete information on the specific photolysis rates of many compounds under different conditions of solar radiation. For the northeastern Alberta region this is especially important due to the large seasonal variation of effective solar radiation. The present authors have estimated average photolysis rates applicable to the northeastern Alberta region, and these are also shown in the Appendix.

From such calculations one hopes to be able to rationalize the ambient concentrations of atmospheric constituents that originate exclusively from chemical reactions in the atmosphere. We will now summarize the status of the major cycles discussed under part B.

The carbon cycle, comprising of the transformation

$$CH_4 \rightarrow CH_2O \rightarrow CO \rightarrow CO_2$$

seems fairly well explained with the existing model. In particular, the model is in agreement with the ambient concentrations of CH_2O and CO and, more importantly, with the natural lifetime of CO.

The nitrogen cycle suffers from the problem that no source of NO_x is firmly established. Soil seems to be the likely origin of NO_x, but as stated before, this theory cannot be proven nor disproven (Rasmussen et al., 1975); the decomposition of organic matter will undoubtedly contribute as well (e.g. silo gas is largely NO_2). Nature is known to supply N_2O and NH_3, for which there are no established chemical reactions to transform them into NO_x under lower tropospheric conditions.

The oxygen cycle, and more specifically, the source of O_3, is an area of active discussion. Photochemical models incorporated in the present scheme predict concentration levels of the correct order of magnitude, given enough NO_x. Another model, which suggests transport from the lower stratosphere into the troposphere, can explain the ozone levels just as well, although quantification seems very difficult, (for a recent discussion on this subject, see Chameides and Walker, (1976); Chatfield and Harrison, (1976)).

The sulphur cycle can be explained with the existing model, although the details of the $SO_2 \rightarrow SO_3$ oxidation are far from conclusively determined.

Another interesting aspect of such model calculations is that they predict radical concentration levels. As mentioned before, the HO radical has very recently been identified in the atmosphere. The other radicals have not been monitored owing to the lack of a suitable monitoring method, even under laboratory conditions. (HO_2 and CH_3O_2 can be monitored by absorption in the UV (Hochanadl et al., 1972; Whitbeck et al., 1976), and IR (Huntziger, 1976) but the methods are still under

Table 2

Concentrations* of major reactive radicals in "clean" air

		HO	HO_2	CH_3O	CH_3O_2
Levy, 1972	calculated at noon, 34°N latitide	1.7×10^7	1.2×10^9	6.1×10^4	5.1×10^8
Crutzen, 1974	calculated for solar zenith angle of 45° (basic model)	2.6×10^6	3.4×10^8	1.2×10^4	3.0×10^8
	including HO_2 removal by aerosols	2.3×10^6	2.6×10^8	1.0×10^4	2.3×10^8
Chameides and Walker, 1976	calculated at noon, 30°N latitude				
	summer	1.5×10^7	1.1×10^9		
	winter	2×10^6	3×10^8		

* All concentrations in radicals/cc

development and for the moment do not look promising for atmospheric application). Table 2 shows the predicted levels of the major radicals under the specific conditions indicated. Such calculations have not been performed for northeastern Alberta conditions. However it has recently been shown that, during summertime latitude should have no major effect on the potential for photochemical smog formation (Nieboer et al., 1976). Since this depends on the potential for radical formation, it seems reasonable to conclude that the data in Table 2 are applicable to northeastern Alberta, at least during summertime.

2.2 OXIDANT CHEMISTRY

The general picture we have outlined for the "clean" atmosphere in fact forms a basis for the oxidant chemistry described here. Oxidant formation is generally associated with combustion processes, in particular automotive combustion, and is therefore considered to be an urban air pollution problem. The first insight into the chemical transformations that play a role in this regard dates from the early 1950s, when Haagen-Smit and coworkers (1951-1954) showed that irradiation of automobile exhaust leads to the formation of ozone and other obnoxious compounds that cause eye-irritation and reduce visibility on otherwise clear, sunny days in the Los Angeles area.

Since these early days a very large amount of work has been performed, leading to an understanding of at least the more fundamental processes which characterize these chemical transformations. In addition to sunlight, the basic ingredients for the formation of oxidants are the presence of higher than normal concentrations of nitrogen oxides, carbon monoxide, and hydrocarbons. Since we can expect that all these ingredients will be injected into the atmosphere in considerable amounts from the oil sand recovery plants it seems warranted to review this type of chemistry here, and point out some of the differences from the conditions most often studied, which pertain largely to Los Angeles type situations. The occurrence of this so-called photochemical smog problem in almost any major urban area in the world has led to extensive research and several review articles (recent review: Finlayson and Pitts, 1976).

As was indicated in the last chapter on "clean" air chemistry, the formation of oxidants is now generally believed to involve homogeneous gas phase reactions, in which small, reactive radicals such as HO, HO_2, RO, and RO_2 (R = alkyl, acyl), are the driving forces. We will first trace the origin of these radicals, and then indicate how they determine the chemical reactions that occur.

2.2.1 Intermediate Species and Their Sources

A general trademark of urban smog situations is the observation of high NO concentrations in the early morning (during morning rush hours mainly NO is emitted, by automobiles). This is followed by a peak in the NO_2 concentration after some two hours while at the same time the NO concentration decreases. The increase in ozone and oxidant concentration roughly starts from the time of the maximum NO_2 concentration. This pattern has been explained by the initial NO → NO_2 conversion and subsequent photodissociation of NO_2 by sunlight to produce NO and ground state oxygen atoms, $O(^3P)$. Subsequently the $O(^3P)$ atoms react with oxygen molecules to form ozone. The three species, NO, NO_2 and O_3, are then interrelated via the basic photostationary state mechanism described in the last chapter:

$$NO \overset{?}{\rightarrow} NO_2$$

$$\left.\begin{array}{l} NO_2 + h\nu \rightarrow NO + O(^3P) \\ O(^3P) + O_2 + M \rightarrow O_3 + M \\ NO + O_3 \rightarrow NO_2 \end{array}\right]$$

The last reaction explains why no rise in O_3 concentration is observed before the NO concentration has fallen to low values. The major oxidation routes of hydrocarbons emitted concurrently with NO were originally assumed to involve reactions with O_3, since the $O(^3P)$ concentration is very low due to the abundance of O_2 molecules. However, from the known rate constants for the O_3-hydrocarbon reactions it became clear that other reactions should occur as well, since the calculated rates of hydrocarbon loss fall far short of observed oxidation rates (Niki et al., 1972; and references therein). Moreover, an explanation had to be found for the initial oxidation of NO to NO_2, since the background concentration of O_3 would be far too low to accomplish this.

The reactive radicals mentioned earlier were suspected to be additional oxidizing species; however, only during the last ten years have rate constants for their reactions (mainly for the HO radical) become available, so that a reasonable quantitative estimate of the correctness of this theory can now be made.

2.2.1.1 Sources of HO radicals

As is the case of an unpolluted atmosphere, one source of HO radicals is the photolysis of O_3 by solar radiation below approximately 320 nm, followed by interaction of $O(^1D)$ atoms with water molecules:

$$O_3 + h\nu(\lambda<320\text{ nm}) \rightarrow O(^1D) + O_2\ (^1\Delta_g)$$
$$O(^1D) + H_2O \rightarrow 2HO$$

Under NO_x-hydrocarbon polluted conditions, this source of HO radicals is only of minor importance once the chemical transformations are under way, especially under high NO concentration conditions, when the O_3 concentration is low. It appears that the major primary source of HO radicals in polluted air is from the photolysis of nitrous acid (Demerjian et al., 1974; Cox and Derwent, 1975).

$$HONO + h\nu(\lambda \lesssim 400\text{ nm}) \rightarrow HO + NO$$

Nitrous acid itself is formed via the following routes (Cox and Derwent, 1975; Simonaitis and Heicklen, 1974a)

$$HO + NO \overset{M}{\rightarrow} HONO$$
$$HO_2 + NO_2 \rightarrow HONO + O_2$$
$$NO + NO_2 + H_2O \rightleftarrows 2HONO.$$

The third nitrous acid-forming reaction is very slow, and therefore is only important under very high NO_x conditions, e.g. in a power plant plume close to the stack (Chan et al., 1976a). The other two reactions do not really constitute primary sources for HO, but are very important as elementary reactions occurring in the ongoing chain of NO-NO_2-O_3 oxidation.

Similarly, an important source of HO radicals is the crucial NO oxidation step (Demerjian et al., 1974).

$$HO_2 + NO \rightarrow HO + NO_2.$$

Finally, but of lesser importance, the photolysis of hydrogen peroxide, which is mainly formed in the atmosphere by recombination of HO_2 radicals, leads to HO radical formation (Calvert and Pitts, 1966).

$$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$$

$$H_2O_2 + h\nu(\lambda \lesssim 370 \text{ nm}) \rightarrow 2HO$$

It thus appears that the major sources for HO radicals under oxidant-forming conditions are reactions involving the HO_2 radical, and no important primary source exists.

2.2.1.2 Sources of HO_2 and RO_2 radicals

The three body recombination reaction of H atoms with molecular oxygen is a very important source of HO_2 radicals.

$$H + O_2 + M \rightarrow HO_2 + M$$

and it appears that the photolysis of formaldehyde is equally important in that it is a major source of H atoms (Calvert et al., 1972).

$$CH_2O + h\nu(\lambda \leq 370 \text{ nm}) \rightarrow H + HCO \text{ (in part)}$$

Formaldehyde is directly emitted into the air from combustion processes and is also formed in atmospheric hydrocarbon oxidation reactions. The formyl radical HCO can undergo two competing reactions with oxygen in the atmosphere:

$$HCO + O_2 \rightarrow HO_2 + CO$$

$$HCO + O_2 \rightarrow H(CO)O_2$$

thus leading also to peroxy radicals. The extent to which both reactions occur under atmospheric conditions is uncertain. The rate constant for the first reaction is fast (Washida and Bayes, 1974), but that of the second is unknown. The $H(CO)O_2$ species conceivably could lead to the formation of peroxyformyl nitrate (PFN) in the presence of NO_2, which has been postulated but never identified in smog mixtures. This might be due to the instability of PFN itself (Demerjian et al., 1974); it has been observed in photolysis of a NO_2-CH_2O-Cl_2 mixture (Niki et al., 1976a, Gay et al., 1976), but not in other spectroscopic work of the H-CO-O_2 system (Hunziker and Wendt, 1976). Osif and Heicklen (1976) indicated that 40% of the reactions of HCO with O_2 lead to $HCOO_2$ formation.

The formyl radical can also be formed by the Photolysis of higher analog aldehydes although the rate is slower due to a blue shift of the absorption spectrum (Calvert and Pitts, 1966):

$$RCHO + h\nu(\lambda \leq 340\ nm) \rightarrow R. + HCO$$

In addition to the formyl radical this reaction produces an alkyl radical which, in the atmosphere, exclusively reacts with O_2 to form an alkyl-peroxy radical (cf. Bascó et al., 1972):

$$R + O_2 + M \rightarrow RO_2 + M$$

Another major source for HO_2 radicals is the interaction of alkoxy radicals with oxygen (Heicklen, 1968; Mendenhall et al., 1975):

$$RCH_2O + O_2 \rightarrow RCHO + HO_2$$

In this reaction an aldehyde molecule is also formed which in turn can photo-decompose to form more peroxy radicals. Alkoxy radicals in oxidant-forming atmospheres find their origin in the important NO oxidation reactions of the general type:

$$RO_2 + NO \rightarrow RO + NO_2.$$

Acylperoxy radicals are formed through the reactions of acyl radicals with O_2, as in the reaction between the formyl radical and O_2 (cf. Weaver et al., 1975):

$$RCO. + O_2 \rightarrow RCOO_2.$$

The origin of the RCO. radicals is H-abstraction from an aldehyde by HO, (Morris and Niki, 1971a) and, to a small extent, by HO_2 radicals:

$$RCHO + HO \rightarrow RCO + H_2O$$

$$RCHO + HO_2 \rightarrow RCO + H_2O_2$$

In general it can be said that H-abstraction from any hydrocarbon will lead to the formation of a peroxy radical:

$$RH + HO \rightarrow R^{\cdot} + H_2O \xrightarrow{O_2} RO_2.$$

2.2.1.3 Sources of $O(^3P)$, $O(^1D)$, NO_3

The source of the oxygen atoms in the atmosphere is purely photochemical. Ground state oxygen atoms are formed by the photolysis of O_3 and NO_2:

$$O_3 + h\nu(\lambda > 320\ \mathrm{nm}) \rightarrow O(^3P) + O_2^*$$

$$NO_2 + h\nu(\lambda < 430\ \mathrm{nm}) \rightarrow NO + O(^3P)$$

Ozone photolysis contributes only little compared to NO_2 since its extinction coefficient is very low in the available wavelength region (Calvert and Pitts, 1966). The photolysis of NO_2 on the other hand is the major source under smog conditions. Almost all $O(^3P)$ atoms thus formed will react with O_2 to form O_3, and thus NO_2 is regarded as the photochemical precursor of O_3.

$O(^1D)$ atoms are only formed by the photolysis of O_3 as discussed in the last chapter.

NO_3 radicals are sometimes considered as important oxidizing species in smog mixtures (cf. Farrow et al., 1975). Very little is known about the rates of oxidation by this radical, although one report indicates that while its reactivity resembles that of the HO radical, the actual rate constants for the NO_3 + olefin interaction are smaller by a factor 10^5, (Japar and Niki, 1975). The NO_3. radical is formed by the interaction of NO_2 with $O(^3P)$ or O_3:

$$NO_2 + O(^3P) + M \rightarrow NO_3 + M$$

$$NO_2 + O_3 \rightarrow NO_3 + O_2$$

However, the first reaction cannot compete with the $O(^3P)$ + O_2 reaction to form O_3 (see above), and the second reaction is slow. Thus only low concentrations of NO_3 are expected in the atmosphere, which makes their role in oxidation reactions of doubtful importance.

2.2.2 Chain Oxidation of NO

As was indicated earlier an important question in the understanding of oxidant-forming chemistry is the way in which NO is oxidized to NO_2. A major breakthrough in the elucidation of the mechanism happened when it was shown that the reaction between HO and CO

$$HO + CO \rightarrow H + CO_2$$

was much more efficient than was previously thought (Heicklen et al., 1969; Stedman et al., 1970). A chain oxidation is then possible for NO oxidation:

$$HO + CO \rightarrow H + CO_2$$

$$H + O_2 + M \rightarrow HO_2 + M$$

$$HO_2 + NO \rightarrow HO + NO_2$$

Although CO concentrations due to combustion processes in polluted atmospheres are substantially higher than the background concentrations, it is believed that a much larger contribution to the NO oxidation is from oxidation by alkyl- and acyl-peroxy radicals, although few direct measurements of such reactions have been reported (Simonaitis and Heicklen, 1974b; Whitbeck, 1975).

From the foregoing discussion on radical sources we can visualize the following scheme:

$$RH + HO \rightarrow R + H_2O$$

$$R + O_2 + M \rightarrow RO_2 + M$$

$$RO_2 + NO \rightarrow RO + NO_2$$

$$RO + O_2 \rightarrow R'O + HO_2$$

$$HO_2 + NO \rightarrow HO + NO_2$$

Hydrocarbon molecules are important because they are sources of several RO_2 radicals. For example, the oxidation/degradation of propylene, initiated by HO radicals, an olefin with 3 carbon atoms, can lead to the formation of at least 8 oxidizing species of general formula RO_2, as theorized by Demerjian et al., (1974) (See Table 3).

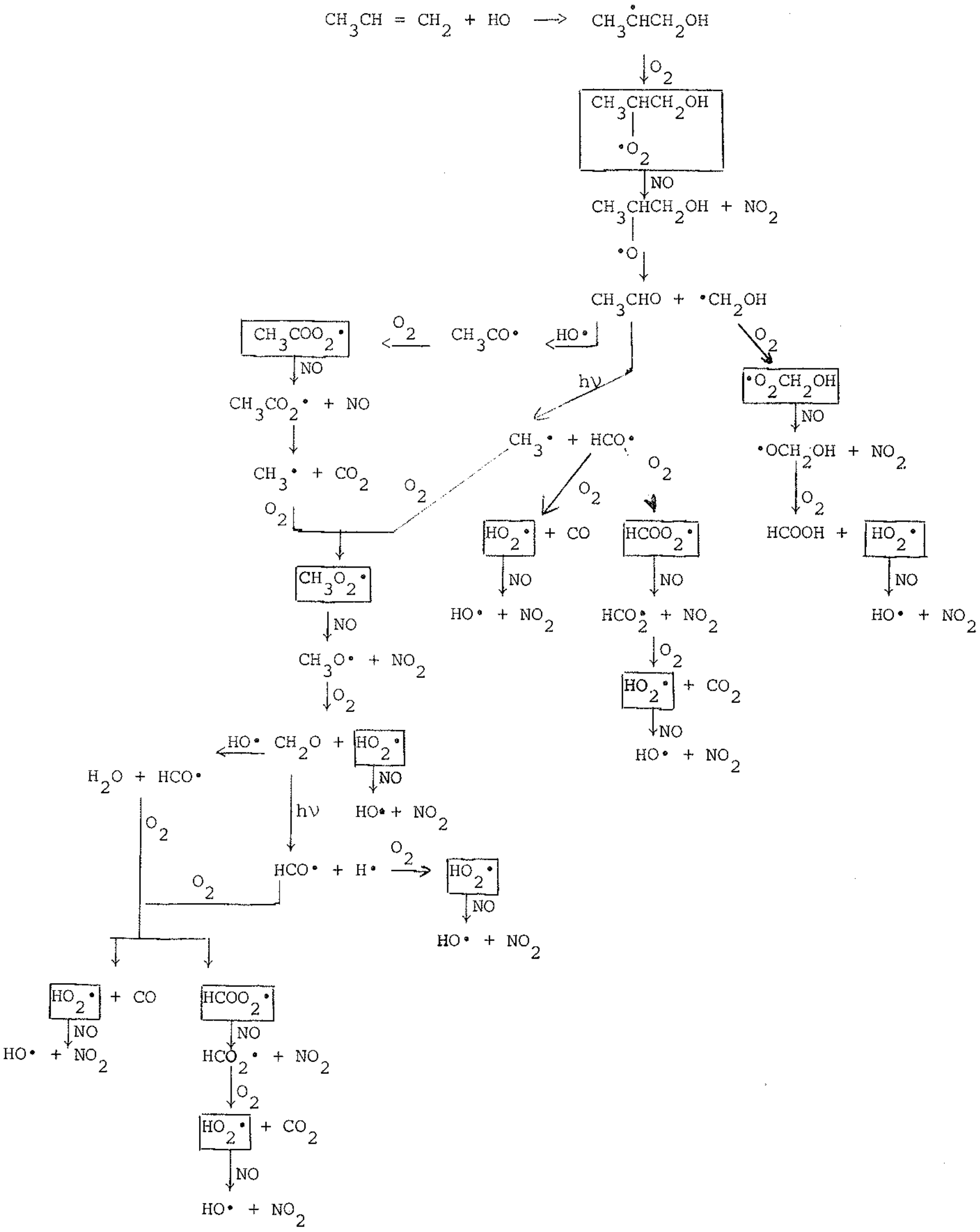
2.2.3 Oxidation Mechanisms of Hydrocarbons

The oxidation of hydrocarbons in a smog mixture is very important since it creates the many radicals necessary for the chain oxidation of NO to NO_2, as indicated in the last section. From current knowledge, it appears that the most important initial reaction is attack by HO radicals (Doyle et al., 1975; Lloyd et al., 1976) and in a later stage O_3 and HO_2 can become important as well. The mechanistic routes along which these oxidations take place are controversial. We will not discuss them in depth here, but indicate some of the complications that are encountered. On the other hand, rate constants for initial attack

Table 3

Possible reactions following HO addition to propylene

(from Demerjian et al., 1974)



by HO and O_3 on hydrocarbons have become available during recent years. This is not true for the HO_2 radical attack, for which the data base is very poor indeed.

2.2.3.1 Reactions of HO with hydrocarbons

HO radicals react essentially with any hydrocarbon that has an abstractable H-atom available, creating a free radical which will probably exclusively react with O_2 in the atmosphere to form a peroxy radical.

The reactions with olefins are very fast, approaching those of diffusion controlled processes (Morris and Niki, 1971b; Wilson, 1972; Atkinson and Pitts, 1975; Davis et al., 1975a; Pastrana and Carr, 1975; Lloyd et al., 1976; Meagher and Heicklen, 1976). There is considerable uncertainty, however, to what extent this reaction involves addition of HO to the double bond, or H-atom abstraction. There is evidence for both routes. Thus Pastrana and Carr (1975) and Slagle et al., (1975) have found evidence that a significant fraction of the reactions proceeds by abstraction of the alkyl hydrogen atom. These studies involved low reactant pressures, however, and Cvetanovic (1976) has indicated that at higher total pressures addition of HO to the double bond is probably the dominant route.

The reactions of HO with alkanes are an order of magnitude slower than with the alkenes (Wilson, 1972; Lloyd et al., 1976; Overend et al., 1976). The reaction involves the abstraction of an H-atom, and the alkyl radical will further react with molecular oxygen to form a peroxy radical. The important consequence of these reactions is that a control strategy based only on reducing the olefinic hydrocarbons levels will not necessarily result in decreasing smog problems, but merely delay the NO to NO_2 oxidation.

Aldehydes will react with HO by H-abstraction as well, and the acyl radicals react further with O_2 to form acyl-peroxy radicals, $RCOO_2$, (Morris and Niki, 1971a; Weaver et al., 1975; Osif and Heicklen, 1976):

$$RCHO + HO \rightarrow H_2O + RCO \xrightarrow{O_2} RCOO_2$$

These radicals can not only oxidize NO to NO_2, but also

These radicals can not only oxidize NO to NO_2, but also can react with NO_2 leading to the obnoxious peroxyacyl nitrates (PANs)

$$RCOO_2 + NO_2 \rightarrow RCOO_2NO_2$$

The PAN compounds have been shown to be strong eye irritants, and moreover to be able to produce severe plant damage (Stephens, 1969).

Reactions of HO with aromatics have lately received some attention, partly because aromatics have been proposed as antiknock additives in gasolines instead of alkyl leads. The initial rates (Doyle et al., 1975; Davis et al., 1975b; Hansen et al., 1975) appear to be comparable to those with olefins. Again addition and abstraction can occur and the contributions from both modes of reaction are essentially unknown. The pressure dependence, however, indicates that even for toluene which has readily abstractable methyl group hydrogens, addition is the major route; however, the observation of benzaldehyde as a minor product in experiments on the toluene-NO_x-air system indicates that abstraction must take place as well (Pitts et al., 1975).

The ultimate fate of the HO-aromatic interaction has important implications in the light of the suggestion of Finlayson and Pitts (1976) that such reactions might lead to long-chain multifunctional compounds which could form nucleating species for organic aerosols.

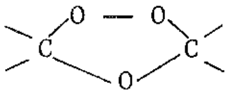
The eventual products of HO-hydrocarbon interactions in the atmosphere are a matter of speculation. Some educated guesses in this regard have been made by Demerjian et al., (1974). We have shown an example of this in Table 3. Similar degradation routes can be constructed for other hydrocarbons. The gist of such schemes is the production of several peroxy radicals, and ultimately the formation of CO, CO_2 and one or two C-atom containing, less reactive, hydrocarbons like formic and acetic acid. The formation of ethylene could be a start for polymerization to organic aerosols, as discussed in Section 2.4.

2.2.3.2 Reactions of O_3 with hydrocarbons

In the gas phase the reactions of O_3 with alkanes are very slow, and considered to be of no importance for atmospheric chemistry. Reactions with olefins and aromatics are moderately fast, but still are about a factor 10^6 slower than the HO-oxidation reactions. However, since the O_3 concentration at low NO concentration is generally a factor 10^4 to 10^5 higher than that of HO, O_3 can effectively compete with HO in reacting with olefins and aromatics under such circumstances.

As far as the O_3-olefin reactions are concerned, many of the important initial reaction rate constants are known with reasonable accuracy, largely from the work of Cvetanovic and coworkers (for recent determinations, see Huie and Herron, 1975; and references therein). The initial product of the reaction is believed to be the highly unstable ozonide. Despite extensive experimental (see Pitts and Finlayson, 1975) and theoretical (O'Neal and Blumstein, 1973; Wadt and Goddard, 1975) research, the ensuing reaction mechanism remains unclear. The well known Criegee mechanism which is able to explain the liquid phase reaction satisfactorily (Criegee, 1975), see Table 4, is not sufficient to explain all observations in the gas phase reactions, e.g. chemiluminescence, and the detection by photoionization mass spectroscopy of HO and HO_2 radicals in addition to a host of stable products (Finlayson et al., 1974; Atkinson et al., 1975). A much more elaborate mechanism, proposed by O'Neal and Blumstein (1973), see Table 5, seems promising in this regard, but more experimental work is warranted to establish the presence of the intermediates and products which this mechanism incorporates.

Generalized valence bond and configuration interaction calculations for the Criegee biradical $H\dot{C}HOO\cdot$ (Wadt and Goddard, 1975) seem to be in agreement with the O'Neal and Blumstein mechanism. It might be mentioned here, that this biradical has been suggested as an important oxidant for SO_2, as we will see in the next section , but this cannot be evaluated since its actual presence has not firmly been established. Niki et al., (1976a) have very recently found spectroscopic evidence for the presence of the secondary ozonide



in a study of the gas phase reaction between olefins and O_3 in the presence of aldehydes, thus reinforcing the original Criegee biradical mechanism.

Table 4

Criegee mechanism for ozonolysis of butene-2

(molozonide)

$$\longrightarrow \quad CH_3\dot{C}HOO\cdot + CH_3CHO$$

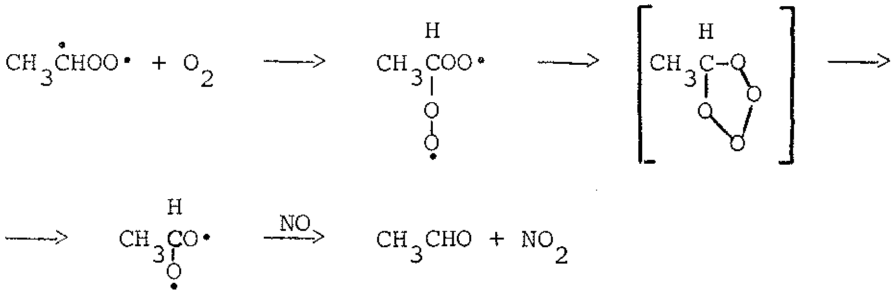
(Criegee biradical)

$$CH_3\dot{C}HOO\cdot \longrightarrow H_2O + CH_2 = C = O$$

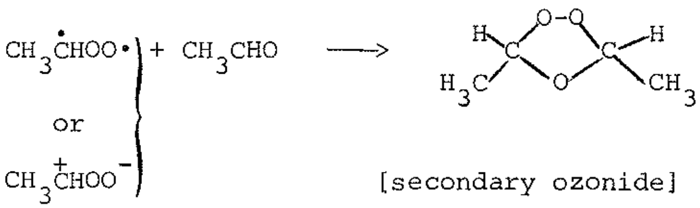
$$\longrightarrow CH_3OH + CO$$

$$\longrightarrow CH_4 + CO_2$$

In air, the Criegee biradical will preferentially decompose as follows, according to Demerjian et al. (1974)



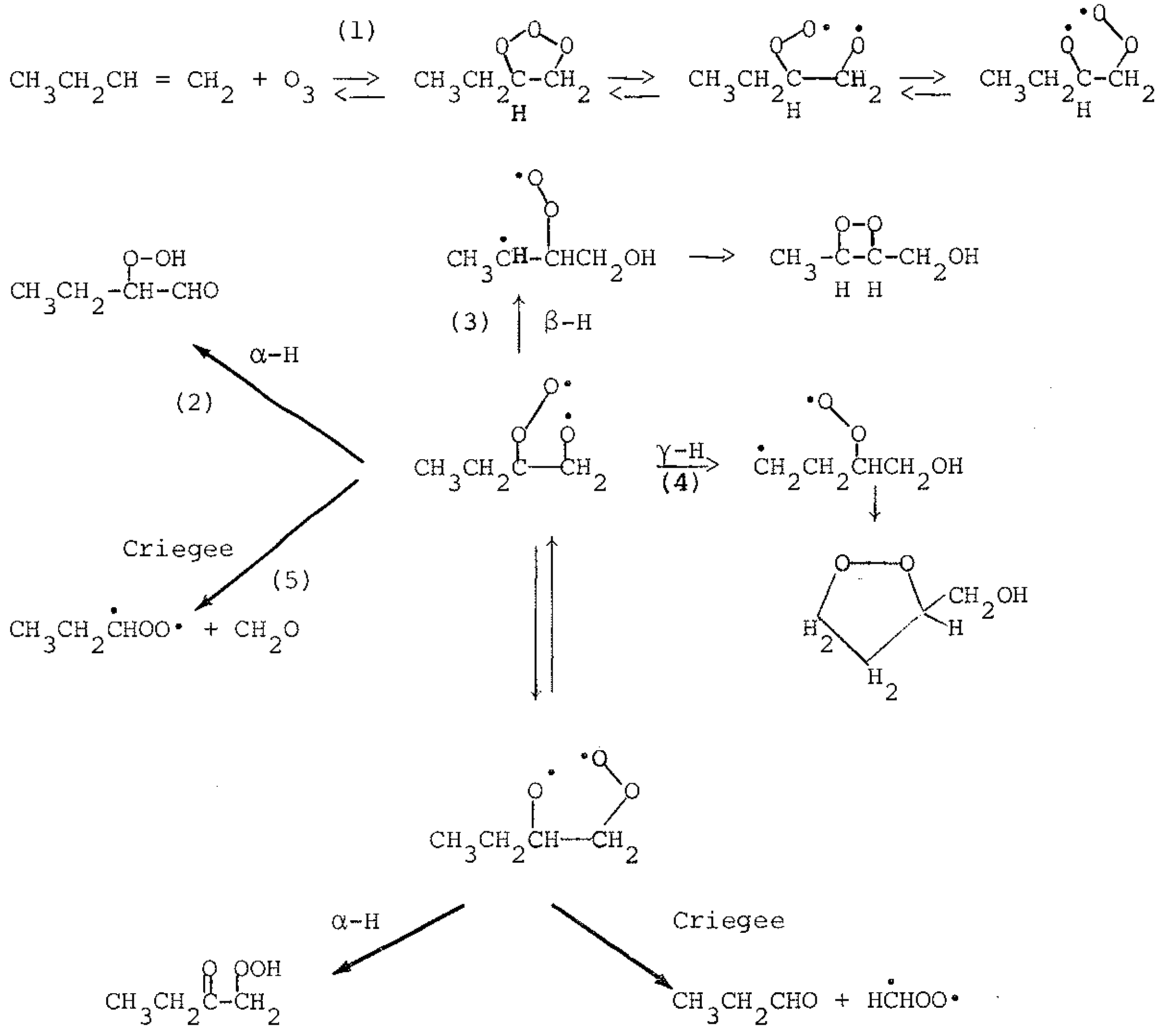
The original Criegee mechanism for liquid phase reactions suggests the following reaction for the biradical (in solution presumed to be in a "zwitterion" state).



[secondary ozonide]

Table 5

O'Neal and Blumstein mechanism for ozonolysis of 1-butene



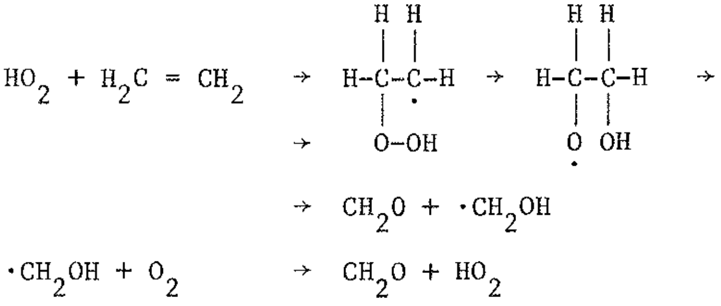
Exothermicity, as calculated by O'Neal and Blumstein:

Reaction	ΔH° (kcal/mole)
(1)	-32.9
(2)	-74.3
(3)	-65
(4)	-80
(5)	$\leqslant$ 4.4

The reaction between O_3 and aromatics has been studied only briefly. It seems that α-dicarbonyl compounds are major products (Nojima et al., 1974). Thus the O_3-benzene reaction leads to glyoxal (CHO-CHO), p-xylene + O_3 produces glyoxal and methyl glyoxal (CH_3COCHO), and o-xylene + O_3 gives glyoxal, methylglyoxal and biacetyl ($CH_3COCOCH_3$). α-Di-carbonyl compounds have been identified as constituents in organic aerosols (O'Brien et al., 1975b), and thus the O_3-aromatic reaction is one possible route of formation of these aerosols.

2.2.3.3 Reactions of RO_2 with hydrocarbons

There is no known unique way of forming HO_2 radicals (Lloyd, 1974), nor an easy method of monitoring these radicals. For this reason the amount of data on HO_2 reactions is very poor, as reviewed recently by Lloyd (1974). Rate constants for initial attack by HO_2 are mainly known within orders of magnitude only, and estimated to be about 10^5 orders of magnitude slower than those of HO reactions with olefins. Consequently there is considerable uncertainty as to how important HO_2 attack on olefins is. It is needless to mention that the mechanism along which eventual degradation takes place, is only speculative. It has been suggested that initial addition to the double bond is the more important reaction path (Lloyd, 1974; Avramenko et al., 1965), although Demerjian et al., (1974) assume that H-atom abstraction might occur as well. Avramenko et al., (1965) suggest that initial addition to ethylene might be followed by isomerization, leading to formation of formaldehyde in a chain reaction:



$$HO_2 + H_2C = CH_2 \rightarrow H-\underset{O-OH}{\overset{H}{C}}-\underset{\cdot}{\overset{H}{C}}-H \rightarrow H-\underset{\dot{O}}{\overset{H}{C}}-\underset{OH}{\overset{H}{C}}-H \rightarrow$$

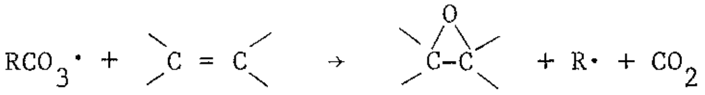
$$\rightarrow CH_2O + \cdot CH_2OH$$

$$\cdot CH_2OH + O_2 \rightarrow CH_2O + HO_2$$

However, Lloyd has questions Avramenko et al.'s results since $O(^3P)$ atoms, and possibly HO as well, were present in their reaction systems.

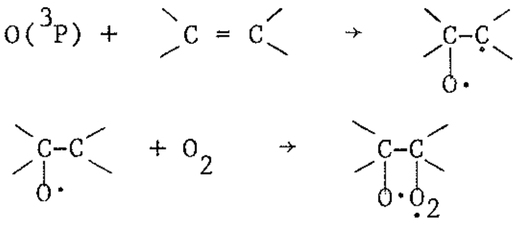
There is no information whatsoever about the possible reactions of HO_2 with aromatics. It seems reasonable to assume that the mechanism of such reactions will be similar to the HO + aromatics case, i.e. addition, followed by ring opening. The rates of initial HO_2 attack are probably again several orders of magnitude slower. Reactions of HO_2 with alkanes and aldehydes proceed by H-atom abstraction, and are thought to be five and two orders of magnitude slower than those with olefins (Lloyd, 1974).

To the authors' knowledge there are no published studies on the reactions between alkyl peroxy radicals with olefins at atmospheric temperatures. Rate constants for some of these reactions have been estimated by Demerjian et al., (1974), which indicate that they are of minor importance; the alkyl peroxy radicals seem to be mainly involved in the oxidation of NO to NO_2. Acyl-peroxy radicals have recently received some attention as well (Ruiz Diaz et al., 1975; Selby and Waddington, 1975). Although studied at temperatures well above normal atmospheric conditions, the proposed interaction is of some importance in that it suggests the formation of highly carcinogenic epoxides (Van Duuren, 1969):

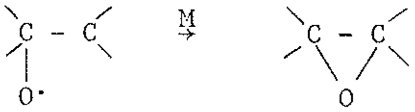


2.2.3.4 Reactions of $O(^3P)$ with hydrocarbons

The reactions of $O(^3P)$ with olefins have been studied extensively, mainly by Cvetanovic and coworkers (Cvetanovic, 1963). Such reactions are now considered of very minor importance, however, since in the atmosphere most of the $O(^3P)$ atoms will react with O_2 to form O_3 leading to low steady state concentrations of $O(^3P)$. The presence of O_2 moreover, will probably mean that the resulting products of the $O(^3P)$ + olefin reaction in the atmosphere are different. Demerjian et al., (1974) suggest that the initially formed biradical most likely will react with O_2, which then makes the products indistinguishable from the O_3 + olefin reactions:



The chance remains, however, that some fraction of the biradical will undergo ring closure and stabilization to form epoxides:



It should be mentioned, however, that to date epoxides have not been identified in polluted atmospheres (Pitts and Finlayson, 1975). The rate of the $O(^3P)$ + olefin interaction, which is 6 orders of magnitude slower than that of the HO + olefin interaction, is the main reason for the unimportance of these reactions. The same reasoning can be applied for the $O(^3P)$ + aromatics interaction, which has recently been studied in depth by Gaffney et al., (1976).

2.2.4 Simulations of Oxidant Chemistry

In the foregoing sections we have treated the more important features of the mechanism of oxidant chemistry and indicated that important information is still missing. Nevertheless, several research groups have used existing data, complemented with estimations of necessary unknown data, to computer simulate the ongoing chemistry of this system. Such simulations can be of multi purpose. In some calculations researchers have tried to achieve a better understanding of the total chemistry involved, for example to establish the relative importance of various reactions. To do this the predicted temporal behaviour of a chemical model was compared with experimental data generally taken from "smog chamber" results. Chemical models as accurate as possible were considered. Such simulation studies have been performed by several groups since the early seventies (Westberg and Cohen, 1969; Niki et al., 1972; Demerjian et al., 1974; McQuigg and Calvert, 1975). Several interesting aspects came to light, such as the important sources for the major radicals (Table 6), and the rates of attack of various reactive intermediates on a hydrocarbon (Table 7). The data in Tables 6 and 7, from Demerjian et al., (1974), were based on the simulation of a model which was more or less validated by comparison with smog chamber data of other groups. Nevertheless, it should again be stressed that the predictions are only as good as the input data, i.e. reaction mechanisms and rate constants.

Table 6

Comparison of theoretical rates of HO radical-forming reactions in a simulated, sunlight irradiated, auto exhaust-polluted atmosphere 1)

(from Demerjian et al., 1974)

A. $HONO + h\nu \longrightarrow HO + NO$

B. $O(^1D) + H_2O \longrightarrow 2HO$

C. $HO_2 + NO \longrightarrow HO + NO_2$

D. $H_2O_2 + h\nu \longrightarrow 2HO$

E. $CH_3CHO_2H \longrightarrow CH_3CHO + HO$ 2)

Rate of HO formation (ppm $min^{-1} \times 10^4$)

Time, min.	A	B	C	D	E
0.05	0.0088	0.0015	28.3	0.0003	1.5
0.5	0.0907	0.0108	29.3	0.0029	1.6
2.0	0.32	0.023	27.8	0.013	1.6
10.0	0.64	0.82	18.5	0.080	1.7
30.0	0.29	0.23	10.0	0.33	1.5
60.0	0.12	0.38	5.9	0.79	0.9
90.0	0.07	0.48	4.0	1.2	0.5
120.0	0.05	0.55	1.2	1.6	0.2

1) The simulated mixture had the following initial conditions: $[NO]^o = 0.075$; $[NO_2]^o = 0.025$; $[\text{trans-2-butene}]^o = 0.1$; $[CO]^o = 10$; $[CH_2O]^o = 0.1$; $[CH_3CHO]^o = 0.06$; $[CH_4]^o = 1.5$; relative humidity: 50%; temperature: 25°C; solar zenith angle: 40°. All concentrations in ppm.

2) CH_3CHO_2H is an intermediate from the $C_4H_8 + HO_2$ interaction in the Demerjian et al. mechanism.

Table 7

Theoretical rate of attack (ppm min^{-1} x 10^4) by various reactive intermediate species on trans-2-butene in a simulated, sunlight irradiated, auto exhaust-polluted atmosphere.*)

(from Demerjian et al., 1974)

Reactive Species

Time, min	$O(^3P)$	O_3	HO_2	HO	CH_3O	NO_3	$O_2(^1\Delta_g)$
2	0.13	0.26	1.69	18.1	0.026	0.00005	0.000029
10	0.20	0.83	1.84	12.5	0.018	0.00051	0.000027
30	0.17	1.58	1.49	5.9	0.008	0.0022	0.000020
60	0.08	1.43	0.88	2.6	0.004	0.0026	0.000012
90	0.03	1.00	0.49	1.2	0.002	0.0090	0.000007
120	0.01	0.65	0.28	0.7	0.001	0.0018	0.000004

*) Simulated mixture same as from Table 6;

Rate of attack = rate constant x concentration of reactive species.

The model of Demerjian et al., updated with more recent rate constant information, was used by the present authors to see what seasonal effects might be expected in the oil sands area (Bottenheim et al., 1976c). The reaction scheme and rate constants used in these calculations are given in the Appendix. Some of the results will be discussed in a later section.

Another approach is to construct a model which is directed to the simulation of actual atmospheric conditions. Not only the chemistry has to be taken into account in such models, but meteorological variables as well. Recently, chemically oriented models have been used to explain actual atmospheric observations (Calvert, 1976b; Graedel et al., 1976), but usually the chemical model is simplified to a limited number of equations, since the inclusion of meteorological variables would make the total model otherwise too complicated. A total airshed model would require as input: i) a detailed emission inventory, ii) meteorological and topographical variables (time of day, wind speed, atmospheric pressure conditions, etc.), and iii) a reliable description of chemical and physical processes that will take place (Eschenroeder and Martinez, 1972). A useful chemical mechanism consisting of approximately 40 reactions is the so called "lumped parameter" model of Hecht et al., (1974), which encompasses most of the chemical particularities determined by the more specific chemical models, such as the Demerjian et al., model.

Finally, a purely statistical approach to air pollution modelling has been developed. In such models monitoring data are collected and a purely statistical model is developed which can more or less predict the expected pollutant concentrations under specified meteorological and emission conditions (Hameed, 1974; Tiao et al., 1975; McCollister and Wilson, 1975). Only a very limited amount of chemical input is required for such models, and actual rate constants used are not from experiment but determined purely by parameter fitting. Of course, such models will only be able to approximate actual conditions, and moreover are only useful for the particular area from which the monitoring data originate.

It appears that modelling studies, which have as their ultimate goal to furnish public authorities with scientifically validated tools to effectively control air pollution, have been almost exclusively directed to urban airsheds. Recently, however, the realization has grown that rural regions have to be considered as well, as we will see in the next section.

At this point we should discuss so-called "smog chamber" research. A smog chamber is in fact a reaction vessel of much larger dimensions than is commonly used in laboratory studies. Several smog chamber facilities exist nowadays, mainly in the United States. In such chambers one tries to study in a more controlled environment the chemical transformations that will take place in air mixed with small quantities of pollutant molecules such as ppm amounts of NO_x, CO, hydrocarbons, and sometimes SO_2. Black lights (Batelle smog chamber, cf. Miller et al., 1976), solar simulators (SAPRC, University of California, Riverside, cf. Pitts and Finlayson, 1975), or natural sunlight (University of North Carolina, cf. Jeffries et al., 1976a) have been utilized as irradiation sources. By "controlled environment" it is meant that the initial constituents of the reaction mixture are known and the rate of production of new chemical species, in particular oxidants like O_3 and PANs are monitored while such environmental variables as irradiation, temperature and pressure are kept under tight control. Such experiments are very valuable for studying chemical transformations, but give no indication of the the effect of meteorological variables. A few studies have been undertaken in which the reaction mixture was diluted with air during the irradiation (Fox et al., 1975; Nieboer, 1975), and the interesting observation was made that dilution might actually increase the total amount of ozone formed (Fox et al., 1975). The latter group in their outdoor smog chamber experiments also noted some interesting enhancement of the chemical transformations due to intermittent irradiation from sunlight (clouds covering the sun) (Jeffries et al., 1976b). Such effects are difficult but not impossible to explain with existing theoretical models of air pollution mixtures. The present authors feel that smog chamber experiments under the conditions prevailing in northeastern Alberta are urgently needed, as will be discussed in some more detail in the last chapter of this report.

2.2.5 High Oxidant Concentrations in Rural Environments

Until the early 1970s, non-urban ozone concentrations were believed to be close to an average of 0.02 ppm. Since then, however, much higher ozone concentrations have been reported from several rural environments, and the question has arisen as to the origin of high rural ozone concentrations (Ripperton et al., 1975; Coffey and Stasiuk, 1975; Cox et al., 1975; Rubino et al., 1976; Lonneman et al., 1976). However, these high ozone concentrations appeared at irregular times, thus making it likely that no actual local increase in background concentrations was observed, but that long range transport mechanisms from originally polluted industrial and urban environments, was involved. Several explanations have been advanced for this phenomenon. Transport of O_3 from the stratosphere, or synthesis from natural precursors, as discussed in the chapter on "clean air" chemistry, were discarded since a more continuous effect would be expected. More reasonable alternatives are O_3 synthesis in polluted environments and subsequent transport to rural areas, or synthesis in transit to rural areas, possibly through additional injection of precursor material from natural sources en route (Ripperton et al., 1975).

At present the latter theory has the most credibility (Lonneman et al., 1976) for the following reasons: when the more reactive olefinic hydrocarbons are consumed, (a "spent" photochemical system), the air remains relatively rich in alkanes and possibly aromatics, which react slower with the active radicals. Under such conditions, even with comparatively low concentrations of nitrogen oxides, these less reactive hydrocarbons will be the sources of peroxy radicals that cause an unbalanced NO to NO_2 ratio, i.e. $NO_2 > NO$, and the previously mentioned photostationary state between NO, NO_2 and O_3 will then predict high O_3 levels. These large O_3 levels, moreover, are now much more stable, since the concentrations of molecules with which it reacts fast (NO and olefins) are now very low.

A consequence of the outlined mechanism is that high O_3 concentrations in rural environments will not necessarily be accompanied by high concentrations of other oxidants like PAN, since other precursors required for their formation (NO_x) are in low concentration. This has indeed been observed in the study by Lonneman et al., (1976); it has therefore been suggested that high PAN levels are a better measure of real photochemical smog situations than high O_3 levels (Nieboer and Van Ham, 1976).

Some other possible mechanisms have recently been suggested (Davis and Klauber, 1975; Chameides and Stedman, 1976). Davis et al., noticed high O_3 concentrations in power plant plumes far downwind, and proposed that a chain oxidation involving SO_2 might be responsible. We will discuss this interesting mechanism in the section on SO_2 oxidation mechanisms. Stedman et al., from computer calculations, proposed that high ozone levels might find their origin from interaction of naturally occurring CH_4 with a spent oxidant mixture. Their calculations have been criticized by Dimitriades et al., (1976) and Jeffries and Saeger (1976), who noted some problems with the mathematical methods used by Stedman et al.

The occurrence of such high ozone levels away from actual polluting sources could have an important bearing on the oil sands area situation. Winter temperature inversions will tend to suppress rapid dilution of emitted pollutants and thus oxidant formation if effective under winter conditions can be of considerable effect over prolonged time spans due to less reactive hydrocarbons. During summer, on the other hand, it can be expected that infusion of terpenes from the wooded surroundings into the original emitted mixtures will maintain a constant rate of oxidant formation even after the originally emitted hydrocarbons have reacted.

2.2.6 Inhibition of Photochemical Smog

Since many of the reactions that lead to oxidant and subsequent aerosol formation involve radical species, it has recently been suggested that addition of radical-trapping compounds to the atmosphere might delay the processes sufficiently so that extensive dilution can occur and smog formation be actually prevented (Heicklen, 1976a). This suggestion has been received with severe criticism among atmospheric chemists (see Science, (1976), 193, 871). For example, some of the originally suggested radical scavengers like aniline have been shown to result in the formation of large aerosols by themselves (Spicer et al., 1974; Nguyen and Phillips, 1975). Heicklen and coworkers showed that diethylhydroxylamine (DEHA) does not induce aerosol formation (Stockburger and Heicklen, 1976), and is effective as a radical-chain inhibitor (Gitchell et al., 1974a,b; Jayanty et al., 1974). Criticisms are not only that the atmospheric effect is uncertain - the observed delay in smog formation might merely result in transferring the problems downwind - but, moreover, the physiological effects of DEHA and its oxidation products on humans are unknown (Finlayson and Pitts, 1976). The latter authors note that DEHA is at least structurally very similar to the notorious carcinogen diethylnitrosamine. The most fundamental argument against the addition of radical scavengers to the atmosphere seems to be expressed in the indicated article from Science: one would use one technology to correct the unwanted side effects of a second one, and thereby introduce a completely new and potentially more serious set of side effects.

2.3 SULPHUR DIOXIDE TRANSFORMATION MECHANISMS IN THE ATMOSPHERE

The transformation chemistry of sulphur dioxide in the atmosphere has been extensively studied in the past few years. It is generally accepted that the atmospheric oxidation of SO_2 results in the formation of sulphates via the formation of SO_3 molecules, which are known to be very hygroscopic and to react very fast with water molecules to form H_2SO_4 (the rate of the homogeneous gas phase reaction $SO_3 + H_2O \rightarrow H_2SO_4$ has recently been measured to be 1.34×10^3 ppm min^{-1}, which leads to a half life of SO_3 at 50% relative humidity (25^oC) of only 2 seconds; Castleman et al., 1975). Sulphates then may be present in the acid form (H_2SO_4, H_2SO_5, $H_2S_2O_8$, etc.) or in the form of salts (especially as $(NH_4)_2SO_4$ due to the natural abundance of NH_3). There is also ample evidence that SO_2 oxidations in the presence of hydrocarbons will lead to the formation of sulphur-containing organic aerosols.

It has been established that moderate levels of SO_2 are hazardous to human health, but even worse effects can be anticipated from the oxidation products of SO_2 especially where the atmosphere has high humidity and particle levels (Amdur, 1971; CHESS, 1974; McJilton et al., 1973, 1976).

Another harmful aspect of SO_2 pollution is the effect on the rural environment ensuing from the acidification of rain water (Likens and Bormann, 1974, Likens, 1976). Existing theories on the global sulphur balance indicate that most of the sulphur compounds emitted into the atmosphere will eventually be deposited back to earth (Kellog et al., 1972), but the empirically determined lifetimes of SO_2 and of its oxidation products in the atmosphere (Eliassen and Saltbones, 1975) seem to be sufficiently long as to allow long range transport. Thus it has been estimated that more than 10% of the total sulphur deposition in Sweden originates from British industrial activity (Fisher, 1975). The acidified rainfall over Scandinavia, resulting from SO_2 emission in major industrial areas of west and central Europe has had very dramatic adverse effects on the aquatic ecosystems while equally serious changes in the forest environment are suspected (Oden, 1976).

Despite intense research efforts into the mechanistic routes along which the oxidation of SO_2 to H_2SO_4 and sulphates take place, no complete picture has emerged. We will now give an overview of the presently existing theories.

A first distinction can be made between homogeneous gas phase reactions, aqueous phase reactions, and heterogeneous processes. Until quite recently it was generally assumed that the major, if not the only, oxidation routes of SO_2 in the atmosphere was in the aqueous phase or heterogeneous reactions. This conclusion was based on the observed slow rates of photo-oxidation of SO_2 in air (Hall, 1953; Gerhard and Johnstone, 1955) as compared to the catalytic influence of certain solids and moisture on the oxidation rate of SO_2 (Johnstone and Coughanowr, 1958, Junge and Ryan, 1958, Johnstone and Moll, 1960; Van den Heuval and Mason, 1963; Foster, 1969; Matteson et al., 1969). Under the conditions that prevailed during some of the major infamous polluting atmospheres such as the London fog of December, 1952, i.e., high humidity, large amount of particles, little wind - this seems to be reasonable. However, in recent years more precise studies into the homogeneous gas phase reaction paths of SO_2 oxidation have lead to a reevaluation of its importance, especially under less severely polluted conditions (Sidebottom et al., 1972; Calvert, 1973, 1974; Payne et al., 1973; Calvert and McQuigg, 1975; Davis and Klauber, 1975; Wood et al., 1975).

We will focus our attention first on these homogeneous gas phase oxidation mechanisms, next consider existing theories on aqueous phase reactions, and then consider heterogeneous oxidation routes. We conclude this section with a review of some plume-studies, in which the oxidation rate of SO_2 has been monitored in the atmosphere.

2.3.1 Homogeneous Gas Phase Reactions of SO_2 in the Atmosphere

There are two types of homogeneous gas phase reactions that SO_2 molecules can undergo and they will be treated separately. Both depend on the presence of sunlight, and thus fall within the category of photochemistry but a distinction will be made between photoexcitation of the SO_2 molecule itself, and the reactions of ground state of SO_2 molecules with small radicals originating in photochemical reactions of other molecules. Finally we will briefly discuss the homogeneous gas phase reactions between SO_2 and NH_3, which are occasionally suggested to be of atmospheric importance.

2.3.1.1 Reactions of electronically excited SO_2

Photodissociation of SO_2 into SO and O atoms requires 135 kcal/mole. Since the wavelength of the solar radiation which reaches the lower atmosphere is greater than 2900 Å (less than 98.6 kcal/mole), only molecular reactions of electronically excited states of SO_2 need to be considered. Recent spectroscopic studies on the absorption (Brand and Nanes, 1973; Hamada and Merer, 1974, 1975; Dixon and Halle, 1973; Brand et al., 1976) and fluorescence (Brus and McDonald, 1973, 1974; Levine and Kaufman, 1974; Bottenheim et al., 1976b) spectra of SO_2 have shown that two excited singlet states of SO_2 are directly accessible in the atmospheric solar region and theoretical calculations (Hillier and Saunders, 1971; Chung, 1974; Lindley, 1976) indicate that three triplet excited states can in principle be populated. Although only one triplet state leads to phosphorescence (Briggs et al., 1975; Bottenheim et al., 1976a), and high resolution triplet absorption spectra provide only indirect evidence for the presence of the other triplet levels (Brand et al., 1973; Hamada and Merer, 1976), there is ample evidence that two (Cehelnik et al., 1971, 1973; Braslavsky and Heicklen, 1972; Luria and Heicklen, 1974; Penzhorn and Filby, 1975; Filby and Penzhorn, 1975) and possibly all three (Fatta et al., 1975; Heicklen, 1976b) triplet levels are photochemically active. At least one singlet excited state is, in principle, chemically active (Cehelnik et al., 1971; Stockburger et al., 1973; Demerjian and Calvert, 1975; Chung et al., 1975) but it has been indicated that photo-oxidation of SO_2 to SO_3 most likely occurs exclusively via triplet excited SO_2 molecules (Okuda et al., 1969). The suggestion by Hellner and Keller (1973) that long-living dimers of SO_2 might be formed in the atmosphere via the interaction of two singlet excited SO_2 molecules has recently been disproven (Bottenheim and Calvert, 1976).

Thus absorption of sunlight can produce two singlet states of SO_2, one or both of which can undergo intersystem crossing (of unknown efficiency) to three triplet states (Bottenheim et al., 1976a); one triplet state is populated by direct (spin forbidden) absorption (Sidebottom et al., 1972), and finally, in principle, at least one singlet state and three triplet states of SO_2 can participate in chemical reactions.

(a) Photooxidation of SO_2 in clean air

As has been indicated, only triplet excited SO_2 is presumed to be active in the SO_2 to SO_3 conversion. Sidebottom et al., (1972) measured the decay kinetics of the $^3B_1$ excited state of SO_2 (i.e. the phosphorescing state) as a function of pressure of different atmospheric constituents. Assuming that each reactive encounter between $^3SO_2$ and O_2 leads to oxidation of SO_2, they were able to estimate a maximum photooxidation rate of the $^3B_1$ state under varying conditions of relative humidity and solar zenith angle. Their data are reproduced in table 8.

Recent developments however have made these data rather unreliable. Sidebottom et al. considered only one singlet state as absorbing in their calculations. Moreover, since their measurements were based on phosphorescence, only the $^3B_1$ state was considered as the active species in photooxidation. It is likely however that another triplet state is the actual reactive state since the quenching rate constant for ${}^3B_1$ deactivation by O_2 is very similar to that by chemically inert molecules such as N_2 and CO_2 (Wampler et al., 1973).

As far as the actual oxidation mechanism is concerned, Sidebottom et al., favor a direct one step reaction,

$${}^3SO_2 + O_2 \rightarrow SO_3 + O({}^3P) \quad (\Delta H = -37.6 \text{ kcal/mole})$$

over the old two step mechanism proposed by Blacet (1952) which invokes a hypothetical SO_4 intermediate. To date however the formation of ozone which would be formed from the reaction

$$O({}^3P) + O_2(+M) \rightarrow O_3(+M)$$

during the photooxidation of SO_2 has never been proven. Another way to establish the efficiency of photooxidation of SO_2 is by measuring the quantum yield of the reaction. The rate of photooxidation can in principle be formulated as:

$$\frac{d(SO_2)}{dt} = K_a \cdot \phi \cdot (SO_2)$$

where K_a is the absorbed light intensity and ϕ is the quantum yield of SO_2 loss following light absorption. Some of the more recent data, shown in Table 9, (for a compilation of older data, see Allen et al., 1972) are widely discrepant. Most values are within an order of magnitude of 10^{-3}. Friend et al., (1973) and Bricard et al., (1972) reported no observable particle formation during the photolysis of SO_2 in clean air and Friend et al., estimated a lower limit of 10^{-9} for ϕ_{SO_3} by direct photooxidation. The latter authors pointed out that most other studies are performed at an unrealistically high SO_2 concentration as far as the atmosphere is concerned, where the reaction

$${}^3SO_2 + SO_2 \rightarrow SO_3 + SO$$

is responsible for SO_2 loss and SO_3 formation, and not oxidation by O_2. It has also been pointed out that in static systems, SO formed above can react further with SO_3 to reform SO_2 (Chung et al., 1975; Skotnicki et al., 1976): thus leading to a lower observed quantum yield

$$SO + SO_3 \rightarrow 2SO_2$$

Table 8

Estimated Theoretical Maximum Rates of Direct Photooxidation of SO_2 in the Atmosphere, from Sidebottom et al. (1972).[a]

Solar zenith angle	Theoretical Maximum rate of homogeneous, direct SO_2 photooxidation in sunlight, assuming all $SO_2(^3B_1)$-O_2 collisions lead to photooxidation.		
rel. hum:	0%	50%	100%
0	2.4	2.1	1.8
20	2.3	1.9	1.7
40	1.6	1.3	1.2
60	0.61	0.50	0.43
80	0.083	0.072	0.065

[a] Rates in $hr^{-1} \times 10^2$

More recent studies performed using ppm concentrations of SO_2 (Clark and Whitby, 1975; Kasahara and Takahashi, 1976) showed that the rate of photooxidation of SO_2 is comparable to that measured in earlier studies at higher concentrations. The low value of Friend et al., is difficult to explain, and photooxidation is now presumed to take place at rates of the order of a few tenth of a percent per hour. It is possible that in rigorously cleaned air, in which very few particles which can serve as nucleation centres are present, the reaction

$$SO_3 \rightarrow SO_2 + O$$

might compete with the reaction

$$SO_3 + H_2O \rightarrow H_2SO_4$$

decreasing the importance of homogeneous nucleation.

Penzhorn et al., (1974a) have used the calculations of Sidebottom et al., and incorporated an average quantum yield of oxidation of 10^{-3} to estimate the photooxidation rates in pure air for central Europe (50°N latitude). Using this value for the quantum yield essentially lowers the rates of photooxidation calculated by Sidebottom, Table 8, by an order of magnitude. Penzhorn et al.'s data are reproduced in Table 10. These authors observed that even though the average solar altitude decreases after June, this effect will initially be counterbalanced by a decrease in the ozone concentration of the upper atmosphere. The rate of photooxidation is therefore constant between May and October, after which it decreases rapidly. In December the estimated rate of photooxidation of SO_2 is only one tenth of its summer value. These calculations are of interest to us, since a similar if not greater effect should take place in northeastern Alberta ($\sim 58^{\circ}$N latitude).

Summarizing, it can be concluded that photooxidation of SO_2 in clean air under optimum conditions will occur at a rate of approximately 0.1 to 1% hr^{-1} (from Table 9). The maximum theoretical rate is somewhat higher (Sidebottom et al., 1972). The exact mechanistic route is as yet unclear; at least one study claims that direct photooxidation is unimportant.

(b) Reactions of photoexcited SO_2 with other atmospheric species

The rate of the reaction

Table 9. Some recent measurements of the SO_2 photooxidation rate*)

Investigator	Conditions	ϕ_{SO_3}	Photooxidation rate	Measurement method
Cox (1972)	static system $\lambda \sim 280-400$ nm	3×10^{-4}	0.02-0.04 % hr^{-1}	Yield of SO_3
Allen, McQuigg, Cadle (1972)	static system $\lambda \sim 280-400$ nm $[SO_2]=19-100$ Torr $[O_2]=50-400$ Torr	$\sim 5.5 \times 10^{-3}$	0.35% hr^{-1} "solar photooxidation rate"	SO_2 disappearance
Friend, Leifer, Trichon (1973)	flow system $\lambda \sim 240-400$ nm $[SO_2] \simeq 0.1-1$ ppm in air	$< 1 \times 10^{-9}$	-	condensation nuclei
Smith and Urone (1974)	static system fluorescent light $[SO_2]=2$ ppm in air	-	initial rate: 1.7×10^{-4} ppm/min overall rate: 0.26% hr^{-1}	SO_2 disappearance
Clark and Whitby (1975)	static system fluorescent light $[SO_2]=0.0491-2.88$ ppm in particle free air	-	0.379 to 0.992% hr^{-1} in noon-day sunlight	increase in H_2SO_4
Kasahara and Takahashi (1976)	flow system black lights $[SO_2]=0.05-10$ ppm in air	8×10^{-3}	0.7% hr^{-1} in noon-day sunlight	H_2SO_4-aerosol growth

*) in all cases, only the data at low rel. humidity are considered.

$$^{3}SO_2 + CO \rightarrow SO + CO_2$$

has been measured (Jackson et al., 1971, Wampler et al., 1972, Cehelnik et al., 1971) but is too slow to be important in the atmosphere.

The experiments of Sidebottom et al., (1972) indicate a very rapid rate of $^{3}SO_2$ deactivation by NO, and a chemical interaction has been proposed although the products of this reaction system have not been analyzed. In earlier studies (Renzetti and Doyle, 1960) where 1ppm NO was added to 0.5 ppm SO_2 in air at a relative humidity of 50% it was noted that aerosol production was suppressed. The reason for this is not clear.

Several studies (Badcock et al., 1971; Sidebottom et al., 1971; Wampler et al., 1973; Demerjian et al., 1974; Demerjian and Calvert, 1975; Wampler, 1976a, 1976b; Cox, 1973a; Penzhorn and Güsten, 1972; Penzhorn et al., 1973; Penzhorn et al., 1975; Jordan and Penzhorn, 1975; Penzhorn and Filby, 1975; Filby and Penzhorn, 1975; Smith and Spicer, 1975; Hirose et al., 1975) have been devoted since the Bufalini review of 1971 to the reactions between photoexcited SO_2 and hydrocarbons. The reactions are generally fast, and accompanied by the formation of copious amounts of aerosols. There is some doubt as to how important the reactions are in the atmosphere, since these later reactions were all performed at relatively high concentrations of hydrocarbons (Penzhorn et al., 1975) whereas in earlier experiments (Johnston and Dev Jain, 1960; Kopczynski and Altshuller, 1962) aerosol formation was not observed when the paraffin concentration was below 0.1 Torr (≈ 130 ppm).

As far as the reactions with alkanes are concerned, the most detailed studies have been performed by Penzhorn and co-workers (1973, 1975; Jordan and Penzhorn, 1975; Filby and Penzhorn, 1975) who explained aerosol formation by a mechanism invoking free radicals, as reproduced in Table 11. The first step in the mechanism is probably H-atom abstraction (Badcock et al., 1971; Penzhorn et al., 1973), and not direct SO_2 insertion into the C-H bond as had been suggested earlier (Dainton and Ivin, 1950; Timmons, 1970). There are strong indications that the reaction involves other triplet states in addition to the

Table 10

Estimated photooxidation rate of SO_2 in the atmosphere at sea level, from Penzhorn et al. (1974a).

Solar zenith angle	SO_2 photooxidation rate in $hr^{-1}x10^2$	
	rel.hum. 0%	100%
80	0.016	0.012
70	0.058	0.044
50	0.25	0.19
30	0.52	0.39

Table 11

Interaction of SO_2 with Alkanes.

(from Filby and Penzhorn, 1975)

$$\begin{array}{rcl} \mathrm{SO_2} + h\nu & \rightarrow & {}^3\mathrm{SO_2} \text{ (via several steps)} \\ {}^3\mathrm{SO_2} + \mathrm{RH} & \rightarrow & \mathrm{R} + \mathrm{SO_2H} \\ & & \mathrm{SO_2} + \mathrm{RH} \end{array}$$

a) radical reactions of major importance in product formation

$$\begin{array}{rcl} \mathrm{R} + \mathrm{SO_2} & \rightleftarrows & \mathrm{RSO_2} \ (K_p \approx 10^{3.8} \text{ atm}^{-1}) \\ 2\mathrm{RSO_2} & \rightarrow & \mathrm{RSO} + \mathrm{RSO_3} \\ & \rightarrow & \mathrm{RSO_2SO_2R} \\ 2\mathrm{RSO} & \rightarrow & \mathrm{RSOSOR} \quad \rightarrow \quad \mathrm{RSO_2SR} \\ \mathrm{RSO_2} + \mathrm{SO_2H} & \rightarrow & \mathrm{RSO_2H} + \mathrm{SO_2} \\ \mathrm{RSO_3} + \mathrm{SO_2H} & \rightarrow & \mathrm{RSO_3H} + \mathrm{SO_2} \end{array}$$

b) radical reactions of minor importance in product formation

$$\begin{array}{rcl} \mathrm{RSO} + \mathrm{SO_2H} & \rightarrow & \mathrm{RSOH} + \mathrm{SO_2} \\ 2\mathrm{R} & \rightarrow & \mathrm{R_2} \end{array}$$

$$\left.\begin{array}{l} \mathrm{RSO_2} + \mathrm{RSO_3} \\ \\ \mathrm{RSO_2} + \mathrm{RSO} \end{array}\right\} \rightarrow \begin{array}{l} \text{Sulphinyl and sulphenyl peroxy} \\ \\ \text{and/or anhydric compounds} \end{array}$$

$$\left.\begin{array}{l} \mathrm{RSO} + \mathrm{RH} \\ \mathrm{RSO_2} + \mathrm{RH} \\ \mathrm{RSO_3} + \mathrm{RH} \end{array}\right\} \rightarrow \text{sulphoxy acids} + \mathrm{R}$$

(R = tert-butyl or isobutyl)

phosphorescing $^3B_1$ state (Demerjian and Calvert, 1975; Filby and Penzhorn, 1975), but the contributions of the different triplet states to the reactions cannot be monitored. Jordan and Penzhorn (1975) have indicated that the actual aerosol formation will probably mainly involve heteronucleation, since they observed that the number of particles formed depends on the rate of RSO_XH- formation; as soon as nucleation has started no new nuclei are formed, but the existing nuclei grow to very large sizes (1.5 - 1.9 μm).

As far as the olefins are concerned, it appears that they are very efficient quenchers of the $SO_2(^3B_1)$ emission, probably indicative of a chemical reaction (Wampler et al., 1973; Wampler, 1976a). Sidebottom et al., (1971) suggested an SO_2-olefin π-complex as intermediate in this case. This suggestion was further corroborated by the studies of Demerjian and Calvert (1975), Cox (1973a) and Penzhorn and Filby (1975), on the cis-trans isomerization of 2-butenes. Aerosol formation was noted (Demerjian and Calvert, 1975; Penzhorn and Filby, 1975) but not when the olefin concentration was in an order of magnitude of 1 ppm or less (Renzetti and Doyle, 1960). No detailed product analysis has yet been performed. In the presence of O_2, several oxygenated organic products have been observed (Hirose et al., 1975), again indicating a reaction mechanism involving organic radicals. The reaction between $^3SO_2$ and acetylene and allene has been studied by Luria et al., (1974a, 1974b; Luria and Heicklen, 1974). It was noted that no physical quenching of triplet excited SO_2 occurred, but chemical reaction took place leading to the formation of aerosols of empirical formula C_5H_8SO. No mechanism was proposed for this reaction.

There is only scanty information on the interaction of photoexcited SO_2 with aromatic molecules. Quenching studies of $SO_2(^3B_1)$ phosphorescence indicate very fast reaction rates (Wampler, 1976b). However, no product analyses, or even aerosol formation studies have appeared in the literature. The reaction between SO_2 and thiophene has been studied (Braslavsky and Heicklen, 1972), but this reaction probably involved photosensitization of thiophene via singlet excited SO_2.

Conclusion

Homogeneous photooxidation of electronically excited SO_2 is in principle a viable route of SO_2 transformation in a clean atmosphere. The rate is too small, however, to explain commonly noted rapid oxidation rates in polluted atmospheres. Aerosol formation through interaction with hydrocarbons is possible, but probably insignificant under commonly noted hydrocarbon concentrations prevailing in the atmosphere.

2.3.1.2 Homogeneous gas phase reactions of ground state SO_2

There is an extensive list of publications in which the effect of addition of SO_2 to a mixture of NO_x and hydrocarbons in air has been studied, and conversely, the effect of such a mixture on the oxidation of SO_2, as reviewed by Bufalini (1971). However important mechanistic progress has only recently been achieved and to a large extent this is due to recent reliable measurements of the rates of reaction of SO_2 with the reactive radical species (RO and RO_2, where R = H, alkyl, acyl) present in such systems. We will focus our attention on these new developments in the understanding of the homogeneous oxidation of SO_2.

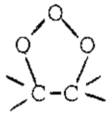
Calvert (1973, 1974), and Calvert and McQuigg (1975), were among the first to quantitatively estimate the rate of homogeneous oxidation of SO_2 by the reactive species that are now presumed to be present in a NO_x-hydrocarbon reaction mixture. Their estimates, updated by recent rate determinations and based on assumptions for the average concentrations of the particular reactive species are shown in Table 12. Recent in situ determinations seem to bear out the correctness for the assumed HO concentration (Wang et al., 1975; Davis et al., 1976; Perner et al., 1976). The HO_2 concentration is based on one measurement of H_2O_2 in the atmosphere, which can only be due to the reaction

$$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$$

(Gay and Bufalini, 1972). The assumed concentrations for CH_3O and CH_3O_2 are those estimated to be present even in clean air on a sunny day (Levy II, 1973; Crutzen, 1974), although it has been suggested that these estimates could be too high since no loss into aerosols was

Table 12

Evaluation of homogeneous oxidation routes of ground state SO_2

Reactant	Concentration ppm	Rate Constant ℓ/mole-sec	Oxidation rate % hr^{-1}	Reference
$O_2(^1\Delta_g)$ (+M)	-	5.7×10^{-5}	0	Penzhorn et al. (1974)
$O(^3P)$ (+M)	10^{-8}	1.1×10^{8}	.014	Atkinson & Pitts (1974) Westenberg & De Haas (1975a)
O_3	-	$< 5 \times 10^{-3}$	0	Davis (1974)
NO_2	-	5.3×10^{-9}	0	Daubendieck and Calvert (1975)
NO_3	-	< 4.2	0	ibid.
N_2O_5	-	$< 2.5 \times 10^{-2}$	0	ibid.
 or $R\dot{C}HOO\cdot$	?	?	$< 0.4 - 3.0$	Cox and Penkett (1972)
HO_2	10^{-4}	1.8×10^{5}	.22	Payne et al. (1973)
HO(+M)	10^{-7}	3×10^{8}	.44	Davis (1974b) Cox(1974) Harris and Wayne (1975) Castleman et al.(1975) Atkinson et al. (1976a)
		[6×10^{8}	.88	Chan et al.(1976b)]
CH_3O_2	2×10^{-5}	$\lesssim 2 \times 10^{6}$	$< .6$	Whitbeck et al. (1976)
CH_3O	10^{-6}	$\sim 2 \times 10^{6}$	$< .1$	Calvert and McQuigg (1975) estimate

assumed (Warneck, 1974).

There is some confusion as to whether the $R\dot{C}HOO.$ radical, presumed to be an important intermediate in the O_3-olefin reaction (O'Neal and Blumstein, 1973; Criegee, 1975), is a reactive species in this regard, as originally proposed by Cox and Penkett (1972). Wilson et al., (1974) have invoked this radical in order to explain the smog chamber experiments involving O_3, olefin and SO_2 of McNelis et al., (1975). They noted that ketene was formed from an ozone + olefin reaction and they propose the following process:

$$R\dot{C}HOO\cdot + R'\text{-}H \rightarrow R = C = O + R'. + H_2O$$

In the presence of SO_2, ketene production was suppressed. Sander and Seinfeld (1976) have also incorporated reactions of this radical intermediate in their model to explain some of the more recent smog chamber studies. However, Calvert and McQuigg (1975) argue that in the atmosphere the biradical will react exclusively with oxygen, leading to RO and RO_2 radicals.

Most other species in Table 12 probably play no role in SO_2 oxidation. Reactions with $O_2(^1\Delta_g)$ Penzhorn et al., 1974b), O_3 (Davis, 1974a), NO_2, NO_3 and N_2O_5 (Daubendieck and Calvert, 1975) are too slow to be of importance. The reaction with $O(^3P)$ atoms will play a role in upper atmospheric chemistry, since it is reasonably fast (Westenberg and De Haas, 1975a), but in the lower troposphere the $O(^3P)$ atoms will react almost exclusively with oxygen to form ozone. It was suggested that this reaction could explain the photochemical oxidation of SO_2 in clean air in the presence of NO_2 (Smith and Urone, 1974; Sander and Seinfeld, 1976) and Friend et al., (1973) suggested that this is the only oxidation reaction of SO_2 in truly clean air. However, Sander and Seinfeld note that the initial inhibition of SO_2 oxidation in the reaction system $SO_2 + NO_2$ + air + light, as noted by Smith and Urone (1974) and Bradstreet (1973), cannot be explained by an initial competition between SO_2 and NO_2 for $O(^3P)$ atoms. This effect cannot be due to the reaction

$$O + SO_3 \rightarrow SO_2 + O_2$$

either, since its rate is too slow (Westenberg and De Haas, 1975b).

To date the products of the important SO_2 + HO reaction have not been examined. Calvert and McQuigg (1975) and Davis and Klauber (1975) have speculated on the mechanism, and their suggestions are shown in Tables 13 and 14 respectively. The salient features of the Calvert and McQuigg mechanism are the proposed formation of organic-sulphur aerosols, and the possiblity of formation of a sulphur acid analog of the notorious peroxy acyl nitrates.

The Davis and Klauber mechanism proposes a new chain-oxidation route for the NO to NO_2 conversion in order to explain the observation of increased ozone concentrations far downwind from a SO_2-NO_x- emitting power plant stack. Altshuller (1974) has argued that the latter effect should be due to other hydrocarbon sources, however, while Calvert (1975a) has questioned the thermodynamic feasibility of the crucial step

$$HSO_4 + O_2 \rightarrow HSO_6$$

Only very little effort has been directed to date to the use of recent data on the homogeneous oxidation of ground state SO_2 in order to explain the varying results of smog chamber studies. Wilson et. al., (1974) computer-simulated the experiments of McNelis et al. (1975), incorporating the $R\dot{C}HOO\cdot$ bi-radical as the main reactive species. Levine and Calvert (1976) were able to explain some of the Battelle smog chamber studies by invoking reactions of HO and HO_2. Graedel (1976) used the Davis and Klauber mechanism to determine its influence on the ultimate ozone formation in polluted atmospheres, and concluded that only marginal effects could be expected. Very recently Sander and Seinfeld (1976) tried to explain some of the recent smog chamber experiments of Smith and Urone (1974), McNelis et al., (1975), Wilson and Levy (1970) and Bradstreet (1973). They concluded that the NO_x-hydrocarbon component of the scheme is adequately explained, but that some important SO_2 oxidation steps are still missing. These authors did not include reactions with CH_3O_2 and CH_3O, however because the relevant kinetic data were not then available. If the recent rate data for the reaction between CH_3O_2 (Whitbeck et al., 1976), shown in Table 12, are correct, then this reaction might actually be the missing link in their overall reaction mechanism. Moreover, it now appears that the rate of HO + SO_2 reaction at atmospheric pressures might be

Table 13

Proposed reactions following the reaction $HO + SO_2 (+M) \longrightarrow HOSO_2 (+M)$
Calvert and McQuigg (1975)

$$\begin{array}{llll}
HOSO_2 & + O_2 & \longrightarrow & HOSO_2O_2 \\
HOSO_2O_2 & + NO & \longrightarrow & HOSO_2O + NO_2 \\
 & + NO_2 & \longrightarrow & HOSO_2O_2NO_2 \quad \text{(peroxysulphuric acid nitrate)} \\
 & + HO_2 & \longrightarrow & H_2SO_5 + O_2 \\
HOSO_2O & + NO & \longrightarrow & HOSO_2ONO \\
 & + NO_2 & \longrightarrow & HOSO_2ONO_2 \\
 & + RH & \longrightarrow & H_2SO_4 + R. \\
 & + >C=C< & \longrightarrow & HOSO_2O\dot{R}H \\
HOSO_2ONO_2 & + H_2O & \longrightarrow & H_2SO_4 + HNO_3 \\
HOSO_2ONO & + H_2O & \longrightarrow & H_2SO_4 + HNO_2 \\
HOSO_2ONO_2 & + h\nu & \longrightarrow & HOSO_2O + NO_2 \\
HOSO_2ONO & + h\nu & \longrightarrow & HOSO_2O + NO
\end{array}$$

$$\left.\begin{array}{l}
H_2SO_4 \\
H_2SO_5 \\
HNO_3 \\
HOSO_2O\dot{R}H
\end{array}\right\} \longrightarrow \text{growing aerosol}$$

Table 14

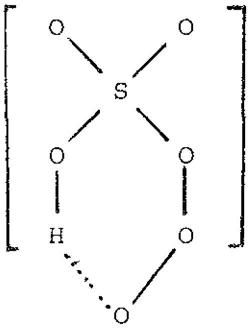
Proposed reactions following the reaction $HO + SO_2(+M) \longrightarrow HOSO_2(+M)$

Davis and Klauber(1975)-mechanism

$HOSO_2 + O_2 \longrightarrow HOSO_2O_2$

$HOSO_2O_2 + NO \longrightarrow HOSO_2O + NO_2$

$HOSO_2O + O_2 \longrightarrow HOSO_2O_3$



$HOSO_2O_3 + NO \longrightarrow HOSO_2O_2 + NO_2$

coupled with:

$NO_2 + h\nu \longrightarrow NO + O(^3P)$

$O(^3P) + O_2(+M) \longrightarrow O_3\ (+M)$

larger by a factor 2 than the value commonly accepted. This follows from the fact that most of the rate determinations for this reaction were determined in competition with

$$HO + CO \rightarrow H + CO_2$$

Recent work (Sie et al., 1976; Cox et al., 1976; Chan et al., 1976b) has shown that the HO + CO reaction is pressure dependent and the newly determined high pressure rate is twice as fast as that in the low pressure region.

Conclusion

Recent work has shown that the homogeneous oxidation of ground state SO_2 is one of the major processes removing SO_2 from NO_x and hydrocarbon polluted atmospheres as well as from clean air. Important rate determinations are only now becoming available, and many potentially important reactions require kinetic and mechanistic analysis. The ultimate fate of the $HOSO_2$ radical is still a matter of speculation. Calvert and McQuigg (1975) claim that all the smog chamber studies to date can be explained by a proper choice of rate constants; however, this would be a sophisticated effort in curve-fitting only, since too many parameters are unknown.

The homogeneous oxidation of ground state SO_2 could potentially be of importance in the northeastern Alberta region. The oil sand plants are expected to emit large amounts of nitrogen oxides in addition to SO_2, while any refinery installation is a source of hydrocarbons in the atmosphere. The importance of this reaction mechanism will probably increase with distance from the plants, since the large amount of particles and high humidity conditions prevailing immediately adjacent to the plants will favor other mechanisms, as will be discussed next.

2.3.1.3 Reactions between SO_2 and NH_3

Recently there has been speculation that the direct interaction between SO_2 and NH_3 might lead to atmospheric removal of SO_2. This reaction, first studied by Döbereiner (1826) results in very low vapor pressure products, and could thus lead to direct particle formation (Scott and Lamb, 1970; Kiang et al., 1973; McLaren et al., 1974;

Scargill, 1971; Haber et al., 1974, Hartley and Matteson, 1975; Landreth et al., 1974, 1975; Birenzvige and Mohnen, 1975; Vance and Peters, 1976a, 1976b). In fact Kiang et al., (1973) reported that the initial product, presumed to be $NH_3 \cdot SO_2$, has a vapor pressure of approximately 10^{-7} Torr at $-70^{\circ}C$ in the presence of trace amounts of water, while NH_3 and SO_2 separately have vapor pressures of 80 and 20 Torr respectively under these conditions. Vance and Peters (1976a, 1976b) found the reaction to be significantly fast at concentrations of 1000 ppm "and much lower", even when traces of water vapor are present, and upon reconsideration of earlier estimates of thermodynamic variables for this reaction, suggest that it could occur under atmospheric conditions. However, their calculations are based on older estimates for thermodynamic constants by Scott and Lamb (1970), and using the two-stage mechanism proposed by Hartley and Matteson (1975):

$$NH_3(g) + SO_2(g) \overset{K_1}{\rightleftarrows} NH_3 \cdot SO_2(g)$$

$$NH_3 \cdot SO_2(g) + NH_3(g) \overset{K_2}{\rightleftarrows} (NH_3.)_2 . SO_2(g)$$

Using the more recent experimentally determined values by Landreth et al., (1975), it can be easily shown that under normal atmospheric concentrations of SO_2 (less than 1 ppm) and NH_3(<< 1ppm), these reactions should be entirely unimportant. This conclusion was also reached by Birenzvige and Mohnen (1975), based on experimental work, and we therefore consider such reactions to be of no consequence for the northeastern Alberta situation. NH_3 does play a role in the atmospheric transformation reactions of SO_2 however, i.e., in the aqueous phase oxidation reactions, to be described next.

2.3.2 Aqueous Phase Oxidation of SO_2

As we have stated earlier, the oxidation of SO_2 in the liquid phase has always been considered to be an important atmospheric process. It appears, however, that kinetic and mechanistic studies of the reaction have not been carried out in detail, although the basic facts are known. There is a bewildering spread in the actual measured oxidation rates, undoubtedly due to the different experimental conditions under which the observations were made. As far as the mechanism is concerned, there is strong evidence that only the sulfite form ($SO_3^=$) of dissolved SO_2 is involved. The oxidation probably involves a chain reaction, but it is not clear whether the reaction is possible in the absence of at least a trace of a metal ion catalyst. This is, of course, not surprising in view of the fact that it is practically impossible to eliminate the presence of trace amounts of metal ions in water (zero concentration is only true insofar as the accuracy of the analytical method will allow one to measure). Nevertheless, we will follow the existing convention and discuss the so-called non-catalyzed oxidation first, and then focus on work in which the catalytic effects of metal ions have been studied. We consider the oxidation in the presence of NH_3 as non-catalytic, since the role of NH_3 is different from that which is normally associated with a catalyst, i.e., NH_3 is only indirectly involved in the oxidation. Under normal atmospheric conditions aqueous phase oxidation will occur in clouds or fogs. Plumes of industrial or power plants form a special case, and we will devote a later section to this subject since actual atmospheric measurements have been made in such plumes.

2.3.2.1 Non-catalyzed aqueous phase oxidation

One of the first considerations in the aqueous phase has to be the form in which dissolved SO_2 exists. It appears from spectroscopic studies (Falk and Giguere, 1958) that very little undissociated sulphurous acid (H_2SO_3) exists and the most abundant species are (hydrated) SO_2, HSO_3^- and $SO_3^=$. The relative amounts of these species depend on the pH of the solution. Below pH = 2 mainly hydrated SO_2 is present, between pH = 2 and pH = 5 mainly HSO_3^-, while above pH = 7 only $SO_3^=$ is found. This is easily derived from the equilibria constants shown in Table 15. Not all these forms of dissolved SO_2 seem to be active in the oxidation itself. It is now generally assumed that most if not all the oxidation involves the sulfite ion ($SO_3^=$). Thus Beilke et al., (1975) noted a decrease of two orders of magnitude in the apparent oxidation rate with a decrease of one pH unit below pH ~ 7.

It seems appropriate to give some attention here to some cloud model studies since this is where in the atmospheric aqueous phase

Table 15

Equilibria of dissolved SO_2, NH_3 and CO_2 in water

(from Scott and Hobbs, 1967, except where noted).

Reaction	$K_{equ.}$	Units	$k_{forward}$
$SO_2(g) + H_2O(\ell) \rightleftharpoons (SO_2.H_2O)$	1.24	M/atm	
$(SO_2.H_2O) \rightleftharpoons HSO_3^- + H^+$	1.7×10^{-2} (a)	M	(3.3×10^{-2} sec^{-1} (b) (3.4×10^{6} sec^{-1} (c)
$(SO_2.H_2O) + OH^{-1} \rightleftharpoons HSO_3^-$	1.26×10^{12}	M^{-1}	2.9×10^{5} M^{-1} sec^{-1} (d)
$HSO_3^- \rightleftharpoons SO_3^= + H^+$	6.24×10^{-8}	M	
$NH_3(g) + H_2O(\ell) \rightleftharpoons (NH_3.H_2O)$	57	M/atm	
$(NH_3.H_2O) \rightleftharpoons NH_4^+ + OH^-$	1.77×10^{-5}	M	
$CO_2(g) + H_2O(\ell) \rightleftharpoons (CO_2.H_2O)$	0.034	M/atm	
$(CO_2.H_2O) \rightleftharpoons H^+ + HCO_3^-$	4.45×10^{-7}	M	
$HCO_3^- \rightleftharpoons H^+ + CO_3^=$	4.68×10^{-11}	M	
$H_2O \rightleftharpoons H^+ + OH^-$	1.008×10^{-14}	M	

(a): from Sillén (1964), Beilke and Lamb (1975)

(b): from Wang and Himmelblau (1964)

(c): from Eigen et al. (1961)

(d): from analogous reaction of CO_2, from Himmelblau and Bobb (1958).

oxidation of SO_2 should take place (for the moment disregarding stack plumes). In their theoretical investigation Scott and Hobbs (1967) assumed that an equilibrium is maintained in atmospheric droplets between gaseous and dissolved SO_2, NH_3 and CO_2 and their associated ions, as shown in Table 15. Based on this assumption one can easily calculate the $SO_3^=$ concentration as a function of the gaseous pressures and pH only. One can then calculate the sulphate formation assuming a first order oxidation rate equation:

$$\frac{d(SO_4^=)}{dt} = k(SO_3^=)$$

Scott and Hobbs, using the experimentally determined rate constant of Van den Heuvel and Mason (1963), found that realistic atmospheric pressures of NH_3($\sim 5 \times 10^{-9}$ atm) would cause a 500 fold increase in the rate of sulphate formation. At reasonable atmospheric abundances of CO_2 ($\sim 3 \times 10^{-4}$ atm; Keeling, 1970) and NH_3 ($\sim 5 \times 10^{-9}$; Beilke and Georgii, 1968) the pH is about 7, while in the absence of NH_3 a pH ~ 5.6 is established from the equilibria of Table 15 and thus Scott and Hobbs' calculations appear to agree with more recent qualitative experiments of Beilke et al., (1975).

Some modifications have been made on the Scott and Hobbs model by McKay (1971) and Miller and De Pena (1972). McKay, in addition to using slightly different values for the equilibria constants, questioned the use of the very qualitative rate constant reported by Van den Heuvel and Mason, and preferred the pH-dependent rate constant for the oxidation step determined by Fuller and Crist (1941), which in practice leads to a 100 fold increase. McKay also observed that the Scott and Hobbs model predicts higher oxidation rates at lower temperatures due to the temperature dependence of the equilibrium constants, even though the actual oxidation rate is slower (McKay assumed an activation energy of 18.3 kcal/mole for the rate constant of this reaction, following Barron and O'Hearn's (1966) value for the copper catalyzed oxidation of SO_2). Miller and De Pena (1972) redetermined the actual oxidation reaction and found a value somewhat comparable to that of Van den Heuvel and Mason (see Table 16). Miller and De Pena suggested that the first dissociation step would actually be rate-determining:

Table 16

Experimental values for first order rate constant of the reaction $SO_3^= + 1/2\ O_2 \longrightarrow SO_4^=$ in the absence of a metal ion catalyst

	k, sec^{-1}
Fuller and Crist (1941), amended by McKay (1971)	$0.013 + 59\ [H^+]^{0.5}$
Van den Heuvel and Mason (1963), calculated by Scott and Hobbs (1967)	0.00167
Miller and De Pena (1972)	0.003
Beilke et al. (1975)	$1.2 \times 10^{-4}\ [H^+]^{-0.16}$

$$SO_2 \cdot H_2O \rightleftarrows HSO_3^- + H^+$$

This was based on the value of $3.2 \times 10^{-2} sec^{-1}$ for the forward reaction, as determined by Wang and Himmelblau (1964). However, this determination is suspect. It is 8 orders of magnitude smaller than that determined earlier by Eigen et al., (1961), and Beilke and Lamb (1975) have reported qualitative evidence to the effect that the value of Wang and Himmelblau is too low by at least a factor 50. More definitive experiments are warranted, however, to unequivocally disregard Miller and De Pena's model, as was noted by Beilke and Lamb. From their semi-quantitative experiments Beilke et al., (1975) conclude that the correct model is that of Scott and Hobbs, using the equilibria constants suggested by McKay and the rate constant for the oxidation step measured by Miller and De Pena. They estimate a removal rate of SO_2 via uncatalyzed oxidation of between ca 10^{-5} and 15% hr^{-1} for pH values between 3 and 6. The important consequence of this estimate is that no oxidation in clouds should be expected, since the pH values in clouds appear to be low, between 3 and 5.6 (Barrie et al., 1975). The latter observation is of interest in itself, since it is not obvious why clouds are so acidic.

Easter and Hobbs (1974) used the basic Scott and Hobbs model in combination with a "wave-cloud" model to estimate if uncatalyzed oxidation is a feasible model to describe worldwide sulphate deposition. They concluded that a residence time of less than 10 minutes of an air parcel containing SO_2(~1 ppb), NH_3(~3 ppb) and CO_2(~10^{-4}) in a cloud is sufficient to result in the necessary sulphate formation. Their calculations also indicate at higher concentrations of SO_2 less sulphate production should be expected, due to the limited buffering capacity of NH_3. The basic weakness of the model of Easter and Hobbs seems to be, however, that it assumes initially neutral clouds (pH~7), whereas actual cloud measurements indicate them to be rather acidic. Moreover, it seems unlikely that pH values of 3 to 5.6 can be attained in this mechanism since the oxidation should be suppressed when enough SO_2 has been oxidized to drop the pH value of the cloud droplets below approximately 6.

Barrie et al., (1975) have extended the Scott and Hobbs model by taking background atmospheric aerosol into consideration, which is assumed to consist in a large part of H_2SO_4. The authors then find that the major function of the SO_2-NH_3 liquid water system is no longer the conversion of SO_2 to sulphate but the conversion of sulphuric acid aerosol and ammonia gas to ammonium sulphate, and thus conclude that uncatalyzed oxidation of SO_2 in clouds is an unimportant process.

The acidity of cloud droplets is explained in a slightly different way by Yue et al., (1976). These authors also used the Scott and Hobbs model, but included a contribution from the homogeneous gas phase oxidation of SO_2. In principle, this is not too different from Barrie et al.'s model, since in practice it also adds an H_2SO_4 term to the set of dissociation equilibria of the Scott and Hobbs model. The difference lies in the fact that Barrie et al., assume all equilibria, including the background aerosol, to be established instantaneously, while in the model of Yue et al., the additional term due to the homogeneous gas phase oxidation of SO_2 is time dependent. Yue et al., assume that the amount of SO_2 not dissolved into the droplets according to the Scott and Hobbs model undergoes homogeneous gas phase oxidation by reaction with HO radicals. Assuming an HO concentration of 10^7 molec/cc and using the rate constant for the $HO + SO_2 + M$ reaction of Castleman et al., (1975) they calculate the amount of oxidized SO_2 in the gas phase and then calculate the rate with which the newly formed particles collide with the aqueous droplets. Of course, such a rate is dependent on the diameter of the aqueous droplets, and the model of Yue et al., therefore predicts that the pH value of the droplets will depend on their actual size: smaller droplets will be more acidic as the reaction proceeds (see Table 17). Considering only the uncatalyzed oxidation of SO_2, the model of Yue et al., is able to explain the acidity of clouds, but in the opinion of the present authors, suffers from the same deficiency as the Easter and Hobbs model in that initially the cloud droplets are supposed to be neutral (and that apparently no H_2SO_4, formed from gas phase oxidation of SO_2, is present in the air parcel which enters a cloud).

It is the present authors' opinion that it is by no means proven that the actual oxidation can occur without the help of a metal

Table 17

Calculated pH value of cloud droplets as function of their size from Yue et al., 1976

Size (cm)	pH[a] A	pH[a] B
10^{-2}	6.1	6.7
10^{-3}	5.5	6.3
10^{-4}	4.5	5.5
10^{-5}	3.5	4.5
10^{-6}	2.5	3.5

A: $[SO_2]$ = 10 ppbv, $[NH_3]$ = 3 ppbv

B: $[SO_2]$ = 1 ppbv, $[NH_3]$ = 3 ppbv

[a] All values calculated assuming 10 minutes oxidation of SO_2 via aqueous and homogeneous gas phase reactions. The cloud is assumed to be at a level of 600 mb and the temperature is 0°C.

ion catalyst. The work of Brimblecombe and Spedding (1974a) has to be mentioned in this regard. These authors argue that in the older studies in "pure" water, oxidation in fact occurs owing to contamination by trace amounts of metal ions. In their studies they calculate an impurity content of ∿5 x 10^{-8}M Fe^{3+} which they consider not unlikely as a trace impurity in carefully deionized water. It might be added that even in very early studies on the catalytic oxidation of SO_2 in water (Titoff, 1903; Reinders and Vles, 1925) it was noted that extremely low concentrations of metal ions had a markedly rate-accelerating effect (in these cases Cu^{2+}, as low as 10^{-12} to 10^{-13} M/1), although it is likely that in these studies trace contaminants in the water used are actually the cause of the observed effects.

With modern analytical methods it should be possible to establish the amount of trace contamination and resolve this question. Only Brimblecombe and Spedding have addressed themselves to this matter, but apparently could not determine a level of 5 x 10^{-8} M/1 Fe^{3+} with the analytical instruments at their disposal.

The mechanism of the actual oxidation step

$$SO_3^= + \frac{1}{2} O_2 \rightarrow SO_4^=$$

could be another indication in this regard, as we will see in a later section.

2.3.2.2 Metal ion catalysis of the aqueous phase oxidation of SO_2

Junge and Ryan (1958) were amongst the first to suggest that trace amounts of metal ions in the atmosphere might exert a strong catalytic influence on the SO_2 oxidation. They found that dilute chloride solutions of Mn^{2+}, Cu^{2+} and Fe^{2+} were the most effective catalysts in decreasing order. However, since their experiments involved bubbling SO_2 through dilute solutions, their results are not directly applicable to the atmospheric conditions of small, liquid droplets since other effects such as mass transfer and mixing, as well as the chemistry involved could influence the rate. Until quite recently most studies were performed at high SO_2 and/or high catalyst concentrations, and therefore are more applicable to plume conditions than to clouds in which case only small, dilute droplets should be expected. Johnstone and Coughanowr (1958) used rather large (0.7 mm diameter) suspended droplets in an SO_2-air mixture and suggested that at high catalyst concentrations the oxidation might occur within a spherical shell at the surface of the drop. This shell becomes thicker as the catalyst concentration decreases, or as the SO_2 concentration at the surface increases, until ultimately the entire drop is involved. The oxidation in such droplets of very high catalyst concentrations or, more properly, deliquescent metal ion-containing particles, has been treated in a detailed theoretical study by Foster (1969).

The essence of Foster's model is as follows. Under high humidity conditions ($\geq$ 95%) catalyst particles are essentially covered by a water film in which absorbed SO_3 promotes dissolution of the catalyst. When SO_2 is absorbed in this layer oxidation occurs, resulting in H_2SO_4 formation. The effect of this will be a slight lowering of the vaporliquid equilibrium around the droplet, which will result in condensation of more water molecules on the droplet, and therefore the formation of H_2SO_4 in the droplet does not initially have a strong acidifying effect. Under these high humidity conditions this process can continue for quite a while, resulting in droplet growth and SO_2 oxidation at moderate rates. At lower relative humidity conditions however the rate of condensation of water is less, the droplets become more acid as H_2SO_4 builds up and the rate of oxidation will be slower due to the higher acidity of the droplets. Moreover, at high acid concentrations in the droplet, part of the catalyst could form stable complexes with H_2SO_4, thus decreasing its effectiveness. In quantifying this model Foster was able to calculate rates of SO_2 oxidation in plumes catalyzed by Mn^{2+} and Fe^{3+} and the values so obtained were qualitatively in agreement with those measured directly by Gartrell et al., (1963). However, since Gartrell et al.'s data are not considered to be very accurate, this result should not be construed as evidence for the soundness of the model.

Matteson et al., (1969) considered the kinetics of the oxidation mechanism using deliquescent $MnSO_4$ particles as catalysts. Their mechanism, shown in Table 18, suggests complex formation between Mn^{++} ions and dissolved SO_2. From theoretical consideration they

Table 18

Mechanism of Mn^{2+} catalyzed oxidation of SO_2 in solution

from Matteson et al. (1969)

$$SO_2 + Mn^{2+} \rightleftharpoons (Mn.SO_2)^{2+}$$

$$2(Mn.SO_2)^{2+} + O_2 \rightleftharpoons \left[(Mn.SO_2)_2^{2+} \cdot O_2\right] \rightleftharpoons 2(Mn.SO_3)^{2+}$$

$$(Mn.SO_3)^{2+} + H_2O \rightleftharpoons Mn^{2+} + HSO_4^- + H^+$$

$$HSO_4^- + H^+ \rightleftharpoons H_2SO_4$$

The second step should be rate-determining.

concluded that the rate of the reaction depends on the square of the initial aqueous Mn^{++} concentration as assumed by Foster. This dependence is in agreement with the experimental observations of Johnstone and Coughanowr (1958), although extrapolation to lower concentrations of catalyst is necessary. Matteson et al., also found that almost no sulphate is formed when the relative humidity is less than 95% and assumed this to be due to insufficient hydration of the aerosol.

Cheng et al., (1971) found the following order of catalytic efficiency: $MnSO_4 > MnCl_2 > CuSO_4 > NaCl$ and also noted that NaCl aerosols at relative humidities of 36-60% would only very slowly oxidize SO_2, whereas the rate rapidly increased at relative humidities above 80%. Following Matteson's suggestion, this is probably related to the fact that in the former case the NaCl particles can be considered to be dry, covered with adsorbed H_2O molecules, and thus true aqueous phase oxidation might be unimportant, while the latter case is a deliquescent salt particle, and thus a concentrated solution.

Barron and coworkers studied the reaction kinetics of the oxidation in dilute solution catalyzed by copper (Barron and O'Hearn, 1966) and cobalt (Chen and Barron, 1972) ions. They found the reaction to be zero order in oxygen, 3/2 order in $SO_3^=$ concentration, and 1/2 order with respect to catalyst concentration. For the actual oxidation they favor a chain mechanism adapted from Backstrom (1934) as we will see in the next section.

Brimblecombe and Spedding (1974a) studied the oxidation in solution using very low concentrations of SO_2 (10^{-5} M) and Fe^{3+} (10^{-6} M), and even under these conditions found the rate to be extremely sensitive to the presence of the catalyst.

Freiberg (1974, 1975) has deduced a rate expression for the iron catalyzed oxidation of SO_2 in aqueous droplets. Considering several equilibrium equations he determined an expression which explains the strong effect of relative humidity and pH on the rate. An increase in relative humidity only increases the pH of the solution according to this model which leads to the following dependence for the rate of oxidation:

$$\frac{d(SO_2)}{dt} \propto \frac{1}{(1\text{-rel.hum})^3\ (H^+)^3}$$

Freiberg's data indicate moreover that a substantial negative temperature effect on the rate constant of the reaction, is to be expected owing to the fact that at lower temperature increased dissolution of SO_2 and dissociation into $SO_3^=$ (see Table 29) more than offsets the decrease in the rate of Fe^{3+} catalyzed oxidation rate of $SO_3^=$. Freiberg (1975) also notes that the Fe^{3+} ion is the actual catalyst, and that if Fe^{2+} is present it must be first oxidized to Fe^{3+} in order to initiate the SO_2 oxidation.

Very recently Barrie and Georgii (1976) studied the absorption of SO_2 in small water drops containing low concentrations of metal ions. Mn^{2+} and Fe^{3+} ions exhibited markedly different reactivities and no rate enhancement was observed in the presence of Cu^{2+} ions in acidic water droplets ($pH \sim 4$). This observation agrees with the work of Bracewell and Gall (1967) who noted that 10^{-5} solutions of Cu^{2+} oxidized SO_2 100 times slower than $10^{-5}M$ Mn^{2+} solutions at $pH \simeq 4.5$, but not with that of Junge and Ryan (1958) who in effect found that Cu^{2+} ions enhanced the rate of oxidation of SO_2 by 50% compared to Mn^{2+} ions at $pH < 4$. The results of Barron and O'Hearn (1966) are not directly comparable since they worked with neutral, unbuffered Cu^{2+} solutions.

Some other interesting observations of Barrie and Georgii should be mentioned here:

- a decrease in the Mn^{2+} catalyzed oxidation of SO_2 by a factor 5 to 10 by lowering the reaction temperature from 25° to $8^\circ C$ was noted. If indeed Barrie and Georgii measured the actual oxidation rate as they claimed (in fact they determined the absorption rate of SO_2 by the droplets as function of time), then this catalyzed reaction must feature a very high activation energy since the equilibrium concentration of $SO_3^=$ should be larger at lower temperature (McKay, 1971).
- a synergistic catalytic effect was noted upon mixing Mn^{2+} and Fe^{3+} ions, i.e., a larger oxidation rate was noticed than could be expected from the sum of the oxidation rates by Mn^{2+} and Fe^{3+} only. In this case moreover, a much smaller temperature effect was observed. Barrie and Georgii suggest that Fe^{3+} ions promote the catalytic ability of Mn^{2+}, and that the overall mechanism of the oxidation might be different.

- the absorption of SO_2 in Mn^{2+}-containing droplets is found to take place in two distinct phases: initially the absorption is rapid, but after a few minutes the rate slows down, and becomes almost zero. The authors suggest that the initial rapid rate involves the formation and build-up of an $SO_3^{=}$-Mn^{2+} complex as suggested by Schmittkunz (1963) and when the Mn^{2+} ions are depleted SO_2 oxidation takes place. The fact that in 10^{-4}M $MnCl_2$ solution the turning point occurs when approximately 3 x 10^{-4}M SO_2 is absorbed, is taken as evidence for a 1:3 catalyzing complex. No explanation is given, however, for the fact that a rapid initial uptake of SO_2 still takes place over the same time interval even when the droplets do not contain a catalyst.

2.3.2.3 Mechanism of the aqueous phase oxidation of SO_2

The oxidation of SO_2 in the aqueous phase is basically thought to involve the following chain mechanism, adapted from Backstrom (1934):

$$SO_3^{\dot{-}} + O_2 \rightarrow SO_5^{\dot{-}}$$

$$SO_5^{\dot{-}} + SO_3^{=} \rightarrow SO_4^{\dot{-}} + SO_4^{-}$$

$$SO_4^{\dot{-}} + SO_3^{=} \rightarrow SO_3^{\dot{-}} + SO_4^{=}$$

or alternatively,

$$SO_5^{\dot{-}} + SO_3^{-} \rightarrow SO_3^{\dot{-}} + SO_5^{=}$$

$$SO_5^{=} + SO_3^{=} \rightarrow 2SO_4^{=}$$

The presence of these radical ions seems very well established from spectroscopic observations (Hayon et al., 1972; Schmittkunz, 1963(?)). Moreover, it appears that $SO_5^{\dot{-}}$ is much more abundant than $SO_3^{\dot{-}}$, and thus the reactions of this species are presumed to be rate limiting (Hayon et al., 1972; Chen and Barron, 1972) in this chain mechanism. However, since the rate of oxidation is dependent on the nature of the catalyst the actual initiation reaction to form the $SO_3^{\dot{-}}$ species is overall rate limiting.

There is less agreement in the literature concerning the nature of the initiation reaction of this chain mechanism. It should be noted that all initiation reactions suggested involve metal ions. Indeed, it is not at all obvious how the radical ion could be formed otherwise; this fact might be construed as an argument for the non-occurrence of the aqueous phase oxidation of SO_2 in the absence of a metal ion catalyst. The only reference to a mechanism for the uncatalyzed process the present authors are aware of is from Basset and co-workers (Basset and Henry, 1935; Basset and Parker, 1951) who conclude that the reaction should proceed via ionic complexes such as $(O_2 \cdot SO_3)^{2-}$ and $(O_2 \cdot S_2O_5)^{2-}$. Similar types of complexes were suggested for the Mn^{2+} ion catalyzed reaction, as was later discussed by Matteson et al., (1969), (cf. Table 18). However, in these studies self oxidation and reduction of the complex was proposed and the $SO_3^{\dot{-}}$ chain mechanism was not invoked.

Several authors have suggested a direct redox reaction between the metal ion $Me^{(n)+}$ and the $SO_3^{=}$ species, following the original suggestion of Backstrom (1934):

$$SO_3^{=} + Me^{(n)+} \rightarrow SO_3^{\dot{-}} + Me^{(n-1)+}$$

Thus Barron and O'Hearn (1966) proposed this initiation for the Cu^{2+} catalyzed reaction, Chen and Barron (1972) invoke $Co(H_2O)_6^{3+}$ as initiator, while Brimblecombe and Spedding (1974a) suggest the FeOOH species (these authors reason that hydroxylated Fe^{3+}, FeOOH, appears to be a better oxidizing agent than Fe^{3+}, since it has a higher redox potential (0.908 V) than Fe^{3+} itself (0.77 V), and moreover a pH in the range 4 to 5 tends to favor formation of the FeOOH species).

Brimblecombe and Spedding also note that part of the $SO_3^{\dot{-}}$ could be effective in regenerating Fe^{3+} from Fe^{2+}. They visualize the following reactions:

$$SO_3^{=} + FeOOH + 3H^+ \rightarrow Fe^{2+} + 2H_2O + SO_3^{\dot{-}}$$

$$SO_3^{\dot{-}} + Fe^{2+} \rightarrow SO_3^{=} + Fe^{3+}$$

Barrie and Georgii (1976) favor the somewhat more elaborate initiation mechanism proposed by Schmittkunz (1963) which is shown in Table 19. It may be seen that in this mechanism three $SO_3^{=}$ ions are required per metal ion to build up the catalyst-complex; Barrie and Georgii have

Table 19

Mechanism of the metal ion-catalyzed oxidation of SO_2 in solution

from Schmittkunz (1963)

a. Catalysis

$$(Me^{+x}\ Y)^{-(6-x)}\ (*) + O_2 \longrightarrow (Me^{+x}\ Y)^{-(5-x)} + O_2^-$$

$$O_2^- + H^+ \longrightarrow O_2H$$

$$(Me^{+x}\ Y)^{-(5-x)} + SO_3^= \longrightarrow (Me^{+x}\ Y)^{-(6-x)} + SO_3^{\overline{\cdot}}$$

b. SO_3^- chain

$$SO_3^{\overline{\cdot}} + O_2 \longrightarrow SO_5^{\overline{\cdot}}$$

$$SO_5^{\overline{\cdot}} + SO_3^= \longrightarrow SO_4^= + SO_4^{\overline{\cdot}}$$

$$SO_4^{\overline{\cdot}} + SO_3^= \longrightarrow SO_3^{\overline{\cdot}} + SO_4^=$$

c. O_2H chain

$$O_2H + SO_3^= \longrightarrow SO_4^= + OH$$

$$OH + SO_3^= \longrightarrow SO_4^= + H$$

$$H + O_2 \longrightarrow O_2H$$

(*) Me^{+x}: metal ion of valence x

Y: $(SO_3^=)_3$ or $(HSO_3^-)_3$

found some evidence for the involvement of three $SO_3^=$ ions as discussed earlier.

Finally, it should be mentioned that the only termination of the $SO_3^{\dot{-}}$ chain that has been suggested to be important is the reaction:

$$SO_5^{\dot{-}} + SO_5^{\dot{-}} \rightarrow \text{inert products.}$$

(Chen and Barron, 1972). Chain termination involving the $SO_3^{\dot{-}}$ species is thought to be unimportant since it reacts much more efficiently with $SO_3^=$ than does $SO_5^{\dot{-}}$, and thus its concentration is very low compared to that of $SO_5^{\dot{-}}$.

2.3.2.4 Aqueous oxidation of SO_2 by other oxidizing species

The effects of some other oxidizing species such as ozone on the oxidation of dissolved SO_2 have been reported. Penkett (1972) used ozone in the range of 3 to 5 x 10^{-6}M in solution and found the oxidation, which he ascribes to bisulfite (HSO_3^-), and not sulfite ($SO_3^=$), to be first order with respect to ozone, and rather fast. In fact, extrapolating his results to typical cloud conditions (10^oC, pH = 5, ~ 1 g/m^3 liquid water content) he determines an oxidation rate of about 0.21%/minute, assuming 7 ppb SO_2 and 50 ppb O_3. The rates of oxidation of SO_2 by O_3 in a fog chamber reported by Penkett and Garland (1974) agree with Penkett's earlier calculations. These data are shown in Table 20.

Barrie (1975) has argued that the Penkett and Garland experiments could equally well be explained by invoking the $SO_3^=$ ion instead of the HSO_3^- ion. This would, in fact, increase the pH dependence of the oxidation rate as shown in Table 20, thus decreasing the efficiency of this oxidation mechanism at lower pH values. Barrie also reported the interesting but not explained observation that the presence of O_3 increased the catalytic effect of Mn^{2+} ions in droplets, while NO_2 seemed to have an inhibiting effect in this regard.

There seem to be no further studies on the effect of other oxidizing reagents on the solution oxidation rate of SO_2. Brimblecombe and Spedding (1974b) noted that traces of H_2O_2 remarkably increased the rate of SO_2 uptake in solution, but they did not indicate if this

Table 20

Rate of Oxidation of SO_2 in solution by dissolved O_3 as function of pH from Penkett and Garland (1974)

pH	$R(O_3)^a$ ppm/min	$R(O_2)^b$ ppm/min	$R(O_3)$measured ppm/min
4	2.1×10^{-6}	7.3×10^{-8}	
5	2.1×10^{-5}	2.5×10^{-7}	
6	2.1×10^{-4}	9.1×10^{-5}	$(2.4 \pm 1.0) \times 10^{-4}$
7	2.1×10^{-3}	4.2×10^{-3}	

a: at $[O_3] = 0.05$ ppm

b: at $[O_2] = 2 \times 10^5$ ppm

actually means an increase in the SO_2 oxidation rate. Lobova et al., (1973) noted that highly concentrated solutions of nitric acid rapidly oxidize SO_2, but it is highly unlikely that such a mechanism is important in the atmosphere since the high vapor pressure of nitric acid will prevent the formation of concentrated HNO_3 aerosol droplets.

Conclusion

It appears that aqueous phase oxidation of SO_2 is a viable atmospheric process. However, as stated earlier, we feel that the presence of metal ions or ozone as catalysts is a prerequisite for such reactions.

Some of the major experimental and theoretical studies discussed in this section are summarized in Table 21. In spite of the widely diverging results and theories it can be concluded that the reactions are highly sensitive to several parameters such as pH, relative humidity, temperature, type and concentration of catalyst. These factors would make the actual atmospheric oxidation of SO_2 highly dependent on existing ambient conditions. Some typical rates in clouds were estimated by Barrie (1975), using concentrations of Mn^{2+} of $\sim 10^{-6}$M/1 and Fe^{3+} of $\sim 10^{-5}$M/1, estimated from aerosol measurements by Jost (1974) in clean Swiss mountain air. Barrie's estimates are shown in Table 22. The present authors are not aware of data on the presence or abundance of such ions in Alberta air.

2.3.3 Heterogeneous Oxidation of SO_2 by "Dry" Particulates

Most of the studies considering dry catalysts in the oxidation of SO_2 have been concerned with the commercial production of sulphuric acid (Duecker and West, 1959) and are of little relevance here because SO_2 concentrations are generally orders of magnitude larger in such processes. In fact, the Fort McMurray stack plumes are expected to be rich in water vapor, and thus dry particulates will probably play a minor role in the overall transformation chemistry of atmospheric SO_2. For completeness however we will briefly discuss some of the facets of these reactions.

Judeikis and Siegel (1973) have estimated that in order for

Table 21

Summary of major aqueous phase SO_2 oxidation studies

adapted from Levy et al., 1976

Author	Type of Mechanism	Rate coefficient and/or equation	Comments
Fuller and Crist (1941)	Sulphite oxidation by O_2 without catalyst	$-\frac{d[O_2]}{dt} = k[SO_3^{2-}]$ $k = 0.013 + 6.6\ [H^+]^{0.5}$	25°C; Rate coefficient later corrected by McKay (1971) suggests very long chain reaction.
Basset and Parker (1951)	Sulphurous acid oxidation by metal salts and O_2	-	Uncatalyzed: formation of $[O_2 \cdot SO_3]^{2-}$, catalyzed: formation of $[O_2 \cdot Mn(SO_3)_2]^{2-}$
Junge and Ryan (1958)	SO_2 oxidation with or without metal ions and with or without NH_3	conversion rate $\sim 1.8 \times 10^{-4}\%\ min^{-1}$	No oxidation in absence of Fe and NH_3; establishes catalyti efficiency of metal chlorides $Mn^{2+} > Cu^{2+} > Fe^{2+}$
Van den Heuvel & Mason (1963)	SO_2 oxidation in presence of NH_3	conversion rate $\sim 2.5\%\ min^{-1}$	Extrapolation to atmospheric conditions for conversion rat
Barron and O'Hern (1966)	Sulphite oxidation in presence of Cu^{2+}	$-\frac{d[O_2]}{dt} = k[Cu^{2+}]^{0.5}[SO_3^{2-}]^{1.5}$ $k \sim 1200$ l/mole-sec	Rapid mixing method. Noticed slight inhibiting effect of C Water purified to better than 10^{-7} M/l ions.

Table 21 Continued - 2

Author	Type of Mechanism	Rate coefficient and/or equation	Comments
Scott and Hobbs (1967)	SO_2 oxidation in presence of NH_3	$d[SO_4^=] = k\ [SO_3^=]$ $k = 0.0017\ sec^{-1}$	25°C; k estimated from Van den Heuvel and Mason. Theoretical model.
Matteson et al. (1969)	SO_2 oxidation catalyzed by metal salts.	$-\frac{d[SO_2]}{dt} = k\ [Mn^{2+}]_0^2$ $k = 2.4 \times 10^5$ l/mole sec	Negligible $SO_4^=$ formation at rel.hum. <95%. Suggested mechanism might be applicable for catalysis by other metal salts.
Foster (1969)	SO_2 oxidation catalyzed by metal salts.	SO_2 conversion rate: 0.09% min^{-1} for Mn^{2+} 0.15 to 1.5% min^{-1} for Fe^{3+}	Theoretical study; rates depend on many factors; Fe^{3+} catalyzed oxidation is pH dependent.
McKay (1971)	SO_2 oxidation in presence of NH_3	$\frac{d[SO_4^=]}{dt} = k\ [SO_3^=]$ $k = 0.013 + 59\ [H^+]^{0.5}$	Theoretical study; k adapted from Fuller and Crist. Suggests large negative temperature effect on overall reaction.
Cheng et al. (1971)	SO_2 oxidation catalyzed by metal salts.	SO_2 conversion rates: ~0.03% min^{-1} with Mn^{2+} levels typical of urban industrial air ~.33% min^{-1} with Mn^{2+} levels typical of coal fired power plant plume.	Oxidation rates estimated through extrapolation. Note strong difference if H_2O is adsorbed on salt particle, or the salt is deliquescent.
Miller and De Pena (1972)	SO_2 oxidation in presence of NH_3	$d[SO_4^=] = k\ [SO_3^=]$ $k \sim .003\ sec^{-1}$ at 25°C	k estimated by fit of experimental data to theoretical curves. Suggests SO_2 dissolution might be rate limiting, based on rate constants that are probably wrong. (Beilke and Lamb, 1975).

Table 21 Continued - 3

Author	Type of Mechanism	Rate co-efficient and/or equation	Comments
Penkett (1972)	Sulphite oxidation by O_3	$-\frac{d[O_3]}{dt} = k\ [O_3][HSO_3^-]$ $k = 3.32 \times 10^5$ l/mole-sec	9.6°C; SO_2 oxidation rate extrapolated to atmospheric conditions. Rate much larger than Scott and Hobbs.
Chen and Barron (1972)	Sulphite oxidation catalyzed by cobalt ions.	$-\frac{d[O_2]}{dt} = k[CO(H_2O)_6^{3+}]^{0.5}[SO_3^=]^{1.5}$	No specific value for k determined. Suggests free radical mechanism; reduction of Co(III) is initiation reaction.
Brimblecome & Spedding (1974a)	SO_2 oxidation catalyzed by Fe^{3+} ions.	$-\frac{d[S(IV)]}{dt} = k[Fe(III)][S(IV)]$ k = 100 l/mole sec	FeOOH is actual catalyst. Suggests trace amounts of Fe^{3+} might be responsible for uncatalyzed oxidation.
Easter and Hobbs (1974)	SO_2 oxidation in presence of NH_3	same as Scott and Hobbs (1967)	Wave-cloud model. Suggests that significant oxidation can occur. Assumes clouds to be initially neutral. Oxidation decreases if SO_2 concentration rises above 10 ppb, due to limited buffering of 3 ppb NH_3
Freiberg (1974)	SO_2 oxidation catalyzed by Fe^{3+} ions	$\frac{d[SO_4^=]}{dt} = \frac{k_o k_s^2 [H_2SO_3]^2 [Fe^{3+}]}{[H^+]^3}$ k_s: 1st dissociation constant of H_2SO_3	Rate increases rapidly with rel. humidity and decreases by about one order of magnitude with 5°C increase in temperature.

Table 21 Continued - 4

Author	Type of Mechanism	Rate coefficient and/or equation	Comments
Penkett and Garland (1974)	SO_2 oxidation by O_3	$-\frac{d[SO_2]}{dt} = k[SO_3^=]$ $k = 4.18 \times 10^{-4} + 1.77[H^+]^{0.5}$ sec^{-1}	Fog chamber experiment. pH = 6 (5.6?) Compares rate with estimations of Penkett (1972) for actual atmosphere.
Beilke et al. (1975)	SO_2 oxidation in presence of NH_3	$\frac{d[SO_4^=]}{dt} = Q.P_{SO_2}$ Q: function of equilibria constants, pH, and k_o, with $\frac{d[SO_4^=]}{dt} = k_o[SO_3^=]$, $k_o \sim 1.2 \times 10^{-4}[H^+]^{-0.16}$ or $\frac{d[SO_4^=]}{dt} = k_o[SO_3^=]^{1.08}$, $k_o = 2 \times 10^{-3}$	Experimental study. Suggests that model of Scott and Hobbs is correct with slight changes in equilibria constants from McKay and rate constant from Miller and De Pena. Removal rate strongly pH dependent, between 10^{-5} and 15% hr^{-1} for pH between 3 and 6.
Yue et al. (1976)	SO_2 oxidation in presence of NH_3	$\frac{d[SO_4^=]}{dt} = k\ [SO_3^=]$ k from Scott and Hobbs, McKay or Miller and De Pena $[SO_3^=]$ depends on equilibria as in Scott and Hobbs + term related to homogeneous gas-phase oxidation of SO_2, following Castleman et al. (1975).	Theoretical study; incorporates collision of H_2SO_4 molecules, formed through homogeneous gas-phase oxidation of SO_2, with water droplets; suggests lower pH values for the drops as function of their diameter.

Table 21 Continued - 5

Author	Type of Mechanism	Rate coefficient and/or equation		Comments
Barrie and Georgii (1976)	SO_2 oxidation catalyzed by metal ions.	$\frac{d[SO_4^=]}{dt} = k[SO_3^=]$		Experimental study; finds evidence for Schmittkunz radical mechanism. Mixture of realistic concentrations of Fe^{3+} and Mn^{2+} is efficient catalyst for SO_2 oxidation even at pH 3 to 4, and low termperature. Suggests that this can explain oxidation in clouds.
		solution	$k[sec^{-1}, 25°C]$	
		$10^{-4}M\ MnCl_2 + 10^{-4}M\ FeCl_2$	140×10^2	
		$10^{-4}M\ MnCl_2$	9.4×10^2	
		$10^{-4}M\ FeCl_2$	5.8×10^2	
		$[SO_3^=]$ depends on pH		

this interaction to be competitive with solution phase oxidation, approximately 1 in 100 gas particle collisions have to lead to reaction. The possible importance of these reactions has been evaluated in a few studies, and it appears that physical processes play a dominant role.

In their study on the interaction of SO_2 with Fe_2O_3 Chun and Quon (1973) indicate that the overall reaction is limited by the amount of active sites on the particles. In the actual oxidation the authors propose the following 5 elementary steps:

1. chemisorption of oxygen on the surface of the particles;
2. diffusion of SO_2 to the surface;
3. reaction between adsorbed SO_2 and chemisorbed O_2;
4. hydration of the resulting SO_3 to form H_2SO_4;
5. partial dissolution of the oxide in H_2SO_4.

The third step would be rate-controlling, in agreement with Corn and Cheng's (1972) suggestion that adsorption of SO_2 is fast, compared to actual oxidation. At relatively low SO_2 concentrations, SO_2 might actually chemisorb on the particle surface, and not be oxidized at all (Smith et al., 1969). Burke et al., (1973) also note that much of the SO_2 loss by interaction with solid particles actually does not lead to oxidation since at later stages SO_2 seems to be released from the particles. These authors moreover indicate that organic material on the particles promotes SO_2 uptake, but only the "cleanest" particles lead to oxidation.

Urone et al., (1968) reported that $CaCO_3$, V_2O_5 and Cr_2O_3 particles are inert with respect to SO_2 oxidation, while oxides of Pb, Fe, Mn, Ca and Al/Ca rapidly take up O_2. As far as CaO is concerned, it might be mentioned that the equilibrium

$$CaO(s) + SO_2(g) + \frac{1}{2}\, O_2(g) \leftrightarrows CaSO_4(s)$$

which is used in flue gas emission control of SO_2 by dry injection of CaO at elevated temperatures is shifted strongly to the right at atmospheric temperatures (Reid, 1970). However, the reaction rate is extremely slow since a large activation energy is apparently involved and the temperature must be such that an optimum balance between a sufficiently high rate for the forward reaction and the desired

Table 22

Expected oxidation rates in clouds, due to particulates from Barrie (1975)

	T (°C)	SO_2 (in ppb)	Mn^{2+} (M/l)	Fe^{2+} (M/l)	$-R_{SO_2}$ (% hr^{-1})
Urban cloud	25	500	10^{-5}	10^{-5}	1
	25	500	10^{-5}	-	0.3
	8	500	10^{-5}	10^{-5}	1
	8	500	10^{-5}	-	0.03
Country air cloud	25	10	10^{-6}	10^{-5}	.75
	8	10	10^{-6}	10^{-5}	.25

Cloud conditions: 0.1 g/m^3 H_2O, pH $\tilde{\sim}$ 3.5, no O_3 present.

equilibrium concentration of $CaSO_4$ can be obtained (Murthi et al., 1971).

The adsorption and conversion of SO_2 on CaO and MgO has also been studied by Low et al., (1971) and Goodsel et al., (1972). Infra red analysis of adsorbed SO_2 indicated that sulfites are initially produced on the surface and then can be oxidized to sulphates upon heating. Lin and Lunsford (1975) also studied the $MgO-SO_2$ system by spectroscopic means (ESR and IR) and found evidence for heterogeneous oxidation on the MgO particles. They identified $SO_3^=$ ions and nonodentate sulfite complexes on the particle surfaces, and suggest that water, absorbed with SO_2, increases the concentration of these ions on the surface thus promoting the conversion rate.

As far as carbon (soot) particles are concerned, Novakov et al., (1974) have presented qualitative evidence to the effect that such particles might be strong catalysts for the oxidation of SO_2 in the atmosphere. High humidity was claimed to lead to more sulphate formation, but no rate data were presented. Corn and Cheng (1971) studied catalysis by activated charcoal. Some conversion rates are given, but it is not clear if the SO_2 oxidation in their experiments actually involved catalysis on the surface of the particles.

Conclusion

It appears from the available data that reactions between SO_2 and solid particles in the atmosphere most likely will not lead to appreciable SO_2 oxidation, but mainly to chemi- or adsorption of SO_2 on the particle surface. Equilibrium considerations as shown for the case of CaO are probably equally applicable for other metal oxides. Since a water film seems to be a prerequisite for catalyzed SO_2 oxidation, it appears not certain whether heterogeneous oxidation is actually occurring, or whether in fact one is dealing with aqueous phase oxidation in a highly concentrated solution of the catalyst. Table 23 summarizes pertinent information from some of the above studies.

Table 23

Summary of studies on heterogeneous oxidation of SO_2 on dry particles

Study	Reaction system	Comments
Urone et al. (1968)	SO_2 (8-14 ppm), particulates (16-30 mg)	Measured tentative conversion rates: $CaCO_3$, Cr_2O_3, V_2O_5, NaCl, Al_2O_3: $< .01\%\ min^{-1}$ CaO, Al_2O_3/CaO, PbO, PbO_2, Fe_3O_4, Fe_2O_3: $> 2\%\ min^{-1}$
Smith et al. (1969)	SO_2 sorption on Fe_3O_4, Al_2O_3, platinum, particle size 0.01 - 0.1 µm	Develops sorption isotherms using the $^{35}SO_2$ technique.
Low et al. (1971), Goodsel et al. (1972)	Adsorption of SO_2 on CaO and MnO	IR study. Identifies sulphites on particle surfaces. Oxidation upon heating observed.
Corn and Cheng (1972)	Adsorption of SO_2 by activated charcoal, Fe_2O_3, MnO_2 (on Teflon beads), monitoring SO_2 effluent flow	With activated charcoal: steady-state rate of conversion/adsorption: .013 µg SO_2/min/mg charcoal (SO_2 = 8 ppm) .021 µg SO_2/min/mg charcoal (SO_2 = 14.4 ppm) With oxides: physical adsorption; fast with Fe_2O_3; $CaCO_3$, V_2O_5, flyash: inert
Chun and Quon (1973)	SO_2(4.7-18.8 ppm) through filter containing Fe_2O_3 particles. Rel. hum. 50-94%	"Capacity limited heterogeneous reaction" oxidation capacity of Fe_2O_3: 62.6 µg/mg Fe_2O_3 rate constant for heterogeneous reaction: $9.4 \times 10^{-3}\ ppm^{-1}\ min^{-1}$
Burke et al. (1973)	SO_2 through column of particles, collected from the atmosphere.	Reversible sorption is major process (30-40% recoverable). Organic contamination promotes sorption, but inhibits oxidation.

Table 23 Continued

Study	Reaction system	Comments
Novakov et al. (1974)	SO_2 with soot particles (through mixing hydrocarbon flame with SO_2)	ESCA study of particles formed. Identifies sulphate and sulphide. Increase in SO_2 or rel. hum. increases sulphate level.
Lin and Lunsford (1975)	SO_2 (25 torr) over MgO and $Mg(OH)_2$	EPR and IR spectra obtained. Identifies sulphite and monodentate sulphite. Heterogeneous oxidation shown to occur.

2.3.4 Plume Studies

At first thought it would appear that a very straightforward way to obtain actual SO_2 oxidation rates would be by direct measurements in stack plumes. Several laboratories have been involved in such studies, but apparently with very little success mainly because several additional factors originating from meteorological variables and therefore essentially noncontrollable, come into play. Moreover, such studies are very difficult to carry out. In a recent critical review Wilson (1976) apparently concludes that all studies published to date should be considered as questionable for one reason or another. Nevertheless important general observations have been made. Some of the major studies of the last 15 years are summarized in Table 24 and Table 25 lists some observed oxidation rates. Very recently SO_2 oxidation in plumes, including many aspects that have been discussed in earlier sections of this chapter have been reviewed by Levy et al., (1976).

The original study by Gartrell et al., (1963) has been used by several authors as a test for proposed theoretical models of atmospheric oxidation of SO_2. This is at least questionable in view of Gartrell et al.'s own observation that "these limited data do not provide a basis for an accurate estimate of the absolute rate of SO_2 oxidation after emission". The important qualitative observation from this study is the low oxidation rate at low relative humidity, (~1 to 3% hr^{-1}) compared to a very high rate at high relative humidity (~30% hr^{-1}).

Newman et al., (1975a,b) used a single-engine aircraft to fly through the plume and employed specially designed high volume samplers for collecting and measuring sulphate and absorption scrubbers to collect SO_2 which was then analyzed isotopically. This technique is based on measurement of the ratio of the two most abundant isotopes of sulphur, $^{32}S/^{34}S$ which "fingerprints" the origin of the sulphur. Newman et al., found that the oxidation rates in plumes of an oil-fired plant were larger than in those from a coal-fired plant. It is entirely possible, however, that this difference is due to different particulate control. In fact, Newman et al., suggest that the low particle content at the coal-fired plant is the major reason for the low oxidation rate. They also suggest that indigenous vanadium could be a potential catalyst at

Table 24

Summary of SO_2 oxidation in stack plumes

(from Levy et al., 1976)

Study	Species measured	Comments
Gartrell, 1963	SO_2, SO_3	Highly variable oxidation rates, positive correlation with humidity.
Dennis et al., 1969	SO_2 relative to SF_6	SO_2 half life from 1.0 to 2.8 hours.
Coutant et al., 1972	SO_2	Laboratory simulation, various fuels, SO_2 loss highly dependent on humidity.
Stephens and McCaldin, 1971	SO_2 relative to submicron aerosol	Oxidation rate dependent on humidity.
Weber, 1970	SO_2 relative to CO_2	Increasing oxidation rate with increasing humidity.
Newman et al. (1975,a, b)	^{32}S, ^{34}S	No specific humidity dependence noted, higher oxidation rates in plumes from oil-fired than from coal-fired plants.
Davis and Klauber (1975)	NO, NO_2, O_3, SO_2	Ozone 'bulge' noted downwind.
Lusis and Wiebe (1976)	SO_2, sulphate	No temperature or humidity effects noted.
MISTT study (see text)	O_3, NO, NO_2, SO_2 b_{scat}, Aitken-nuclei, sulphate	Oxidation rate increases after 1 to 2 hours aging. Different stage of oxidation at edge of plume than at centre.

Table 25

Summary of some SO_2 oxidation rates, measured in plumes.

Study	Location	Type	Rate (% hr^{-1})	$t_{1/2}$ (hrs)	rel.hum. %
Katz (1950)	Sudbury	smelter stack	2.1	-	-
Shirai (1962)	Tokyo	urban air	11.7	-	-
Gartrell et al. (1963)	TVA	power plant	0-4 8-55	- -	45-70 73
Dennis et al. (1969)		coal fired power plant	-	1.0-2.8	36-53
Weber et al. (1970)	Frankfurt	ground level sampling downwind power plant	-	0.3-1	-
Stephens and McCaldin (1971)		power plant	- 0	1.2-2.4 -	40-80 < 35
Coutant et al. (1972)	laboratory simulation	different fuel types	-	1-6	40-90
Granat and Rodhe (1972)	Stockholm	oil fired power plant	4.3	-	-
Newman (1975a)	New York State	oil fired power plant	-	10	-
Newman (1975b)	Pennsylvania	coal fired power plant	small	-	-
Roberts and Friedlander (1975)	Los Angeles	urban air	2-13	-	-
Lusis and Wiebe (1976)	Sudbury	smelter stack	1	-	-
Whitby et al. (1976)	St. Louis	coal fired power plant	1.5-5	-	~ 75

the oil-fired plant but this seems unlikely in view of the apparent low catalytic efficiency of vanadium, as discussed in the last section. Finally, it should be mentioned that Newman et al., are of the opinion that homogeneous gas phase or aqueous phase oxidation mechanisms are inconsistent with their data.

Davis and Klauber (1975) did not measure oxidation rates but observed increased ozone levels some 50 km downwind of the plant. As indicated earlier their proposed mechanism is questionable.

Lusis and Wiebe (1976) studied the plume of the large INCO nickel smelter stack near Sudbury using sampling techniques similar to those designed by Newman et al., (1975a,b). Sulphate and SO_2 were determined using standard wet chemical methods but the large errors in their data could not allow assessments of significant temperature or humidity effects. The average value for the oxidation rate was of the order of 1% hr^{-1} and a slight decrease in the oxidation rate with plume age was tentatively observed. The authors also noted that within the first 100 km of transport usually less than 10% of the sulphur in the plume is in the form of sulphate.

Roberts and Friedlander (1975) used total filter and cascade impactor aerosol samples from several sites in Los Angeles and performed calculations to estimate gas-to-particle conversion rates for SO_2 in urban polluted air. The oxidation rates obtained were rather large compared with other plume studies; these results may be artifacts, depending on the method of calculations, but are not entirely unreasonable when it is realized that under such circumstances all the possible oxidation mechanisms discussed in earlier sections will now be operative.

Finally, the most thorough and far-reaching study to date, on a power plant stack plume in the vicinity of St. Louis (the Midwest Interstate Sulphur Transport and Transformation (MISTT) study) is not yet completed, but promises to give major insights into the understanding of plume processes. Several research groups collaborate under the aegis of the U.S. Environmental Protection Agency (Charlson, University of Washington, Seattle; Whitby, University of Minnesota, Minneapolis; Husar, Washington University, St. Louis; Blumenthal, Meteorology Research Inc.; Wilson, Environmental Protection Agency). Some initial results have been presented at several scientific meetings during 1976 (Whitby et al., 1976; Wilson et al., 1976; Husar et al., 1976) and it seems appropriate to devote some attention to them here.

The basic aims and modus operandi of the project were described by Wilson et al., (1976). The following improvements and extensions from earlier plume studies are noted. More gas and aerosol parameters were determined. The gas parameters O_3, NO, NO_x and SO_2 were continuously monitored and aerosol parameters such as particulate sulphur samples were collected for each plume traversal, and analyzed by a specially developed highly sensitive method (flash vaporization-flame photometry; Husar et al., 1975). Continuous light scattering (b_{-scat}) was monitored and a combination of an optical counter and electrical aerosol analyzer provided in situ particle size distributions from grab samples. The monitoring aircraft made several traversals through the plume at different altitudes at discrete distances from the stack in order to measure horizontal and vertical profiles. The data are interpreted in terms of total mass flow instead of ratios and the background air mixing with the plume was characterized at each measuring location. Measurements were made in approximately the same air mass as it moved downwind.

The large amount of monitoring equipment made it possible to characterize the plume with much greater accuracy at each measuring location. In fact, on some occasions the plume could be followed over more than 24 hours, representing travelling distances of the order of a few hundred kilometers. Some of the major findings that have been reported so far are:

- the conversion rate of SO_2 to sulphate appears to be slow during the first two hours of travelling time, and then <u>increases</u> (see Table 26, from Whitby et al., 1976). All three aerosol parameters measured follow this trend (see Figure 2 in Whitby et al., 1976).
- there is strong evidence that at the edges of the plume the conversion chemistry is at a different stage than at the centre of the plume. This is easily observed from the Aitken-nuclei count for a transversal through the plume (cf. Figure 2 in Wilson et al., 1976). A probable explanation is that at the edges of the plume homogeneous

Table 26

Plume aerosol flow rates and calculated sulphur conversion assuming the aerosol is H_2SO_4 in equilibrium with water vapor for one run at the Labadic power plant, near St. Louis. From Whitby et al., 1976.

Distance km	Time hrs	Aerosol volume flow above background cm^3/sec	SO_2 converted*) %	SO_2 conversion rate %/hr
0	0			
10	0.7	185	1.1	
				1.5
21	1.49	388	2.3	
				1.8
32	2.29	640	3.7	
				4.9
45	3.17	1378	8.0	

*) based on average SO_2 flow of 4.08 kg/sec and rel. humidity 75%.

gas phase reactions from mixing with background air are more important. At the centre of the plume the ozone concentration is low due to reaction with NO (which is usually present in large amounts in power plant plumes), and thus comparatively little radical chemistry is expected initially;

- from the total sulphur balance it appears that the fraction of SO_2 converted does not depend on the SO_2 concentration, but on the total amount in the atmosphere and its time of residence;
- it seems that the total fraction of SO_2 converted is actually surprisingly small, i.e. of the order of 10%. This conclusion was also reached by Lusis and Wiebe (1976);
- most of the sulphate aerosol is formed in the accumulation mode (see the next section on aerosols). Particles in this size range have very long atmospheric lifetimes since their deposition velocity is definitely smaller than that for gaseous SO_2 (Sehmel, 1971, 1973; Whelpdale and Shaw, 1974). Long range transport of sulphates is thus predicted.

The last observations have a critical impact on the environmental consequences of the use of tall stacks. When SO_2 is emitted close to the ground, surface removal mechanisms will remove most of it before considerable oxidation occurs. Tall stacks, emitting SO_2 high in the air, will provide for increased dilution of SO_2 and sulphate, and thus reduce the impact of emissions in the vicinity of the source. However, the residence time of the total amount of SO_2 emitted will be much larger in the atmosphere and thus more conversion to sulphates will occur, leading to larger amounts of sulphates that can be traced over long distances. In this regard it is interesting to mention that abnormally high sulphate aerosol concentrations were once observed over Greenland. The history of the particular air mass indicated that the INCO stack at Sudbury was a possible origin (Flyger et al., 1973; Whitby, 1975).

The MISTT project has also studied the long range effects of the St. Louis urban plume (White et al., 1976a, 1976b) and the initial data seem to indicate the same effects.

In view of the uncertainties in comparing the published plume data it seems somewhat premature to try to construct adequate theoretical models to explain all the observations. Certainly, the models by Foster (1969) and Matteson et al., (1969) described in the section on the aqueous phase oxidation of SO_2 have import but testing such models on actual measurements can not be always reliable. In this respect the very detailed modelling study by Freiberg (1976) should be noted. This model predicts strong effects from relative humidity and temperature, for which some evidence exists from plume measurements; not all of the emitted SO_2 will be converted to H_2SO_4, in agreement with Lusis and Wiebe (1976) and the MISTT study; however it is predicted that most of the oxidation will take place during the first hour of plume travel. Freiberg's model is not directly applicable to the relatively clean plume which was studied in the MISTT project, however, since he considered Fe^{3+} catalyzed oxidation as the only conversion mechanism, and furthermore assumed rather high concentrations of Fe^{3+} (0.12×10^{-3} M/l Fe^{3+} and up) and relative humidity (90%).

2.4 AEROSOLS

In earlier sections of this review we frequently indicated that the ultimate fate of many atmospheric transformation reactions is the formation of aerosols. Although most properties of aerosols are determined by physical parameters, it will be useful to devote some attention to these atmospheric constituents here. The revised version of the Handbook on Aerosols (Dennis, 1976) treats many of the physical aspects of these compounds, and the reader is referred to this treatise for a thorough review in this respect. Some of the major concerns about the presence of aerosols relate to their influence on the reduction of visibility and their detrimental effect on human health. It appears that so-called secondary aerosols, i.e. aerosols that result from chemical reactions in the atmosphere and that are not due to primary emission such as metal and soot particles from industrial operations or blowing dust, are the major culprits in this regard. This is due to the fact that secondary aerosols usually end up in the size range of 0.1 to 1 μ (1000 to 10,000 Å) diameter, which experimentally has been determined to be the most efficient light scattering range, and moreover falls within the physical dimensions of particles which can reach the inner tracts of the human lung (Williamson, 1973).

The mechanism of aerosol formation, which is largely determined by physical parameters, is an area of active theoretical (cf. Chu and Seinfeld, 1975; Seinfeld and Ramabhadran, 1975; Takahashi et al., 1975; Hamill, 1975; Nair and Vohra, 1975) and experimental (cf. Clark and Whitby, 1975; Kasahara and Takahashi, 1976) research today. Kinetic rate data concerning the actual aerosol formation are almost nonexistent, although recently some experiments have been performed by Heicklen and coworkers (Luria et al., 1974a, 1974b; Heicklen and Luria, 1975; Miller et al., 1975; Olszyna et al., 1974, 1976).

2.4.1 Physical Considerations

Aerosols are defined as particles suspended in the atmosphere, of such a size that Brownian motion and other collisional processes prevent them from direct settling due to gravitational forces. The size of most aerosol particles ranges from ~0.001 to 50 μ diameter. Some very important discoveries have been made during the last six years concerning the distribution of particles within this range. It now appears that the atmospheric size distribution is almost always bimodal in surface or volume, and frequently trimodal near sources of fresh combustion (Whitby et al., 1972; Willeke and Whitby, 1974; Whitby et al., 1975). This observation has led to the following distinction in the description of aerosol particle distributions (Whitby and Cantrell, 1975):

- coarse (giant) particle mode: this mode contains particles of diameter larger than ~2 μ. Particles in this mode originate from direct emission into the atmosphere, by industrial operations or dust storms. Although they are generally responsible for 2/3 of the total aerosol mass, the coarse particles form only a small part of the total number of particles.
- fine particle mode: particles of diameter less than ~2 μ. This mode may show two distinct surface area modes (leading to the earlier mentioned trimodal distribution).
- transient (Aitken) nuclei mode: particles of diameter less than 0.1 μ (average diameter: ~0.02 μ). Particles in this mode result primarily from the direct emission of primary particles from

combustion processes. Moreover, if homogeneous nucleation (vide infra) takes place, then new nuclei will be found in this range as well.

- accumulation mode: particles with a diameter between 0.1 and 2 μ. Particles in this mode are not due to primary emission processes, but result from coagulation of primary particles or condensation of chemical reaction products with secondary aerosols.

The physical parameters which lead to particles in the accumulation mode seem to be responsible as well for the significant observation that there is very little exchange of mass between the accumulation and coarse modes. The important consequence of this observation is that the ratio of fine to coarse particles can be utilized to establish some of the history of an air mass.

Particles in the accumulation mode are by far the most important from an air pollution point of view. It appears that these particles account for most visibility phenomena and contain most of the chemical compounds having biological effects, a large fraction of liquid, most of the free acids, and practically all of the aerosol mass resulting from chemical reactions in the atmosphere.

It seems logical that analysis of aerosols with respect to air pollution studies should focus on particles in the accumulation mode. Unfortunately this appears to be a difficult task. Two of the more recent instruments that seem to be able to analyze particle distributions with reasonable accuracy are the optical particle counter (Liu et al., 1974a) and the electrical aerosol analyzer (Liu et al., 1974b). We will discuss some of the problems of aerosol analysis later in this section.

The formation of fine particle aerosols can generally take place along two routes:

- homogeneous nucleation processes: nucleation can occur spontaneously if the reagent vapor is supersaturated in the atmosphere, so that small clusters of molecules can condense out. In this process vapor pressure thus plays a deciding role, and two different routes can be distinguished in this regard. Homonucleation is a process where identical molecules combine to form the initial particles, while in heteronucleation different chemical species condense out. The latter process usually dominates in the atmosphere, where one of the species is H_2O. Its importance is readily grasped from the fact that the vapor pressure of pure H_2SO_4 is approximately two orders of magnitudes larger than 98% H_2SO_4 in H_2O. Another example of a powerful heteronucleating mixture is the combination of NH_3 and SO_2, as discussed in the last section.

Homogeneous nucleation will lead to particles in the transient nuclei mode. Their lifetime is usually very short since collisional processes will rapidly lead to particle growth into the accumulation mode. The fact that in atmospheric monitoring the transient mode is usually only observed in regions very close to combustion sources, had led to speculation that homogeneous nucleation is an altogether unimportant atmospheric process. However, such atmospheric measurements are not commonly performed *in situ* and it is conceivable that the short lifetime of particles in this mode is the reason for the lack of observation of the transient mode. By careful analysis of monitoring data Whitby (1977) has recently found evidence that this might indeed be so, thus reinforcing the probability that homogeneous nucleation is a viable atmospheric aerosol formation route.

It should be mentioned that due to the very low vapor pressures necessary for homogeneous nucleation, this process cannot be important for nitrate-containing and most organic aerosols.

- *heterogeneous nucleation processes*: condensation on existing particles, so-called heterogeneous nucleation, is the major route of formation of atmospheric aerosols. No supersaturated vapor is necessary for this process, and it can thus lead to the formation of HNO_3 and organic aerosols. The rates with which these processes take place depend on diffusion rates of particles and gases in the atmosphere, and rates of irreversible sorption processes (absorption, adsorption, chemisorption). During supersaturation conditions, which depend on the chemical formation rate of the nucleating species, diffusion limited growth can occur, and homogeneous nucleation can compete with heterogeneous nucleation.

Thermodynamic considerations have to be taken into account as well. According to Kelvin's relation, the vapor pressure of a condensable species is larger for particles with very small radius. It appears that due to surface tension of a range of materials, condensation will not take place on particles with a diameter less than approximately 0.05 to 0.1 μ (Heisler et al., 1973; Hidy, 1973). Thus heterogeneous nucleation seems to be dependent on the presence of particles in the accumulation mode, and will, through further coagulation, lead to an increase in the volume of this mode.

2.4.2 Primary Aerosols

Of concern to us here are the particles that reach the atmosphere as a result of the oil sand plant activities. At the writing of this review few monitoring data were available. We will limit ourselves therefore to a short discussion of what might generally be expected.

Chemical analysis of fly ash from the stacks contains several metal oxide and soot particles in addition to a large quantity of water vapor. The amount and size distribution of the particle emission will of course depend in part on the particle control methods that will be incorporated. It seems reasonable to expect that sufficient submicron-size particles will be emitted, so that aqueous phase metal ion catalyzed oxidation mechanisms for the SO_2 transformation could be operative, but from the discussion of actual plume measurements in the last section it appears that one has to be careful not to overestimate the importance of these processes. It should be reiterated that Newman et al., (1975b) found very little evidence for SO_2 oxidation in a reasonably clear (low particle count) plume from coal fired power plant, whereas the MISTT-study, which also reported data from a well controlled power plant stack, points to the likelihood that the homogeneous gas phase oxidation of SO_2 might be an important mechanism.

The very fact that these emissions also contain large amounts of water vapor makes purely heterogeneous oxidation mechanisms probably of little importance, but homogeneous aqueous phase mechanisms should be expected to play a role. It would be mentioned though that carbonaceous particles (soot) have recently been suggested to be very efficient oxidation catalysts. The carbon particle-catalyzed oxidation of NO to NO_2 (Heicklen and Cohen, 1968; Chang and Novakov, 1975) and of SO_2 to SO_3

(Novakov et al., 1974) is supposed to be highly efficient and much faster than the homogeneous gas phase rates.

Even if no chemical reaction occurs, adsorption of gas molecules on particulate matter can be important since the adsorption spectrum of the adsorbed species can be markedly shifted, thereby altering the photochemistry. Thus Daubendieck and McMillan (1973) reported that 1,3 pentadiene adsorbed on pyrex glass could be photoisomerized with 3660 Å radiation, even though this compound does not absorb light above 2900 Å in the gas phase. This type of process has received no attention to date in atmospheric studies.

The importance of the above processes can only be assessed when actual monitoring data become available, however.

2.4.3 Secondary Aerosols

Although the distinction is not realistic, three types of secondary aerosols can be classified: sulfates, nitrates and organic. As far as the chemistry is involved, we are interested in the actual constituents of aerosols, and the chemical reactions that lead to these aerosols. We will describe the current status of knowledge for each of the three classes of aerosols. Many of the mechanistic details of the reactions have already been discussed in earlier chapters.

Nitrate-containing Aerosols

Such aerosols result from oxidant-type pollution chemistry. From modelling studies, Calvert (1973) has shown that the major formation path of HNO_3 in the atmosphere is the reaction

$$HO + NO_2(+M) \rightarrow HNO_3(+M)$$

Under conditions of low radical concentration, i.e. during night, the gas phase reaction

$$N_2O_5 + H_2O \rightarrow 2HNO_3$$

becomes important, although its rate is much slower. There are indications however, that a more rapid heterogeneous reaction can occur on surfaces (Morris and Niki, 1973). N_2O_5 would be formed via the scheme:

$$O_3 + NO_2 \rightarrow O_2 + NO_3 \xrightarrow{NO_2} N_2O_5$$

Nitric acid is fairly stable in the atmosphere and will not by itself lead to aerosols since its vapor pressure is fairly high, even over water solutions (Toon and Pollack, 1973). However, HNO_3 readily reacts in the gas phase with NH_3, leading to the much less volatile ammonium nitrate. This reaction and the ensuing aerosol formation have been extensively studied by Heicklen and coworkers (De Pena et al., 1973; Olszyna et al., 1974, 1976). It was established that under atmospheric conditions the equilibrium

$$HNO_3 + NH_3 \rightleftarrows NH_4NO_3$$

is shifted to the right side. The critical pressure needed to initiate nucleation is approximately 0.4 ppb($\sim 10^{10}$ molec/cc). In an atmosphere containing HNO_3 and NH_3, these authors established the following condensation mechanism:

$$HNO_3 + C_n \rightleftarrows C_n.HNO_3$$

$$C_n.HNO_3 + NH_3 \rightarrow C_{n+1}$$

where C_n represents a particulate species consisting of nNH_yNO_3 molecules. The frequent identification of NH_4NO_3 in aerosols from oxidant-forming pollution indicates the importance of those reactions, although the direct application of the results of Heicklen's group is somewhat difficult since they used much higher concentrations of NH_3 and HNO_3 than will be present in the atmosphere.

Another route to nitrate-containing aerosols is dissolution of nitrogen oxides in water droplets. With the exception of NO, which dissolves very little in water, the other nitrogen oxides (NO_2, NO_3, N_2O_5) are readily dissolved in water (Hidy and Burton, 1975). Nash (1970) and Borok (1960) for instance, showed that trace amounts of NO_2 are readily absorbed in water, leading to nitrite and nitrate ions. Nitrite ions will then probably be oxidized to nitrate ions via analogous routes to SO_3^{2-} oxidation, Table 27.

Another route for nitrate formation seems to be via interactions with H_2SO_4. Bourbigot et al., (1973) noticed the formation of particles of empirical formulae $HNSO_5$ and $S_2O_7(NO)_2$ during photolysis of an SO_2-NO_2-moist air mixture. Similar products have been observed by Urone et al., (1970) in the photolysis of SO_2 and NO_2 in dry air,

Table 27

Aqueous reactions of nitrogen oxides*)

$$N_2O_5 + H_2O \rightleftharpoons 2H^+ + 2NO_3^-$$

$$2NO_2 + H_2O \rightleftharpoons H^+ + NO_3^- + HNO_2$$

$$HNO_2 + OH^- \longrightarrow H_2O + NO_2^-$$

$$2NO_2^- + O_2 \longrightarrow 2NO_3^-$$

$$NO_2^- + O_3 \longrightarrow NO_3^- + O_2$$

$$NO_3 + H_2O \longrightarrow H^+ + NO_3^- + OH^-$$

$$NO + NO_2 + H_2O \longrightarrow 2H^+ + 2NO_2^-$$

*) from Hidy and Burton, 1975.

Paul et al., (1972) from the reaction of N_2O_4 and SO_3 in liquid SO_2, and Daubendieck and Calvert (1975) from the gas phase reaction between SO_3 and NO_2. $HNSO_5$ could well be nitrosyl sulphuric acid formed by absorption of NO_2 into H_2SO_4, while Daubendieck and Calvert postulate that $S_2O_6(NO)(NO_2)$ might be nitrosyl nitryl pyrosulphate, which has been synthesized by others (cf. Stopperka and Kilz, 1968). The presence of NH_3 seemed to suppress the formation of these products in the experiments of Bourbigot et al. No indication of the efficiencies of such reactions are known and more definite studies in this field should be performed.

Finally, organic nitrates can result from oxidant chemistry reactions of the type:

$$RO. + NO_2 \rightarrow RONO_2$$

$$RO. + NO_2 \rightarrow RO_2NO_2$$

with R=H, alkyl, acyl. These compounds are volatile when low molecular weight alkyl/acyl groups are involved but longer carbon-carbon chains could result in the atmosphere, as we will see shortly. Moreover, these compounds seem to readily hydrolyze in an aqueous medium, leading to nitrite ions.

Organic Aerosols

Very little information exists pertaining to the mechanisms of chemical reactions that lead to such aerosols. Analysis of organic aerosols (the definition is usually implied to mean that part of an aerosol which is soluble in benzene) has shown an overwhelming array of compounds: organic nitrates, carboxylic acids and their esters, carboxyl compounds, alcohols and polymeric peroxides have been identified (Grosjean and Friedlander, 1975; O'Brien et al., 1975a, 1975b; Grosjean, 1975) as well as long chain alkanes, alkenes and dicarboxylic and fatty acids (Schuetzle et al., 1973, 1975).

O'Brien et al., (1975a) have performed some laboratory studies with the aim of identifying possible precursors for the carboxylic acids, and conclude that diolefins or cyclic olefins play a dominant role in this respect. Finlayson and Pitts (1976) have argued that an additional path for the formation of multifunctional compounds might be the oxidation of aromatic compounds, which would explain the presence of significant amounts of unsaturated organics in particulate matter, as observed by Grosjean and Friedlander (1975).

It has been observed that particle formation takes place concurrently with increasing ozone concentration (Hidy and Burton, 1975), thus prompting the suggestion that ozone might play an important role in the chemical reactions leading to organic aerosols. As noted elsewhere, the mechanism of ozonolysis of olefins in the gas phase, although being still a matter of wide controversy, has been suggested to include steps that lead to carboxylic acid formation. Moreover, the many radical intermediates that are present in such systems would constitute excellent initiators for polymer formation. Thus, Calvert (1975b) has suggested that in a "spent" oxidant mixture (i.e. when most of the NO → NO_2 conversion has taken place, the ozone concentration increases, and higher analogue olefins are largely degradated to ethylene), the following polymer formation mechanism is quite conceivable:

$$\begin{array}{ll} HO + C_2H_4 \rightarrow HOC_2H_4\cdot & \text{(initiation)} \\ HOC_2H_4 + O_2 \rightarrow HOC_2H_4O_2\cdot &) \\ HOC_2H_4O_2\cdot + C_2H_4 \rightarrow HOC_2H_4O_2C_2H_4 &)\text{(propagation)} \\ HO(C_2H_4O_2)_n\cdot + NO_2 \rightarrow HO(C_2H_4O_2)_nNO_2 & \text{(termination)} \end{array}$$

The aerosols over forested rural areas most likely originate from similar reactions. Thus, Lillian (1971) noticed the formation of large amounts of aerosols while studying the reaction between ozone and α-pinene. Schwartz (1974) found multifunctional compounds in the aerosol extracts from similar experiments, containing two or more of the carbonyl, alcohol, carboxylic acid, and nitrate functions. Interestingly, pinoic acid was subsequently found in atmospheric aerosols.

It appears from this short discussion that even from simple model systems (Schwartz, 1974; O'Brien et al., 1975a) enormous complex product mixtures are to be expected and a complete analysis of organic aerosols, let alone a description of mechanistic detail, will still need a large amount of further research.

Sulphur-containing Aerosols

These secondary aerosols have received the most attention. We have already extensively discussed the possible mechanisms for atmospheric oxidation of SO_2 to SO_3 which, in the atmosphere, will react very fast with water molecules to form H_2SO_4. The reaction may also take place in the liquid phase.

Formation of H_2SO_4 aerosols is possible by homogeneous nucleation, contrary to the cases of nitrate and organic aerosols since the vapor pressure of H_2SO_4 is very low, and in recent years several studies have been published that shed some light on the mechanisms of formation (Cox, 1973, 1974; Clark and Whitby, 1975; Smith et al., 1975; Kasahara and Takahashi, 1976; Shen and Springer, 1976). All these studies used the photooxidation of SO_2 as a route to particle formation. The following observations are made: initially there is a rapid increase in the total number of particles until a maximum concentration is reached, after which stage prolonged irradiation does not lead to an increase in the number of particles (in fact, a decrease is observed); however, the total <u>volume</u> of the aerosol increases, probably in a linear fashion (Clark and Whitby, 1975).

It is easily recognized that the initial increase in the number of particles can be identified with homogeneous nucleation due to supersaturation of the newly formed H_2SO_4. The rate of particle formation is probably a complex function of the rate of H_2SO_4 formation (which will depend on light intensity, SO_2 concentration, and relative humidity) and of actual nucleation. The maximum number of particles formed is strongly dependent on the same parameters (Kasahara and Takahashi, 1976; Shen and Springer, 1976). The latter authors deduce the following empirical relation:

$$N_{max} = A \times (SO_2)_{t=o} \times (\text{rel.hum.})^2_{t=o}$$

where A is presumably a function of the light intensity.

This relation however cannot be fitted to the data of Smith et al., (1975), and, according to these authors, not to the data of Cox (1973) as well. The latter results seem to indicate that N_{max} is independent of initial SO_2 concentration or of relative humidity. However, much higher concentrations of SO_2 were involved in these experiments, which makes a comparison rather doubtful, as discussed by Shen and

Springer (1976). It is quite conceivable that a species other than H_2SO_4 is the nucleating agent in the work of Smith et al., (1975), for example, the elusive SO_4 radical, as suggested by these authors. It might be significant that their constant N_{max} is considerably lower ($\sim 0.6 \times 10^5$ particles/cm^3) than that obtained in the other studies at lower SO_2 concentration (depending on $(SO_2)_{t=0}$ and relative humidity, of the order of magnitude of 10^6 particles/cm^3).

After the maximum number of particles has been reached and when the total number of particles decreases, coagulation and condensation should be responsible for the increase in aerosol volume. Clark and Whitby (1975) suggest that this phenomenon is caused by a faster rate of condensation as compared to the rate of photochemically formed H_2SO_4 molecules, thus leading to a drop in the H_2SO_4 vapor pressure below the supersaturation level. The actual decrease in the total number of particles is then explained by coagulation of existing particles. The fact that at this stage the average diameter of the particles slowly increased with reaction time constitutes supporting evidence for this mechanism. It was also noted that the particle surface reaches an equilibrium value, which was correlated with the rate of increase of particle volume. This interesting relation seemed to be purely determined by an equilibrium between the physical processes of coagulation and condensation and is in agreement with the atmospheric observation that particles in the accumulation mode do not grow to the range of the coarse particle mode. No chemistry seems to play a role, since quite different aerosol formation processes, e.g. aerosol formation during irradiation of terpene vapors in initially particle-free air, follow exactly the same relationship. This effect was also found in the theoretical calculations by Takahashi et al., (1975) on the mechanism of sulphuric acid aerosol formation, and explains why sulphuric acid aerosols generally are limited in particle size to a diameter of the order of 0.1 μm to 1 μm.

It is interesting to note that these studies generally agree only within 2 orders of magnitude on the estimated partial pressure of H_2SO_4 vapor necessary before homogeneous nucleation will start. The values range from $\sim 10^{-9}$ Torr H_2SO_4 (Cox, 1973) to approximately 10^{-7}

Torr H_2SO_4 (Clark and Whitby, 1975; Smith et al., 1975). Stauffer et al., 1973) estimate a theoretical value of 10^{-8} Torr H_2SO_4, while Mirabel and Katz (1974) arrived at a slightly higher estimate ($\sim 10^{-7}$ Torr). This means that under polluted conditions, i.e. SO_2 concentrations of the order of 0.1 ppm, homogeneous nucleation of H_2SO_4 aerosols could indeed be important (H_2SO_4 formation rates of 1 - 10 ppb hr^{-1}, Cox (1973); 10^{-8} Torr H_2SO_4 corresponds to approximately 0.01 ppb in air), while under more "clean air" conditions ($\sim$0.005 ppm SO_2) only heterogeneous nucleation on existing particles will be of importance.

The question might arise as to how concentrated sulphuric acid aerosol particles will be. As has been indicated before, from supersaturation considerations it is likely that homogeneous nucleation will actually involve heteronucleation between H_2SO_4 and H_2O molecules, whereby 90% H_2SO_4 constitutes the most favorable conditions. It was shown recently, however, that continued contact with water in the atmosphere will very rapidly lead to dilution of the original particles, since the establishment of a droplet-vapor equilibrium can take place in a matter of milliseconds (Carabine and Maddock, 1976) contrary to earlier suspicions that this process might be severely rate limited (Coutarel et al., 1967). This fact probably means that inhalation of highly concentrated H_2SO_4 aerosols is not as damaging for human health as suspected before, since considerable dilution will occur before the particles can reach the lung tissue.

Some aerosol formation routes other than via the SO_2-SO_3-H_2SO_4 route, but also involving SO_2, have been mentioned in the section on oxidation mechanisms for SO_2, and will be briefly summarized here.

The reaction between photochemically excited SO_2 and hydrocarbons has been shown to produce large amounts of aerosols consisting of sulphur-containing acids (sulfonic, sulfinic, sulfenic acids) that can grow to considerably large particles (Penzhorn and Jordan, 1975). In the presence of oxygen oxygenated organic compounds were also identified in accord with the involvement of organic radicals in the SO_2-hydrocarbon-irradiation experiments (Hirose et al., 1975). However, the reactions are probably of little atmospheric consequence when other radical reactions are dominant.

The homogeneous reactions of SO_2 with the RO and RO_2 radicals have been indicated to be major oxidation routes of SO_2. It was suggested that RO radicals will mainly add to SO_2 and it is quite conceivable that a fraction of the $RO_2 + SO_2$ interaction will also lead to addition as well as oxygen transfer to SO_3 and RO. Although nothing is really known about the fate of such addition products, it has been speculated that aerosols ultimately consisting of SO_2-organic molecules are formed. Thus, analysis of aerosols observed in the ozone-olefin-SO_2 system has shown the presence of organic sulphur compounds which might well have arisen from such addition reactions (Schulten and Schurath, 1975a).

The direct reaction between SO_2 and NH_3 is another potential route to homogeneous aerosol formation. However, as we have indicated earlier, thermodynamic considerations appear not to favor this reaction under normal atmospheric conditions. Very high concentrations of SO_2 and NH_3 seem to be necessary, and even though such concentrations might prevail within the stack exhaust (Claus-process exhaust?), other reactions should be dominant.

2.4.4 Other Chemical Aspects Related to Aerosols

Analysis

We have briefly indicated many of the perplexing problems which have thus far hindered orderly development in the understanding of the mechanism of formation and properties of aerosols. A further complication is encountered in the field of analytical techniques for determining particle samples. There is a large body of published analytical methods, mainly for the determination of sulphate particles. Ideally, information on particle size and number distribution, quantitative data on the different types of sulphates (H_2SO_4, bisulphate, sulphate, sulphite, type of cation etc.), and their temporal behavior are required. The presently available methods have recently been reviewed (Dharmarajan et al., 1975; Tanner and Newman, 1976) and range from endless classical wet chemical methods to more elaborate techniques such as X-ray fluorescence (Gilfrich et al., 1973), Electron Spectroscopy (ESCA) (Novakov et al., 1972), Fourier Transform Infrared Spectroscopy

(FTSIR) (Cunningham et al., 1974), field desorption mass spectroscopy (Schulten and Schurath, 1975b) and so on. Without going into detail it appears that no completely satisfactory methods which can distinguish between the different types of sulphates are available. A much worse problem is inherent to essentially all the methods, i.e. sample collection. In all the analytical methods devised to date the aerosols are collected on a filter. In addition to the engineering problems related to the sampling medium, as reviewed by Fuchs (1975), there are two important chemical considerations that have to be taken into account, as summarized by Tanner and Newman (1976):

- acidic sulphate can undergo neutralization reactions with the filtration medium, with basic material collected on the filter surface, and with basic gases (NH_3) in the sampled air during particle collection.
- gaseous SO_2 can undergo catalytic oxidation reactions initiated by the filter material or particles collected thereon.

As a measure of the importance of these processes it might be mentioned that Friend (1974) reported that measurable amounts of $SO_4^=$ are formed when humid, particle-free air containing 1 ppm each of SO_2 and NH_3 is passed through a plug of clean glass wool. It seems, therefore, that any quantitative analysis of sulphate content will have an inherent large uncertainty. Quoting Tanner and Newman: "it is regretfully axiomatic that the only way to eliminate interaction of collected sulphate-containing particles with reactive gases (e.g. SO_2, NH_3) or other particles in the sampled air would be to determine the particulate sulphate *in situ* without filter collection." However, no such methods seem to have been developed to the stage of practical application.

Another example of this filter effect concerns the measurements of nitrates. Spicer (1975) has suggested that reports of high particulate nitrate levels in polluted urban atmospheres are probably seriously in error due to trapping of gaseous nitric acid on the particle collection medium.

Effects of aerosols on atmospheric chemistry

Although aerosols can be considered as end stations in atmospheric chemistry, they will influence the mechanisms of atmospheric reactions. We have already indicated the catalytic role which primary aerosols can play in the photochemical reactions, and oxidation routes for molecules like SO_2 and NO_2.

The presence of aerosols will also influence photochemical reactions by scattering of the sunlight. The effect of aerosols on solar radiation has been studied quite extensively, but the main focus of these studies was the possibility of climatic changes (Liou and Sasamori, 1975; Cogley and Boruclei, 1976; and references therein). However, photochemical reactions will equally be influenced since they depend on the total amount of radiation available for absorption. This radiation, the so-called actinic irradiance, is a complex function of direct, scattered, and reflected solar light (Leighton, 1961; Peterson, 1976). Aerosols will reflect and possibly absorb this light, thereby altering the effective wavelength and intensity distribution of light available for photochemical reactions. The blue haze over wooded areas (Went, 1960) and brown color of Los Angeles smog (Husar and White, 1976) have been ascribed to scattering and absorption due to aerosol layers. A theoretical treatment of the aerosol effect on atmospheric photochemical reactions has not yet been performed. Peterson (1976) has reevaluated the solar irradiance, i.e. the amount of sunlight available for atmospheric photochemical reactions, incorporating new information on light scattering and absorption due to aerosols. This work was performed to establish reasonable estimates of solar irradiance for use in simulation studies, however, and does not focus primarily on the aerosol effect.

It was recently suggested that aerosols might also play a role in the typical radical reactions associated with polluted and unpolluted atmospheres. Warneck (1974) has argued that the average daily concentration of HO radicals, as calculated by Levy (1974) and others, ($\sim 2 \times 10^6$ molec/cc) should be lower by a factor of 5 to 10 in order to explain the observed global CO mixing ratios and the rate of nitrate precipitation in the northern hemisphere. From theoretical calculations, Warneck concludes that HO_2 radicals can be effectively scavenged by ambient aerosols, and that this would result in a lowering of the HO concentrations by competition with HO-reformation reactions involving HO_2 radicals.

If Warneck's arguments are correct, then aerosols should have an effect on the chemistry in polluted atmospheres as well. Indeed, modelling studies performed at Bell Laboratories (Farrow et al., 1975; Graedel et al., 1975; Graedel et al., 1976) support this conclusion. These authors have shown that diurnal variations of air pollution episodes in the New Jersey-New York region are much more satisfyingly explained when heterogeneous interaction between aerosols and some of the active radicals, in particular the peroxy radicals (HO_2, RO_2, R=alkyl, acyl) and the NO_3 radical, are included in the overall reaction scheme. To our knowledge no experimental data exist concerning the radical scavenging effect of aerosols, although such experiments are clearly warranted to confirm these suggestions. Certainly an added complication lies in the fact that specific interactions are suggested with the HO_2 and NO_3 radicals, for which no simple (and unique) formation routes nor monitoring methods are known.

3. SURVEY OF AIR POLLUTION STUDIES UNDER CLIMATIC AND GEOGRAPHICAL CONDITIONS SIMILAR TO THE ALBERTA OIL SANDS REGION

In this chapter we will indicate some of the air pollution studies that have direct relevance to the potential environmental problems of the Alberta oil sands region. As far as the chemistry is concerned there are two factors that will have to be considered here: temperature and solar altitude. The temperature affects the rates of the reactions that take place and the solar altitude, on the other hand, will determine the intensity and wavelength distribution of light available for photochemical reactions. In addition to these factors, which directly affect the chemical transformations, meteorological aspects specific to the almost arctic conditions during winter will be of consequence. Finally, the location of the plants in a nearly clean, rural environment might lead to peculiar chemical transformations.

We have computer-scanned the pollution abstracts data base for the literature on air pollution studies under comparable conditions. Using the combination of pollution key words like sulphur dioxide, sulfuric acid, aerosols, oxidants, with geographical key words like Arctic, Alaska, Fairbanks, northern Canada, N.W.T., Siberia, Norway, Sweden, etc., only a few reports were found. We also scanned the data base from the Boreal Institute for Northern Studies ("Northern titles"), with little more success. We were equally unsuccessful in finding reports in the Russian literature: it appears that whatever work has been done in Russia is not listed in the indicated data bases, or has not appeared in the open literature. As far as the western European work is concerned, this almost exclusively relates to urban air pollution studies and is of no relevance to the present problem. From the North American work, only some studies on air pollution in Alaska, more particularly Fairbanks, seem to have some bearing on the prevalent conditions around Fort McMurray. We will discuss this work shortly.

We can extrapolate some of the results from other studies to the northeastern Alberta conditions and make some rough predictions with regard to the possible polluting effects of the oil sand plants but it is obvious that a major interdisciplinary research effort must be initiated in order to establish meaningful guidelines.

Effect of Temperature

It appears that no studies on the effect of temperature on the chemistry of air pollution have been performed except one modelling study by the present authors (Bottenheim et al., 1976c). In this work it was shown that on the basis of the known and estimated temperature dependence of chemical reactions that occur in an oxidant-forming reaction mixture, only small effects should be expected from a lowering of the ambient temperature from +25 to -15°C. The reason is that the reactions in such a mixture feature small activation energies (from almost zero to only a few kcal/mole), as in the case of most radical reactions. No smog chamber studies have been reported which corroborate or contradict these theoretical predictions. However, an indirect effect of temperature on the importance of homogeneous gas phase reactions can be expected. At the much lower winter temperatures, evaporation of hydrocarbons, e.g. from naturally-occurring terpenes, the oil sand formations, or storage tanks at the oil sand plants, will be unimportant as a source of hydrocarbons in the atmosphere. Since these hydrocarbons are essential for the radical-chain reactions which characterize the homogeneous reactions, they should be expected to play a much less important role in winter.

As far as SO_2 oxidation is concerned, we have already indicated that many reactions are temperature-dependent, although few investigations have specifically studied such effects. The photooxidation of SO_2 is probably slightly temperature dependent, considering the $^3B_1$ state as the precursor state in this regard, since Wampler et al., (1973) reported an activation energy of ~ 3 kcal/mole for the collisional deactivation of this state by O_2. The reactions of $SO_2(^3B_1)$ with hydrocarbons have even lower activation energies (essentially zero in the case of olefins). The reaction of ground state SO_2 with HO radicals is pressure dependent (Davis, 1974b) and thus will probably show a negative temperature effect, i.e. the reaction will be faster at lower temperature. Since the average HO concentration is expected to be lower during winter (vide infra), a somewhat faster reaction rate due to low winter temperatures will probably be offset.

There is no information on the temperature dependence of the $HO_2 + SO_2$ reaction. It seems reasonable that the reaction features a small activation energy which, coupled with lower average HO_2 concentrations in winter, would indicate that this reaction is less important.

Turning to the aqueous phase oxidation of SO_2, much stronger temperature effects should be expected. Estimates of the room temperature oxidation rate of SO_2 in aqueous solution, i.e.

$$SO_3^{=} + \frac{1}{2} O_2 \rightarrow SO_4^{=}$$

vary widely, and McKay (1971) suggests that the activation energy is high, 18.3 kcal/mole. Yue et al., (1976) calculated the resulting rate constants, listed in Table 28. Moreover, all the equilibrium constants in the mechanism for dissolution of SO_2 in water to $SO_3^{=}$ are highly temperature dependent (McKay, 1971; Yue et al., 1975) see Table 29. The effect of lower temperatures on the metal ion-catalyzed oxidation is not clear. Freiberg (1974, 1975), on the basis of theoretical considerations, has argued that an increase in the actual oxidation rate of the ion catalysed-oxidation should be expected at lower temperature. No experimental studies which could corroborate such temperature effects are known. However, the work of Barrie (1975) on the rate of SO_2 oxidation catalyzed by manganese ions in droplets indicates that the oxidation rate is considerably lower.

Finally, the rate of aerosol formation should be faster at lower temperatures, owing to the lower vapour pressures of aerosol precursors. However, it is doubtful whether such effects would be noticeable in the atmosphere, since the rate of formation of aerosol precursors is usually rate determining. The lower vapour pressures might cause homogeneous nucleation to become a more important route to aerosol formation since lower concentrations of precursors are now required.

In conclusion, although no experimental studies seem to have been focussed specifically on the role of temperature on the evolving chemistry of an air pollution mixture it is probable that a somewhat slower rate of oxidant formation, mainly due to lower concentrations of ambient hydrocarbons, and a possible shift in the mechanism of aerosol

TABLE 28

Rate constant in sec^{-1} for the reaction

$$SO_3^{=} + \frac{1}{2} O_2 \longrightarrow SO_4^{=}$$

at different temperatures.

From Yue et al., 1976.

Author	25°C	15°C	10°C	0°C	-3°C
Scott and Hobbs	0.0017	0.00058	0.00033	0.0001	0.000069
McKay*)	0.032	0.011	0.00628	0.00192	0.00133
Miller and De Pena	0.003	0.001	0.0059	0.00018	0.000124

*) Calculated for pH = 7.

formation might result from a lowering of the ambient temperature. It is not possible at present to assess the effect on the oxidation of SO_2.

Effect of Solar Altitude

The solar spectrum does not seem to have been measured in Alberta. However, the amount of sunlight available for photochemical reactions in the atmosphere can be reasonably accurately estimated as outlined by Leighton (1961) and Peterson (1976). It then becomes apparent that during the winter not only less hours of sunshine can be expected but moreover, the ultraviolet cut-off is shifted to higher wavelength. An important result will be that the photolysis of O_3 to yield $O(^1D)$ atoms

$$O_3 + h\nu\ (\lambda \lesssim 320\ \text{nm}) \rightarrow O(^1D) + O_2$$

is much less effective in winter (Bottenheim et al., 1976c). Since this reaction forms the basis of the clean air radical chemistry, and is an HO radical source in polluted air as well (although of less importance), some seasonal changes have to be expected.

During summer the amount of ultraviolet light is more comparable to that available at lower latitudes, and no major change in the chemical transformation routes should be expected. Thus, Nieboer et al., (1976) have shown that, in fact, comparable amounts of PAN under similar air pollution conditions can be expected in Los Angeles (34°N), Rotterdam (51°N) and Fairbanks (65°N). The seasonal variations in the photochemical oxidation rates of SO_2 have been estimated by Penzhorn et al., (1974a), as discussed earlier.

It appears that the effects of solar altitude, i.e. seasonal variations in the solar spectrum, on air pollution chemistry have been little investigated experimentally. Some studies have appeared in which natural sunlight is used as radiation source, and thus the solar altitude and resulting light intensity changes with time of day. Of particular interest in this regard are some of the smog chamber studies performed at the University of North Carolina by Jeffries and coworkers (Fox et al., 1975; Jeffries et al., 1976a, 1976b). An outdoor smog chamber was used in this work, in which certain air pollution mixtures were followed over the period of a day. Quite interesting effects were noted, such as an increase in the maximum O_3 concentration when the reaction mixture was slowly diluted with ambient rural air, and an increase in the $NO \rightarrow NO_2$ conversion when sunlight was intermittently disrupted by cloud cover. Such effects are not easily quantified with purely chemical models, but point to the necessity of more studies on the effect of controlled light intensity variation. The effect of solar altitude is expected to be more pronounced than a lowering of the temperature as far as the oxidant chemistry is concerned. The present authors have shown (Bottenheim et al., 1976c) that taking average values for temperature and solar altitude, the so called photostationary state (Stedman and Jackson, 1975; Calvert, 1976a) predicts a lower O_3 concentration in winter. Thus from the photostationary state mechanism:

$$(O_3) = \frac{k_1(NO_2)}{k_3(NO)}$$

k_1 is the rate constant for the reaction

$$NO_2 + h\nu \rightarrow NO + O$$

and is dependent on solar altitude, and k_3, the rate constant for the reaction

$$NO + O_3 \rightarrow NO_2 + O_2$$

is temperature dependent. Both rate constants will decrease under winter conditions, and have opposing effects on the steady state O_3 concentration. Nevertheless, a decrease of 30% to 40% is calculated, assuming a drop of temperature from $+25^\circ$ to $-15^\circ C$, combined with an average solar altitude decrease from 50° to 10°.

Air Pollution Studies in Fairbanks, Alaska

The only directly relevant studies concerning air pollution under comparably severe winter conditions have been performed in the Fairbanks region. Although Fairbanks is only a comparatively small urban community (less than 20,000 inhabitants), several recent studies have noted that very high CO concentrations (Holty, 1973; Gilmore and Hanna, 1974; Jenkins et al., 1975) and particulate matter (Holty; Jenkins et al.,) can be present for prolonged periods in winter. In fact, on several occasions the U.S. Ambient Air Quality standards are drastically exceeded. High CO and hydrocarbon levels comparable to

TABLE 29

Temperature dependence of equilibrium constants for the SO_2-H_2O system

From Yue et al., 1975

$$SO_2 + H_2O \overset{K_1}{\rightleftharpoons} SO_2 \cdot H_2O$$

$$SO_2 \cdot H_2O \overset{K_2}{\rightleftharpoons} HSO_3^- + H^+$$

$$HSO_3^- \overset{K_3}{\rightleftharpoons} SO_3^= + H^+$$

Temperature (°C)	K_1 (M/atm)	K_2 (M)	K_3 (M)
25	1.24	.0174	6.3×10^{-8}
15	1.83	.0219	7.9×10^{-8}
10	2.25	.0247	8.9×10^{-8}
0	3.46	.0319	11.4×10^{-8}
-3	3.97	.0346	12.4×10^{-8}

Los Angeles have been correlated with automobile traffic, whereas the high particle count seems to be the result of necessary heating requirements. No data are available on oxidant concentrations, nor on the actual chemical composition of the particulates. These serious conditions occur when strong temperature inversions promoted by the low ground level temperatures are present, and can persist for several days. Another phenomenon, ice fog, is quite often present at the same time, and will be discussed briefly.

Benson (1970) defined ice fog as a form of air pollution which appears at temperatures below -35°C in populated regions where topography, combined with strong inversions, causes air to stagnate. In the Fairbanks area there are two types of sources for the formation of ice fog: automobile exhaust, which generally leads to much smaller ice particles than those from the other type of sources, power plants, cooling water ponds and furnaces. These sources could play a role in the oil sands area as well. It should be mentioned that -35°C as a limiting temperature is not as absolute as it might seem to be: pure water droplets would not generally freeze at temperatures above -40°C, while automobile exhaust compounds other than water seem to become effective as ice-forming nuclei at temperatures around -30°C, (Bowling, 1975). In addition to the strong reduction in visibility in ice fogs, another unpleasant side effect is that it traps other pollutants (Bowling mentions that the Fairbanks ice fog appears to have the same basic chemical ingredients as the Los Angeles smog, along with the accompanying eye irritation), and has a stabilizing effect on the unwanted temperature inversions.

These air pollution problems in Alaska are very relevant to winter conditions in the oil sands area, since the topographic (river valley) and climatologic (high frequency of light winds) conditions are favorable for temperature inversions and frequent occurrence of ice fogs, as has been noted by the Conservation and Utilization Committee, Oil Sands Climatological and Hydrological Research Task Force of the Alberta Government (OSCHRTF, 1974). Moreover, it is quite conceivable that the large amount of water vapor from the oil sand plants, together with high particle counts, will lead to ice fogs at temperatures even higher than

than $-30^{\circ}C$, since another prerequisite, supersaturation of the air with water vapor, is very easily established at low temperatures.

It has been suggested that the ice fogs which could possibly be formed in the oil sands region could be extremely dangerous due to the large amount of SO_2 emission, and be similar in their effect to the infamous London-type killer fog of December 1952 (OSCHRTF, 1974; Smith, 1975). On the other hand, the recent report of AOSERP (Croft et al., 1977) concludes that significant fog-pollutant interaction will not occur in the oil sands area. In any case, this serious suggestion has not been substantiated by experimental data, and urgently needs to be studied. It has been claimed that the Fairbanks type ice fog contains lacrimators, the origins and types of which are by no means clear, however, since the author (Bowling) describes similarities with Los Angeles type smog, in which PAN-type compounds are thought to be responsible for eye irritation. However, PANs are considered to be formed via photochemical reations which during the ice fog season in Fairbanks are unimportant because of the very low solar altitudes in Alaskan winters. Holty (1973) noted much higher SO_2 levels during ice fog episodes in Fairbanks, a fact which is compatible with the demonstrated efficiency of ice fogs in trapping pollutants. However, one could speculate that the accompanying low temperatures have an inhibiting effect on the rate of the aqueous phase oxidation of SO_2, as indicated in an earlier section of this chapter, and thus the increase in the SO_2 concentration could, in principle, reflect the inefficiency of oxidation. Furthermore, it is not known whether SO_2, trapped in ice particles (most likely together with air in that case) will be oxidized or not, and if so, at what efficiency.

Air Pollution in Rural Atmospheres

The oil sand plants are located in an essentially rural, wooded area, and will release pollutants into relatively clean air. The notion that a high enough stack will result in sufficient dilution of pollutant gases so that no major problems can be expected is too simplistic, as discussed earlier, and moreover could be exemplified by the barren areas around the Sudbury INCO stack. Plumes from industrial complexes in mainly rural environments can be identified over very large distances, as shown in the St. Louis (Missouri) air pollution studies (MISTT-study, cf. Whitby et al., 1976; Wilson et al., 1976). Especially during summer, when higher temperatures will lead to increased rate of discharge of hydrocarbons from various sources in the rural air, homogeneous oxidation of SO_2 and oxidant formation can be expected to occur. We have already mentioned that in the U.S. very high O_3 levels have been identified in rural areas, and seem to originate from the interaction of "spent" photochemical air pollution mixtures (i.e. low in industrial hydrocarbons and NO_x) with local hydrocarbons. Not only has naturally occurring methane been suggested as a possibility in this regard (Chameides and Stedman, 1976), but more importantly the terpenes could be very effective in this regard, as has recently been shown (Boyle, 1975). It is noteworthy in this regard that recently determined values of rate constants for the HO + terpenes reactions are very high indeed (Winer et al., 1976). Several unknown but possibly very unpleasant aerosol products could be the result of such reactions.

Conclusions

The authors conclude that many air pollution problems peculiar to the oil sand plants might be expected, for which basic chemical information is essentially unknown.

During summer, photochemical type air pollution is likely and homogeneous oxidations will be important. Interactions with naturally occurring terpenes can also occur but no information exists as to the formation of harmful aerosols. In particular, the SO_2 + terpene + NO_x reactions have not been studied. Aqueous phase oxidation reactions will probably take place close to the stacks of the oil sand plants, but its importance can not be assessed at the present time.

During winter photochemical reactions are probably less important, and heterogeneous chemistry will be dominant. The likelihood of ice fogs in which pollutants are trapped and possibly react (presumably slowly) to form hazardous substances is quite unsettling, but before jumping to conclusions a detailed study on the chemical events that might occur in an ice fog should be made.

4. FURTHER RESEARCH REQUIREMENTS

From the preceding literature review on the chemical transformation mechanisms in the atmosphere, the reader might have the impression that in almost all major areas of importance many unresolved problems exist, and that further research is needed. Although this is correct in principle, the actual situation is not so very disturbing and many of the basic mechanistic problems have been at least partly elucidated during the last decade. In the research outlines that we suggest, we have focussed on subjects that will probably be relevant with respect to the expected emissions from the oil sand recovery plants. In particular, emphasis will be given to the chemistry of SO_2 and the particular effects that might be expected from low temperatures and the large spread in solar irradiance in northern areas, as discussed in chapter 3 of this report or preceding chapter. The outlines are divided into four subheadings which reflect some differences in financial expenditures, time involved to complete the projects, the manpower involved and finally the degree of cooperation with other branches of physical sciences which will be required.

4.1 BASIC RESEARCH

There are many chemical reactions occurring in the atmosphere for which very little information is available. The required data may be the absolute reaction rates, the nature of the products formed, extinction coefficients, for example, and most of the projects can be immediately initiated in the authors' laboratories which are well equipped for such studies.

Many of the projects suggested as basic research projects ultimately involve the reactions of SO_2. We feel that in view of the high concentrations of SO_2 that are expected in the oil sands region, a better understanding of its transformation chemistry is of the utmost importance.

4.1.1 SO_2 - Reactions

4.1.1.1 Radical reactions

From the outlines in the text it becomes clear that homogeneous gas phase interactions between SO_2 and reactive radicals are probably very important steps in the oxidation chemistry of SO_2. It is somewhat discouraging that the data base on which this prediction is based is rather limited. In particular the following problems merit immediate attention:

- the $HOSO_2$ radical: this radical is probably formed by the interaction of HO radicals with SO_2 (Section 2.2.1.2) although this has not yet been definitely proven. In fact there have not been any spectroscopic or chemical studies performed on this radical and in view of the importance of the HO + SO_2 reaction under certain atmospheric conditions, a kinetic-spectroscopic investigation of the formation and decay kinetics of $HOSO_2$ is warranted.
- the SO_2 and CH_3O reaction: estimates shown in Table 12 predict a possible rate of 0.1% hr^{-1} for this reaction in the atmosphere, even though the reaction

  $$CH_3O + O_2 \rightarrow CH_2O + HO_2$$

  is considered to be dominant. The latter reaction is fairly slow, and therefore reactions of CH_3O with pollutants at the sub-ppm to ppm level are by no means impossible in the atmosphere, since they should be very rapid. A study of the $CH_3O + SO_2$ reaction therefore is very necessary and relevant.
- the $SO_2 + RO_2$ reaction: only one rate determination has been published for the reaction

  $$HO_2 + SO_2$$

  (Payne et al., 1973), while for the reaction

  $$CH_3O_2 + SO_2$$

  (Whitbeck et al., 1976) only a tentative upper limit has been reported. Referring to Table 12 it can be seen that these reactions might well constitute some of the most important oxidation steps of SO_2 in the atmosphere. Further studies into these reactions are therefore of the utmost importance for a clearer picture of the importance of homogeneous gas phase oxidation routes of SO_2.

4.1.1.2 Reactions of SO_2 + terpenes in air

We have indicated the strong possibility that natural terpenes evolved in the forested areas surrounding Fort McMurray might become involved in atmospheric transformation reactions, especially during summer when their concentrations are expected to be higher. It appears however that only the initial reaction rates of O_3 or HO with terpenes have been determined. We suggest a study of the products that are formed in such reactions, especially in the presence of SO_2. Since aerosols will be formed during these reactions, auxiliary studies will have to be undertaken on the chemical composition of the aerosols, the number, volume and surface distribution of the aerosol particles, the chemical precursor reactions that lead to aerosol formation and the influence of light.

4.1.1.3 SO_2 oxidation in the aqueous phase

As we have noted earlier SO_2 oxidation in the aqueous phase will probably be of major importance during the winter, since relatively little sunlight will be available to produce reactive radicals for homogeneous gas phase oxidation reactions. It was noted that several important factors for a proper evaluation of the actual importance of such oxidation routes of SO_2 are still poorly understood, and we will suggest some areas where improvement is most warranted. We might add here that from reviewing the existing literature we have the impression that aqueous phase oxidations of SO_2 have mainly been studied by investigators having a rather poor background in pure chemistry.

- noncatalysed oxidation of SO_2 in water: we have expressed our doubts as to whether oxidation of SO_2 in water will take place at all without the presence of at least traces of metal ions, and in this regard given attention to the work by Brimblecombe and Spedding (1974a). Modern analytical tools should enable one to establish the amount of trace contamination in water to levels of better than 5 x 10^{-8} M/l, which was apparently below the detection limit of these authors.
- temperature dependence of SO_2 oxidation in water: we have indicated in chapter 3 that strong temperature effects on the aqueous phase oxidation of SO_2 should be expected. However the experimental basis for this expectation is very poor indeed. The suggested activation energy for the true overall oxidation step

$$SO_3^{=} + \frac{1}{2} O_2 \rightarrow SO_4^{=}$$

is based on one particular study only, i.e. the copper-ion catalyzed oxidation of SO_2 in water (Barron and O'Hearn, 1966). Its implications are far-reacting however, (see discussion Chapter 3, pp. 141-142), and we feel a more thorough study in this field to be of the utmost importance.

- influence of other atmospheric pollutants on aqueous phase oxidation of SO_2: Barrie (1975) reported that O_3 increased the catalytic effect of Mn^{+2} ions upon aqueous phase oxidation of SO_2, while NO_2 had an inhibiting effect in this regard. In view of our expectations that the emission from the oil sands complex will increase the NO_x concentration of the air well above background levels, and that sizeable amounts of O_3 will also be present, we suggest that this aspect of the catalyzed aqueous phase oxidation of SO_2 should be studied in more detail.

4.1.2 Heterogeneous Reactions

Heterogeneous chemistry is rather poorly understood, compounded as it is with factors other than chemical reactions. Two areas in this field which seem to merit attention with respect to the understanding of the atmospheric chemistry in the Fort McMurray area are photochemical reactions of gases on particle surfaces (p. 104), and the scavenging of radicals by aerosols (p. 106).

4.1.3 Reactions of Peroxy Radicals

Studies of reactions of peroxy radicals (HO_2, CH_3O_2, etc.) with hydrocarbons are of high priority for a proper understanding of air pollution chemistry in general. This is also applicable to the oil sands area, in particular since calculations of the present authors (Bottenheim et al., 1976c) indicate that a substantial decrease in the rate of $NO \rightarrow NO_2 \rightarrow O_3$ conversion, and moreover the decrease in ultimate oxidant formation might be expected in this area during the winter. The main reason for this appears to be the fact that the peroxy radical chain reactions are not compensated for in winter, in contrast with the HO chain reactions. Studies on HO_2 reactions therefore should include the effect of temperature on the reaction rates.

4.1.4 Ice Fog Chemistry

We have discussed in Chapter 3 that in the oil sands area ice fogs might be formed during the winter. Although we indicated that it is very unlikely that large amounts of SO_2 will be trapped in these ice fogs, we feel that the chemistry of SO_2, NO_x, hydrocarbons etc. in ice fogs warrants attention in order to assess its probable effects. The occurrence of Los Angeles type lacrimators in Fairbanks ice fogs is rather mysterious, to mention one aspect. To our knowledge no studies at all have been reported which shed some light on the chemical reactions that could occur when pollutants are trapped in an ice fog, and it is therefore impossible to predict whether Fort McMurray area ice fogs are merely an aesthetic nuisance, compounded by high concentrations of primary pollutants due to a concomittant persistant temperature inversion, or that other much more harmful components are formed as well.

4.2 SMOG CHAMBER RESEARCH

It appears to us that there is an urgent need for experimentation with a smog chamber in order to study, in a controlled fashion, the complicated overall transformations that might occur in the oil sands area. No smog chamber studies at low temperatures have been reported, nor studies of chemical reactions in ice fogs. There are two basic reasons why such studies should be done with a smog chamber: (a) wall reactions, which would introduce a large heterogeneous interfering component in the reactions under consideration, can be reduced to a great extent by the much smaller surface to volume ratio in a smog chamber as compared to a conventional laboratory apparatus and (b) a smog chamber would enable one to monitor, (e.g. through multiple pass FTSIR) reactants and products at lower, and thus more realistic concentrations. While stressing the need for such studies it should be stated that smog chamber research is very costly. Thus, we are of the opinion that before embarking on such a project, an extensive background analysis is warranted in order to prevent a waste of time and money through basic construction errors. Input from other disciplines (engineering, physics) will also be required in order to develop a smog chamber facility equipped with such instrumentation from which unequivocal answers can be obtained regarding problems mentioned earlier. The building of a smog chamber facility has to be considered a long term project, involving several highly trained personnel. Such a project therefore requires a long term financial commitment from a sponsor and would only be initiated after a special report on a cost-benefit analysis of smog chamber research has been prepared.

4.3 MODELLING STUDIES

We have already initiated some modelling studies on the effects of low temperature and variations in solar irradiance on air pollution mixtures in northeastern Alberta (see Bottenheim et al., 1976c). We propose to continue and expand this work by considering contributions from molecules that were not included in our initial model, e.g. SO_2, NH_3 and H_2S. Such studies are extremely valuable in order to establish the importance of key reactions in atmospheric transformation chemistry. Moreover they should be considered as guidelines for evaluation of smog chamber experiments and as such form a necessary component of these experiments. The required manpower for simulation experiments is small and the main cost factor is the required computer time. The computer facilities of the University of Alberta are adequate in order to carry out the proposed computations.

4.4 IN SITU MONITORING

Although it is trivial to state that direct monitoring of the atmosphere should provide the final answers as to which reaction mechanisms are prevailing in the transformation chemistry, this is a vital and intensive aspect of atmospheric research in terms of retrievable information, manpower and funding. In particular we feel the following projects need to be considered with high priority.

4.4.1 Solar Spectrum Measurements and Albedo Factors

For a proper evaluation of the importance of photochemical reactions it is necessary to know the amount of sunlight available for such reactions. Although this can be reasonably well estimated by standard calculation methods, it would be better to measure this quantity for the northeastern Alberta region directly. Commonly, calculated results are compared with measurements by Nader and White (Envir. Sci. Techn., 3, 848 (1969)), which were performed at a much lower latitude (Cincinnati, Ohio, ~40°N). Such measurements should preferably not only establish total sunlight energy, but also establish the wavelength-intensity distribution of the sunlight, especially in the important cut off region around 3000 Å. Surface reflection (the albedo factor) is another variable which is important in this respect. It has been shown that the albedo factor is wavelength dependent (Coulson and Reynolds, J. Appl. Meteorol., 10, 1285 (1971)), being much lower at the shorter wavelength region of the solar spectrum around 3000-4000 Å, than at higher wavelengths. In this regard especially a good determination of the (wavelength dependence of) reflectance of snow is required.

4.4.2 Background Measurements

For a proper evaluation of the air pollution chemistry that will develop in the northeastern Alberta atmosphere we feel that it is extremely important to determine background levels of the atmosphere. The gaseous composition, in particular with respect to NO_x, O_3, CO, and hydrocarbons as well as SO_2, H_2S, and NH_3 should be known to be able to determine if future "air pollution episodes" are really due to the operation of the oil sand plants, and to which extent the natural background plays a synergistic role. Moreover, the particle content, and the occurrence of natural aerosols (summer time) should be measured. We have to stress again that such data should be collected during different seasons since meteorological conditions might have profound effects on the chemical constitution of the background atmosphere.

4.4.3 Plume Studies

In the introduction to this report we mentioned that the plume exhausted from an oil sand recovery plant would probably constitute an ideal system for the study of the developing chemical reactions from a pollution source in really clean air, and thus offer important advantages over other plumes that have been studied elsewhere so far. We suggest therefore that a major plume study project be undertaken. Such a study should comprise not only determination of meteorological data, so SO_2

and total sulphate, but also measurement of other gaseous constituents such as NO_x, O_3, hydrocarbons, and a fairly complete set of aerosol parameters. This report is not the place to go into details of the methodology of such a study, nor to do a cost-benefit analysis. As in the case of smog chamber research, such a project is costly, involves long range planning, and input from many scientific disciplines.

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6. APPENDIX

In this appendix are reproduced two tables showing the reactions and rate constants that have been used by us (Bottenheim et al. 1976c) to estimate the effect of solar altitudes and temperature on a general oxidant forming air pollution mixture. Table I shows average specific absorption rates for photochemical reactions as a function of the season. Table II shows the non photochemical reactions, where applicable as functions of temperature. Many of the rate constants in Table II were estimated, as described in detail in the original paper.

Table I. Specific Absorption Rates[a] of Photochemical Reactions.

		Winter	Spring	Summer	Autumn
P1.	$NO_2 + h\nu \rightarrow NO + O$	.098	.33	.48	.33
P2.	$HNO_2 + h\nu \rightarrow OH + NO$	.0057	.019	.028	.020
P3.	$HNO_3 + h\nu \rightarrow OH + NO_2$	$2x10^{-7}$	$9x10^{-6}$	$3x10^{-5}$	$1x10^{-5}$
P4.	$H_2CO + h\nu \rightarrow H_2 + CO$	$7.7x10^{-4}$	$3x10^{-3}$	$4.9x10^{-3}$	$3.1x10^{-3}$
P5.	$\rightarrow H + HCO$	$2\ x10^{-4}$	$9.4x10^{-4}$	$1.7x10^{-3}$	$1.0x10^{-3}$
P6.	$CH_3CHO + h\nu \rightarrow CH_4 + CO$	$2x10^{-6}$	$1.2x10^{-5}$	$2.4x10^{-5}$	$1.3x10^{-5}$
P7.	$\rightarrow CH_3 + HCO$	$3.4x10^{-5}$	$2.4x10^{-4}$	$4.8x10^{-4}$	$2.7x10^{-4}$
P8.	$O_3 + h\nu \rightarrow O(^1D) + O_2$	$1.1x10^{-6}$	$1.1x10^{-4}$	$6.3x10^{-4}$	$2x10^{-4}$
P9.	$\rightarrow O(^3P) + O_2$	$2.6x10^{-3}$	$7.3x10^{-3}$	$1\ x10^{-2}$	$7.7x10^{-3}$
P10.	$CH_3ONO + h\nu \rightarrow CH_3O + NO$	$1.8x10^{-2}$	$6.2x10^{-2}$	$9.2x10^{-2}$	$6.3x10^{-2}$
P11.	$H_2O_2 + h\nu \rightarrow 2OH$	$2.1x10^{-4}$	$8.4x10^{-4}$	$1.4x10^{-3}$	$8.8x10^{-4}$

[a] in min^{-1}

Table II Nonphotochemical Reactions and their Rate Constants[a]

No,	Reaction	Rate constant
1	$O_3 + O \longrightarrow 2O_2$	$2.8 \times 10^4 \exp(-2300/T)$
2	$O_3 + HO \longrightarrow O_2 + HO_2$	$2.4 \times 10^3 \exp(-1000/T)$
3	$O_3 + HO_2 \longrightarrow 2O_2 + HO$	$1.5 \times 10^2 \exp(-1250/T)$
4	$O_3 + NO \longrightarrow O_2 + NO_2$	$5.1 \times 10^3 \exp(-1533/T)$
5	$O_3 + NO_2 \longrightarrow O_2 + NO_3$	$1.8 \times 10^2 \exp(-2450/T)$
6	$O_3 + C_4H_8 \longrightarrow C_4H_8O_3$	$1.1 \times 10^2 \exp(-1100/T)$
7	$O + O_2 + M \longrightarrow O_3 + M$	$2.4 \times 10^{-6} \exp(510/T)$
8	$O + NO + M \longrightarrow NO_2 + M$	$1.1 \times 10^{-4} \exp(940/T)$
9	$O + NO_2 \longrightarrow O_2 + NO$	$2.5 \times 10^4 \exp(-300/T)$
10	$O + NO_2 \xrightarrow{M} NO_3$	2.9×10^4 (2nd order limit)
11	$O + CH_2O \longrightarrow HCO + HO$	$2.5 \times 10^4 \exp(-1400/T)$
12	$O + CH_3CHO \xrightarrow{O_2} CH_3COO_2 + HO$	$4.9 \times 10^4 \exp(-1400/T)$
13	$O + C_4H_8 \longrightarrow C_4H_8O$ (epoxide)	6.8×10^3
14	$O + C_4H_8 \xrightarrow{O_2} C_4H_8O_3$	2.7×10^4
15	$O(^1D) + H_2O \longrightarrow 2HO$	5.1×10^5
16	$O(^1D) + M \longrightarrow O + M$	8.5×10^4

Table II (continued)

17	$2NO + O_2 \longrightarrow 2NO_2$	1.2×10^{-10} exp(530/T)
18	$NO + NO_2 + H_2O \longrightarrow 2HONO$	2.2×10^{-9}
19	$NO + NO_3 \longrightarrow 2NO_2$	1.3×10^{4}
20	$NO + HO \xrightarrow{M} HONO$	8.2×10^{3} (2nd order limit)
21	$NO + HO_2 \longrightarrow NO_2 + HO$	7.3×10^{4} exp(-1200/T)
22	$NO + CH_3O_2 \longrightarrow NO_2 + CH_3O$	4.9×10^{3} exp(-500/T)
23	$NO + CH_3O \longrightarrow CH_3ONO$	1×10^{2}
24	$NO + CH_3O \xrightarrow{O_2} NO + CH_2O + HO_2$	1.7×10^{1}
25	$NO + HCOO_2 \longrightarrow NO_2 + HCO_2$	4.9×10^{3} exp(-500/T)
26	$NO + HCOO_2NO_2 \longrightarrow 2NO_2 + HCO_2$	4.9×10^{3} exp(-3000/T)
27	$NO + CH_3COO_2 \longrightarrow NO_2 + CH_3CO_2$	4.9×10^{3} exp(-500/T)
28	$NO + CH_3COO_2NO_2 \longrightarrow 2NO_2 + CH_3CO_2$	4.9×10^{3} exp(-3000/T)
29	$NO + CH_2\dot{O}\dot{O} \longrightarrow NO_2 + CH_2O$	4.9×10^{3}
30	$NO + CH_3CH\dot{O}\dot{O} \longrightarrow NO_2 + CH_3CHO$	4.9×10^{3}
31	$NO + C_4H_8(OH)(O_2) \xrightarrow{O_2} NO_2 + C_2H_4(OH)(O_2)$ $+ CH_3CHO$	2.4×10^{3} exp(-500/T)
32	$NO + C_2H_4(OH)(O_2) \longrightarrow NO_2 + HCOOH$ $+ CH_3O_2$	4.9×10^{3}

Table II (continued)

33	$NO + C_4H_8(HO_2)(O_2) \longrightarrow NO_2 + C_4H_8(HO_2)(O)$	$2.4 \times 10^3 \exp(-500/T)$
34	$NO + C_4H_8(CH_3O)(O_2) \xrightarrow{O_2} NO_2 + C_2H_4(CH_3O)(O_2) + CH_3CHO$	$2.4 \times 10^3 \exp(-500/T)$
35	$NO + C_2H_4(CH_3O)(O_2) \longrightarrow NO_2 + CH_3O + CH_3CHO$	4.9×10^3
36	$NO + C_4H_8(CH_3O_2)(O_2) \longrightarrow NO_2 + CH_4H_8(CH_3O_2)(O)$	$2.4 \times 10^3 \exp(-500/T)$
37	$NO + C_4H_7(O_2)(O_2) \longrightarrow NO_2 + C_4H_7(O_2)(O)$	$2.4 \times 10^3 \exp(-500/T)$
38	$NO_2 + NO_3 \longrightarrow N_2O_5$	5.6×10^3 (2nd order limit)
39	$NO_2 + NO_3 \longrightarrow NO + NO_2 + O_2$	$3.4 \times 10^2 \exp(-1000/T)$
40	$NO_2 + HO \longrightarrow HONO_2$	1.2×10^4 (2nd order limit)
41	$NO_2 + HO_2 \longrightarrow HONO + O_2$	4.4×10^1
42	$NO_2 + CH_3O \longrightarrow CH_3ONO_2$	4.8×10^2
43	$NO_2 + CH_3O \longrightarrow HONO + CH_2O$	4.8×10^1
44	$NO_2 + HCOO_2 \longrightarrow HCOO_2NO_2$	4.8×10^2
45	$NO_2 + CH_3COO_2 \longrightarrow CH_3COO_2NO_2$	4.8×10^2
46	$NO_3 + HO_2 \longrightarrow HONO_2 + O_2$	2.5×10^3
47	$NO_3 + CH_2O \longrightarrow HONO_2 + HCO$	$2.4 \times 10^3 \exp(-2250/T)$
48	$NO_3 + CH_3CHO \xrightarrow{O_2} HONO_2 + CH_3COO_2$	$1.2 \times 10^3 \exp(-2250/T)$

Table II (continued)

49	$NO_3 + C_4H_8 \longrightarrow HONO_2 + C_4H_7\cdot$	$7.3 \times 10^3 \exp(-2250/T)$
50	$N_2O_5 \longrightarrow NO_2 + NO_3$	$3.4 \times 10^{16} \exp(-10600/T)$ (1st order limit)
51	$N_2O_5 + H_2O \longrightarrow 2HONO_2$	2.5×10^{-3}
52	$HONO_2 + HO \longrightarrow NO_3 + H_2O$	$8.8 \times 10^2 \exp(-400/T)$
53	$HONO + HO \longrightarrow NO_2 + H_2O$	3.1×10^3
54	$2HONO \longrightarrow NO + NO_2 + H_2O$	$3.5 \times 10^3 \exp(-4365/T)$
55	$CH_4 + HO \xrightarrow{O_2} CH_3O_2 + H_2O$	$3.5 \times 10^3 \exp(-1710/T)$
56	$CH_2O + HO \longrightarrow HCO + H_2O$	2.1×10^4
57	$CH_2O + HO_2 \longrightarrow HCO + H_2O_2$	$1.2 \times 10^3 \exp(-3250/T)$
58	$CH_3CHO + HO \xrightarrow{O_2} CH_3COO_2 + H_2O$	2.2×10^4
59	$CH_3CHO + HO_2 \xrightarrow{O_2} CH_3COO_2 + H_2O_2$	$6.1 \times 10^2 \exp(-3250/T)$
60	$H_2O_2 + HO \longrightarrow HO_2 + H_2O$	$2.5 \times 10^4 \exp(-910/T)$
61	$HO + HO + M \longrightarrow H_2O_2 + M$	9.1×10^{-3}
62	$HO + HO \longrightarrow H_2O + O$	$1.5 \times 10^4 \exp(-550/T)$
63	$HO + HO_2 \longrightarrow H_2O + O_2$	$1.2 \times 10^5 \exp(-500/T)$
64	$HO + CO \xrightarrow{O_2} CO_2 + HO_2$	2.1×10^2
65	$HO + C_4H_8 \xrightarrow{O_2} C_4H_8(OH)(O_2)$	9.8×10^4
66	$HO + C_4H_8 \longrightarrow C_4H_7\cdot + H_2O$	1.2×10^4
67	$HO_2 + CH_3O_2 \longrightarrow CH_3O_2H + O_2$	1×10^2

Table II (continued)

68	$HO_2 + HO_2 \longrightarrow H_2O_2 + O_2$	$4.4 \times 10^4 \exp(-500/T)$
69	$HO_2 + HCOO_2 \longrightarrow HCOO_2H + O_2$	$2.1 \times 10^2 \exp(-500/T)$
70	$HO_2 + CH_3COO_2 \longrightarrow CH_3COO_2H + O_2$	$2.1 \times 10^2 \exp(-500/T)$
71	$HO_2 + C_4H_8 \xrightarrow{O_2} C_4H_8(HO_2)(O_2)$	$1.2 \times 10^3 \exp(-1100/T)$
72	$HO_2 + C_4H_8 \longrightarrow C_4H_7\cdot + H_2O_2$	$3.8 \times 10^3 \exp(-2810/T)$
73	$CH_3O_2 + CH_3O_2 \longrightarrow 2CH_3O + O_2$	1×10^2
74	$CH_3O_2 + CH_3O_2 \longrightarrow CH_3O_2H + \cdot CH_2O_2\cdot$	1×10^2
75	$CH_3O_2 + HCOO_2 \longrightarrow CH_3O + HCO_2 + O_2$	3.9×10^1
76	$CH_3O_2 + CH_3COO_2 \longrightarrow CH_3O + CH_3CO_2 + O_2$	3.9×10^1
77	$CH_3O_2 + C_4H_8 \xrightarrow{O_2} C_4H_8(CH_3O_2)(O_2)$	$7.8 \times 10^2 \exp(-1050/T)$
78	$CH_3O_2 + C_4H_8 \longrightarrow C_4H_7\cdot + CH_3O_2H$	$7.8 \times 10^2 \exp(-3000/T)$
79	$CH_3O + O_2 \longrightarrow CH_2O + HO_2$	$2.4 \times 10^2 \exp(-3300/T)$
80	$CH_3O + C_4H_8 \xrightarrow{O_2} C_4H_8(CH_3O)(O_2)$	$4.9 \times 10^2 \exp(-550/T)$
81	$CH_3O + C_4H_8 \longrightarrow C_4H_7\cdot + CH_3OH$	$7.6 \times 10^2 \exp(-2430/T)$
82	$HCO + O_2 \longrightarrow CO + HO_2$	8.4×10^3
83	$HCO + O_2 \longrightarrow HCOO_2$	1×10^2
84	$CH_2\dot{O}\dot{O} + O_2 \longrightarrow HCO_2 + HO_2$	$6.1 \times 10^2 \exp(-2040/T)$
85	$CH_3CH\dot{O}\dot{O} + O_2 \longrightarrow CH_3CO_2 + HO_2$	$6.1 \times 10^2 \exp(-2040/T)$
86	$HCOO_2 + HCOO_2 \longrightarrow 2HCO_2 + O_2$	3.8
87	$CH_3COO_2 + CH_3COO_2 \dashrightarrow 2CH_3CO_2 + O_2$	3.8

Table II (continued)

88	$HCOO_2 + CH_3COO_2 \longrightarrow HCO_2 + CH_3CO_2 + O_2$	3.8
89	$HCO_2 \xrightarrow{O_2} HO_2 + CO_2$	$1.9 \times 10^{15} \exp(-3500/T)$
90	$HCOO_2NO_2 \longrightarrow HONO_2 + CO_2$	$1.9 \times 10^{13} \exp(-2500/T)$
91	$CH_3CO_2 \xrightarrow{O_2} CH_3O_2 + CO_2$	$6 \times 10^{15} \exp(-2500/T)$
92	$C_4H_8O_3 \longrightarrow CH_3CHO + CH_3\dot{C}H(O_2)\cdot$	$1.9 \times 10^{16} \exp(-7500/T)$
93	$CH_3\dot{C}H(O_2)\cdot + O_2 \longrightarrow CH_3CH\dot{O}\dot{O} + O_2$	1×10^{4}
94	$CH_3\dot{C}H(O_2)\cdot + O_2 \longrightarrow O_3 + CH_3CHO$	$2.4 \times 10^{3} \exp(-500/T)$
95	$\cdot CH_2O_2^{:}+O_2 \rightarrow CH_2\dot{O}\dot{O} + O_2$	1×10^{4}
96.	$\cdot CH_2O_2^{:}+O_2 \rightarrow O_3 + CH_2O$	$2.4 \times 10^{3} \exp(-500/T)$
97.	$C_4H_8(HO_2)(O) \rightarrow HO + 2CH_3CHO$	$1.9 \times 10^{16} \exp(-7500/T)$
98.	$C_4H_8(CH_3O_2)(O) \rightarrow CH_3O + 2CH_3CHO$	$1.9 \times 10^{16} \exp(-7500/T)$
99.	$C_4H_7 \xrightarrow{2O_2} C_4H_7[O_2][O_2]$	$3.2 \times 10^{11} \exp(-5500/T)$
100.	$C_4H_7[O_2][O] \rightarrow HCO + CH_2O + CH_3CHO$	$1.9 \times 10^{14} \exp(-2500/T)$

[a] in units min^{-1} (1st order), $ppm^{-1}\ min^{-1}$ (2nd order), $ppm^{-2}\ min^{-1}$ (3rd order); preexponential factors tabulated at 25°C.

7. LIST OF AOSERP REPORTS

1		AOSERP First Annual Report, 1975
2	AF 4.1.1	Walleye and Goldeye Fisheries Investigations in the Peace-Athabasca Delta- 1975
3	HE 1.1.1	Structure of a Traditional Baseline Data System
4	VE 2.2	Preliminary Vegetation Survey of the AOSERP Study Area
5	HY 3.1	Evaluation of Wastewaters from an Oil Sands Extraction Plant
6		Housing for the North - Stackwall System Construction Report
7	AF 3.1.1	Synopsis of the Physical and Biological Limnology and Fishery Programs within the Alberta Oil Sands Area
8	AF 1.2.1	Impact of Saline Waters upon Freshwater Biota (A Literature Review and Bibliography)
9	ME 3.3	Preliminary Investigation into the Magnitude of Fog Occurrence and Associated Problems in the Oil Sands Area
10	HE 2.1	Development of a Research Design Related to Archaeological Studies in the Athabasca Oil Sands Area
11	AF 2.2.1	Life Cycles of Some Common Aquatic Insects of the Athabasca River
12	ME 1.7	Very High Resolution Meteorological Satellite Study of Oil Sands Weather, a Feasibility Study
13	ME 2.3.1	Plume Dispersion Measurements from an Oil Sands Extraction Plant
14	HE 2.4	Athabasca Oil Sands Historical Research Project (3 volumes) (in preparation)
15	HE 3.4	Climatology of Low Level Air Trajectories in the Alberta Oil Sands Area
16	ME 1.6	The Feasibility of a Weather Radar near Fort McMurray, Alberta
17	AF 2.1.1	A survey of Baseline Levels of Contaminants in Aquatic Biota of the AOSERP Study Area
18	HY 1.1	Alberta Oil Sands Region Stream Gauging Data(in preparation)
19	ME 4.1	Sulphur Dioxide Concentrations at Ground Level (in preparation)
20	HY 3.1.1	Evaluation of Organic Constituents (in preparation)
21		AOSERP Second Annual Report, 1976-77
22	HE 2.3	Maximization of Technical Training and Involvement of Area Manpower(in preparation)
23	AF 1.1.2	Acute Lethality of Mine Depressurization Water on Trout, Perch and Rainbow Trout (in preparation)
24	ME 4.2	Review of Dispersion Models Possible Applications in the Alberta Oil Sands Area (in preparation)
25	ME 3.5.1	Review of Pollutant Transformation Processes Relevant to the Alberta Oil Sands Area
26	AF 4.5.1	An Interim Report on an Intensive Study of the Fish Fauna of the Muskeg River Watershed of Northeastern Alberta (in preparation)

For information regarding any of these publications of the Alberta Oil Sands Environmental Research Program, please contact the Program Office.

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