ATMOSPHERIC CHEMISTRY: OVERVIEW AND FUTURE CHALLENGES

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Химические механизмы атмосферы (ХМА) являются основными компонентами в моделях переноса аэрозолей в атмосферной химии. В статье представлен обзор газовой химии пограничного слоя атмосферы и свободной тропосферы, которая должна быть включена в ХМА. Возникает необходимость в усовершенствовании существующих ХМА. Объясняются стоящие проблемы и дается описание основного направления исследований.

1. Introduction

For regional scale problems, tropospheric chemistry can be divided into two main groups: the chemistry of the background and polluted troposphere [1, 2]. The chemistry of the background troposphere is quite simple, if biogenically emitted organic compounds are not considered, due to the low concentrations of urban air pollutants. On the other hand, the polluted air cases, especially with highly varying Volatile Organic Compounds (VOCs), give rise to very complicated chemical reaction schemes.

A large variation of anthropogenic emissions into the atmosphere has been recognised as crucial for the Earth's climate and the atmospheric chemical composition [3]: combustion of biomass, coal production and use, petroleum production and use, natural gas production and use, and industrial processes. These emissions add chemical reactive sulfur-, nitrogen- and carbon-containing compounds, and atmospheric particles to the troposphere. Aside from the anthropogenic impact there is also a natural atmospheric source of sulfur-containing compounds from biological decay, combustion of organic matter and sea spray [1, 2].

The most important anthropogenic emitants in relation to tropospheric gas-phase chemistry are the nitrogen- and carbon-containing compounds. Among the nitrogen compounds NO and NO_2 are the most important from a chemical point of view, because these are highly active catalysts in most atmospheric chemical chains. NO_3 is very important for nighttime chemistry.

The major atmospheric gas-phase carbon-containing compounds are CO, CO_2, CH_4 and VOCs. CO_2 is inactive, CO and CH_4 react with HO resulting in the formation of HO_2 and CO_2, and CH_3O_2 and H_2O, respectively. This simple chemistry correspond to that of the background troposphere which is discussed in *Section 2.* On the other hand, the atmospheric composition

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and chemistry of VOCs are rather complex. It consists of a broad spectra of compounds containing almost all the different organic functional groups. Therefore, VOCs have a major impact on almost all the concentration levels of the important species in the polluted atmosphere, this is described in *Section 3*.

Particulate matter can either be solid or liquid. Particulate matter in the atmosphere may affect the atmospheric chemical production, reduce visibility, fog formation and precipitation, and reduce the solar radiation. For example, high concentrations of SO_2 can form sulfuric acid droplets by oxidation. This can serve as condensation nuclei for formation of small fog droplets, and a large range of heterogeneous processes can take place on particle surfaces, e.g. SO_2 and SO_4 are important chemical compounds in aerosol and cloud chemistry, and soot can interact with a number of gas-phase species including NO_2, O_3 and SO_2. This can affect the production of air pollutants.

There exist several future scientific challenges where the understanding of atmospheric chemistry should be improved. In *Section 4* some of these challenges are described. It is recognised that one of the central part in Atmospheric Chemistry Aerosol Transport Models (ACATMs) is the Atmospheric Chemical Mechanism (ACM) [4, 5]. The current state of the ACMs used in ACATMs today is described in *Section 5*. Finally, in *Section 6* a summary is given.

2. Chemistry of the Background Troposphere; an Overview

The chemical composition of the background troposphere is controlled by the chemistry of nitrogen oxides and its connection with that of O_3, CO, the simplest alkane methane (CH_4) and water vapour. The chemical interaction of these compounds can be described by the HO_x ($= HO+HO_2$) and NO_x ($= NO+NO_2$) cycles illustrated in fig. 1.

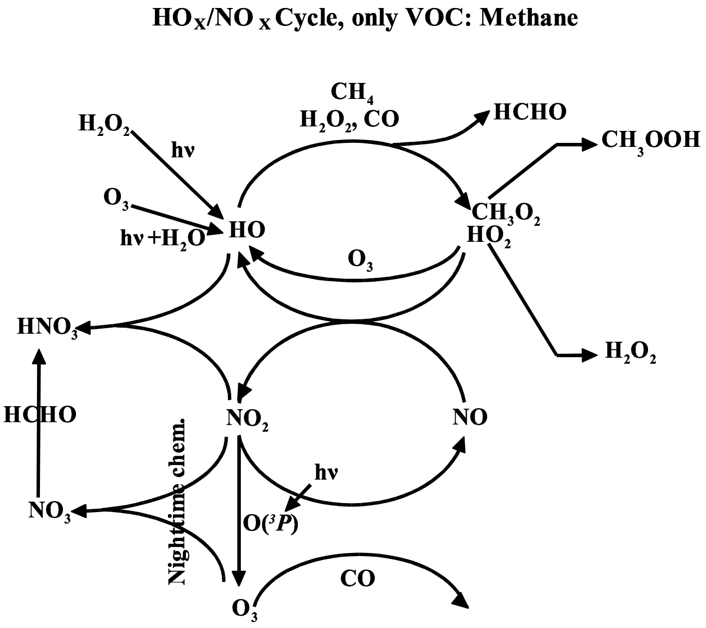


Fig. 1. Simplified illustration of the chemistry of the background troposphere.

2.1. Ozone, O_3

The major contributor to tropospheric O_3 is the termolecular recombination reaction:

$$O(^3P) + O_2 + M \rightarrow O_3 + M, \tag{1}$$

where M is an inert atom or molecule, in the atmosphere primarily O_2 or N_2. In order to form O_3 from this reaction we need $O(^3P)$ which is obtained from the photolysis of NO_2:

$$NO_2 + h\nu \rightarrow O(^3P) + NO \tag{2}$$

therefore reaction 1 will not be active during nighttime. Some of the formed O_3 is destroyed by reactions with NO, but this reaction then forms NO_2:

$$O_3 + NO \rightarrow NO_2 + O_2. \tag{3}$$

We see that reactions 1–3 are a closed cycle and therefore O_3 is not produced by these three reactions alone. These reactions show the conversion between NO_2 and NO with an interplay of O_3, and it illustrates the most important tropospheric source of O_3. The main atmospheric source of NO comes from combustion processes. NO is the dominant emitant from these processes, because approximately 90 % of anthropogenic emitted NO_x is NO. NO_2 is then formed by chemical reactions between peroxide radicals and NO as described in fig. 1. Even very low concentrations of atmospheric NO_2 initiate complex series of chemical reactions that produce photochemical smog.

O_3 has an important chemical impact in the troposphere even though only about 10 % of all atmospheric O_3 is located there. The reason is that O_3 determines the oxidation capacity by being the major source of HO:

$$O_3 + H_2O + h\nu \rightarrow O(^1D) + O_2 + 2\ HO. \tag{4}$$

HO is an important species in the troposphere since they initiate the oxidation of many gaseous hydrocarbons, organosulphur compounds, CO, NO_2, SO_2, etc. (see also *Section 3*).

The formed NO_2 in reaction 3 will in the daytime be removed according to the photolysis reaction 2. But during the nighttime it is possible that NO_2 reacts with O_3 forming NO_3 that together with NO_2 form an equilibrium with N_2O_5 or react further with HCHO making HNO_3. This does not occur during the daytime because NO_3 is rapidly removed by photolysis.

2.2. Carbon Monoxide, CO

As it was the case for O_3, the concentration level of HO is also strongly influenced by the presence of NO and NO_2 species. The background tropospheric concentration level of CO is around 100 to 120 ppbV [1, 2], therefore the reaction of HO with CO can initiate one of the atmospheric catalytic reaction chains: $HO \hookleftarrow\!\!\rightarrow HO_2$ followed by $NO \hookleftarrow\!\!\rightarrow NO_2$, (initial step CO+HO)

$$CO + 2\ O_2 \overset{HO \leftrightarrow HO_2,\ NO \leftrightarrow NO_2}{\rightarrow} CO_2 + O_3. \tag{5}$$

This reaction chain occurs in the presence of sufficiently large concentrations of NO.

For low NO conditions, it is more likely that the much less reactive reaction between HO_2 and O_3 will be the dominant reaction. This creates an $HO \leftrightarrow HO_2$ catalytic reaction chain that destroys O_3 instead of creating it (initial step CO+HO):

$$CO + O_3 \overset{HO \leftrightarrow HO_2}{\rightarrow} CO_2 + O_2. \tag{6}$$

At 298 K the second reaction chain will dominate when the concentration of O_3 is approximately 4050 times higher than that of NO. The primary chemical source of NO in the background troposphere comes from the photolysis of NO_2, while the dominant removing reactions of NO are reaction 3 and $HO_2+NO \rightarrow HO+NO_2$ (sub-reaction in the first chain). Within the rural and urban limit, the dominant reaction chain will almost always be the NO rich chain. Another important chain mechanism initiated again by reaction CO+HO also occurs:

$$2\ CO + O_2 \overset{HO \rightarrow HO_2 \rightarrow H_2O_2 \rightarrow HO}{\longrightarrow} 2\ CO_2. \tag{7}$$

The highly reactive and important atmospheric species HO, HO_2, H_2O_2, NO and NO_2 only acts as catalysts in these chain mechanisms. These mechanisms therefore compete with each other and two other possible O_3 destruction reactions: $O_3 + HO \rightarrow O_2 + HO_2$ and $O_3 + HO_2 \rightarrow 2\ O_2 + HO$. Both HO_2 and H_2O_2 are water-soluble and are therefore important agents in cloud-chemistry and water containing aerosols. Furthermore, HO_2 is a highly active chemical agent, whose self-reaction undergoes $\rightarrow H_2O_2 + O_2$. HO_2 react also with organic peroxy radicals.

2.3. Methane, CH_4

CH_4 chemistry is initiated by HO forming another radical, CH_3. The CH_3 starts chain reactions similar to the CO+HO case. Again we have two cases depending on the NO concentration. In the NO rich regime a rapid formation of O_3 and HCHO occurs:

$$CH_4 + 4\ O_2 \overset{NO \hookleftarrow NO_2,\ HO \hookleftarrow HO_2}{\longrightarrow} HCHO + H_2O + 2\ O_3. \tag{8}$$

In the NO poor regime, two competing chain reactions can occur

$$CH_4 + O_2 \overset{HO \hookleftarrow HO_2,\ HO_2 \hookleftarrow HO}{\longrightarrow} HCHO + H_2O \tag{9}$$

or

$$CH_4 + HO + HO_2 \rightarrow HCHO + 2\ H_2O. \tag{10}$$

The reactions that determine the switch between the high and low NO regimes are $CH_3O_2 + NO \rightarrow CH_3O + NO_2$ and $CH_3O_2 + HO_2 \rightarrow CH_3O_2H + O_2$ from chains 8 and 9/10, respectively. The magnitude of the rate constants for these two reactions show that all three chains dominate under “clean” and polluted conditions. For the two low regime cases, reactions $CH_3O_2H + h\nu \rightarrow CH_3O + HO$ and $CH_3O_2H + HO \rightarrow HCHO + H_2O + HO$ are the chain determining reactions. We see that the time of day determines which of the chains are the important one.

Both the low and high NO concentration regimes form the simplest peroxy radical, CH_3O_2. Due to this peroxy radicals' similarity with HO_2, it triggers similar reactions such as:

$$CH_3O_2 + HO_2 \rightarrow CH_3O_2H + O_2; \tag{11}$$

$$CH_3O_2H + HO \rightarrow CH_3O_2 + H_2O. \tag{12}$$

CH_3O_2 self-reaction is much more complicated than that of HO_2. Experimental investigation shows that four reaction channels are observed [6]:

$$CH_3O_2 + CH_3O_2 \rightarrow \begin{cases} 2\ CH_3O + O_2, \\ CH_2O + CH_3OH + O_2, \\ CH_3OOCH_3 + O_2, \\ CH_3OOH + CH_2O_2 \end{cases} \tag{13}$$

but due to the complexity of this self-reaction, many open questions remain [7, 8].

In reactions 8–10 HCHO is formed. HCHO is also a primary pollutant and therefore the chemistry of that compound is important. In this context the following reactions of HCHO exists: HCHO + $h\nu$ and HCHO + HO, both reactions produce HO_2 and CO, and NO_3 formed during nighttime can react with aldehydes forming HNO_3 and peroxy radicals (see fig. 1).

3. Chemistry of the Polluted Atmosphere; an Overview

In polluted air a large variety of VOCs from anthropogenic sources must be incorporated in the description of the chemistry. The CMD group under EUROTRAC made an European emission inventory with 68 different VOCs [9, 10], i.e. polluted air chemistry is very complex. In figs. 2 and 3 a schematic description of the most important polluted air chemistry is presented.

3.1. Alkane Chemistry

Alkanes can be transported over long distances due to their chemical stability, therefore they play an important role in tropospheric chemistry, e.g. the approximate residence time of CH_4 is 7 years[1]. HO can either attack alkanes on a terminal or internal carbon atom and thereby form alkyl peroxy radicals ($R\dot{O}_2$)

$$RH + HO + O_2 \rightarrow R\dot{O}_2 + H_2O. \tag{14}$$

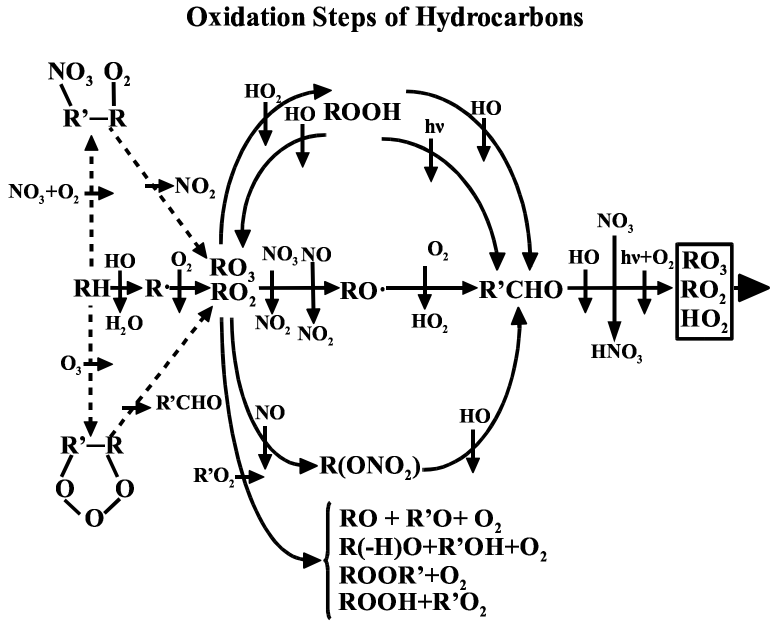

Oxidation Steps of Hydrocarbons

Fig. 2. Schematic presentation of the most important oxidation steps of atmospheric hydrocarbons in the polluted atmosphere. The reactions described by the dashed lines are only relevant for alkenes and alkynes.

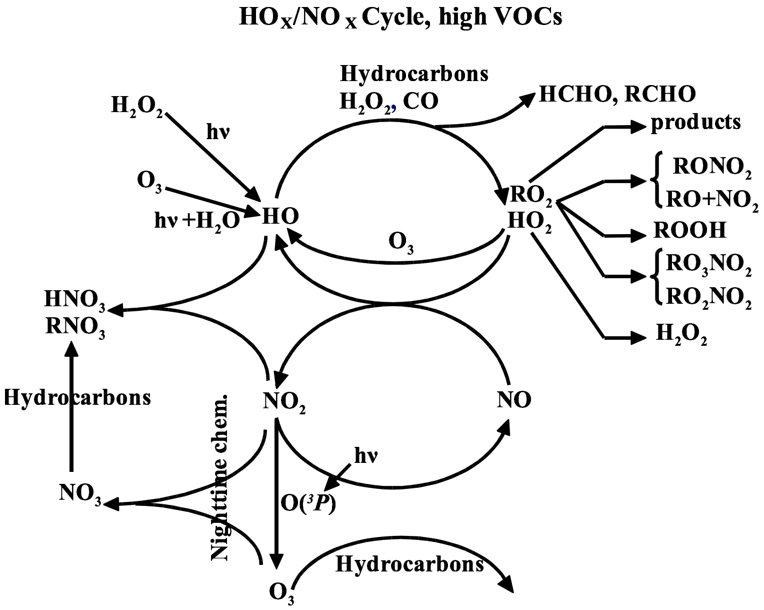


Fig. 3. Simplified illustration of the chemistry of the polluted atmosphere.

These alkyl peroxy radicals are highly reactive and can react with a large variety of atmospheric chemical compounds [11]:

$$\mathrm{R\dot{O}_2 + NO} \begin{cases} \overset{\mathrm{M}}{\rightarrow} \mathrm{RONO_2}, \\ \rightarrow \mathrm{R\dot{O} + NO_2}; \end{cases} \tag{15}$$

$$\mathrm{R\dot{O}_2 + NO_2 \overset{M}{\rightarrow} RO_2NO_2}; \tag{16}$$

$$\mathrm{R\dot{O}_2 + NO_3 \rightarrow R\dot{O} + NO_2 + O_2}; \tag{17}$$

$$\mathrm{R\dot{O}_2 + HO_2 \rightarrow ROOH + O_2}; \tag{18}$$

$$\mathrm{R\dot{O}_2 + R'\dot{O}_2 \rightarrow products}. \tag{19}$$

The alkoxy radicals ($\mathrm{R\dot{O}}$) either react with O_2, decompose or change to another isomer of $\mathrm{R\dot{O}}$. The $\mathrm{R\dot{O}} + O_2$ reaction leads to the formation of a carbonyl compound and HO_2. It can also decompose to a carbonyl compound and an organic peroxy radical after addition of O_2. Finally, it can undergo an isomerization that, after reaction with O_2 and NO, leads to the formation of a carbonyl and HO_2.

The chemical reaction of peroxy radical + peroxy radical is rather complex and will therefore not be described in detail in this paper. Its complexity involves a large number of different kinds of RO_2 that can be formed from emitted VOCs. Furthermore, many different kinds of reaction products can be formed from these different interactions between the peroxy radical + peroxy radical. For a more detailed description see Ref. [7, 8, 11, 12].

3.2. Alkene and Alkyne Chemistry

In contrast to alkanes, alkenes have a double bond, therefore these compounds are very reactive. Many different atmospheric chemical species can be added to the double bond: e.g. HO, O_3 and

NO_3 [1, 2, 8, 11]. For monoalkenes, dienes and trienes with non-conjugated double bonds, HO can be added to the double bond and followed by a rapid reaction with O_2 [8, 11]:

$$\mathrm{RCH{=}CHR' + HO} \overset{\mathrm{M}}{\rightarrow} \begin{cases} \mathrm{RCH(HO){-}\dot{C}HR'}, \\ \mathrm{R\dot{C}H{-}CH(HO)R'}; \end{cases} \tag{20}$$

$$\begin{aligned} \mathrm{RCH(HO){-}\dot{C}HR' + O_2} &\overset{\mathrm{M}}{\rightarrow} \mathrm{RCH(HO){-}CH(\dot{O}_2)R'}, \\ \mathrm{R\dot{C}H{-}CH(HO)R' + O_2} &\overset{\mathrm{M}}{\rightarrow} \mathrm{RCH(\dot{O}_2){-}CH(HO)R'}. \end{aligned} \tag{21}$$

We see that alkyl peroxy radicals are formed in both channels, and these can react as described under alkane chemistry.

Alkenes can react with O_3 and form a highly energy-rich ozonide as an intermediate. This ozonide decomposes automatically to a carbonyl compound and a highly energy-rich Criegee intermediate [2]:

$$\mathrm{R_1R_2C{=}CR_3R_4 + O_3} \rightarrow \begin{cases} \mathrm{R_1C(O)R_2 + R_3R_4COO^*}, \\ \mathrm{R_3C(O)R_4 + R_1R_2COO^*}. \end{cases} \tag{22}$$

The highly energy-rich Criegee intermediate can either be de-excited to a stable molecule or further decomposed:

$$\begin{aligned} \mathrm{R_1R_2COO^*} &\begin{cases} \overset{\mathrm{M}}{\rightarrow} \mathrm{R_1R_2COO}, \\ \rightarrow \text{products}, \end{cases} \\ \mathrm{R_3R_4COO^*} &\begin{cases} \overset{\mathrm{M}}{\rightarrow} \mathrm{R_3R_4COO}, \\ \rightarrow \text{products}. \end{cases} \end{aligned} \tag{23}$$

Refs. [8, 11] gives examples of products formed from different highly energy-rich Criegee intermediates. The stable Criegee intermediates react primarily with H_2O producing either HO or H_2O_2 plus products of the Criegee intermediate's aldehyde, carboxylic acid, ester and ether [12].

NO_3 is added to the double bond in alkenes in the same manner as HO [8, 11] followed by a reaction with O_2 which result in formation of peroxy radicals:

$$\mathrm{RCH{=}CHR' + NO_3} \overset{\mathrm{M}}{\rightarrow} \begin{cases} \mathrm{RCH(NO_3){-}\dot{C}HR'}, \\ \mathrm{R\dot{C}H{-}CH(NO)R'}; \end{cases} \tag{24}$$

$$\begin{aligned} \mathrm{RCH(NO_3){-}\dot{C}HR' + O_2} &\overset{\mathrm{M}}{\rightarrow} \mathrm{RCH(NO_3){-}CH(\dot{O}_2)R'}, \\ \mathrm{R\dot{C}H{-}CH(NO_3)R' + O_2} &\overset{\mathrm{M}}{\rightarrow} \mathrm{RCH(\dot{O}_2){-}CH(NO_3)R'}. \end{aligned} \tag{25}$$

The reactive part in the β-nitratoalkyl peroxy radicals formed by reaction 25 are the peroxy radical. This can react with NO, HO_2, and $R\dot{O}_2$ in a manner similar to that described in reactions 15, 18 and 19. The alkoxy radicals formed from β-nitratoalkyl peroxy radicals interaction with NO and peroxy radicals can either react with O_2, decompose or isomerize as described in section *Alkane Chemistry*. Contrary to alkane chemistry, β-nitratoalkyl peroxy radicals interact reversibly with NO_2 forming a thermally unstable nitrato peroxynitrate.

Knowledge of alkynes' impact on atmospheric chemistry is rather limited. Alkynes have a triple bond, therefore it is reasonable to believe that alkynes' chemistry is similar to that of the alkenes', but only alkynes' interaction with HO is considered to be important.

3.3. Carbonyl Chemistry

A large variety of carbonyl containing compounds exist in the troposphere since these compounds are both emitted from anthropogenic sources and formed chemically. In this section the most important chemistry of aldehydes, ketones and dicarbonyls are discussed.

3.3.1. Aldehydes

The three simplest aldehydes are the most important in the troposphere. HCHO and CH_3CHO are photolyzed as follows:

$$\mathrm{RCHO} + h\nu \rightarrow \begin{cases} \mathrm{R} + \mathrm{HCO}, \\ \mathrm{RH} + \mathrm{CO}, \end{cases} \tag{26}$$

while only the upper channel is important for CH_3CH_2CHO. Aldehydes react with HO and form alkoxy radicals

$$\mathrm{RCHO} + \mathrm{HO} \rightarrow \mathrm{R\dot{C}O} + \mathrm{H_2O} \tag{27}$$

and these radicals react further with O_2. For $\mathrm{H\dot{C}O}$ we have that

$$\mathrm{H\dot{C}O} + \mathrm{O_2} \rightarrow \mathrm{HO_2} + \mathrm{CO}, \tag{28}$$

while for higher aldehydes we obtain peroxy radicals,

$$\mathrm{R\dot{C}O} + \mathrm{O_2} \rightarrow \mathrm{RC(O)\dot{O}_2}. \tag{29}$$

These peroxy radicals can react with NO, making

$$\mathrm{RC(O)\dot{O}_2} + \mathrm{NO} \rightarrow \mathrm{RC(O)\dot{O}} + \mathrm{NO_2} \rightarrow \mathrm{\dot{R}} + \mathrm{CO_2} + \mathrm{NO_2} \tag{30}$$

with NO_2, forming

$$\mathrm{RC(O)\dot{O}_2} + \mathrm{NO_2} \overset{\mathrm{M}}{\rightarrow} \mathrm{RC(O)OONO_2} \tag{31}$$

and with HO_2, forming

$$\mathrm{RC(O)\dot{O}_2} + \mathrm{HO_2} \rightarrow \begin{cases} \mathrm{RC(O)OOH} + \mathrm{O_2}, \\ \mathrm{RC(O)OH} + \mathrm{O_3}. \end{cases} \tag{32}$$

Further reactions with alkyl peroxyl radicals occur, as described in section *Alkane Chemistry*. If $R = CH_3$ in reaction 31, PAN is formed.

3.3.2. Ketones

Photolysis data of $CH_3C(O)CH_3$ are the only ones available for ketones. $CH_3C(O)CH_3$ photolyzes to an acetyl peroxy radical and CH_3

$$\mathrm{CH_3C(O)CH_3} + h\nu \rightarrow \mathrm{\dot{C}H_3O} + \mathrm{\dot{C}H_3}. \tag{33}$$

The reactions between ketones and HO form

$$\mathrm{RC(O)R'} + \mathrm{HO} \rightarrow \begin{cases} \mathrm{\dot{R}[\text{-}H]C(O)R'} + \mathrm{H_2O}, \\ \mathrm{RC(O)\dot{R}'[\text{-}H]} + \mathrm{H_2O}. \end{cases} \tag{34}$$

These products depend highly on which H-atom is extracted from the ketones, see for instance Refs. [8, 11]. We see that reaction 34 forms carbonyl radicals where the carbonyl group remains intact. This reaction controls the isomer product formation. Therefore, the chemistry of these carbonyl radicals follows the chemistry described in the section *Alkane Chemistry*.

3.3.3. Saturated Dicarbonyls

Within the class of saturated dicarbonyls, glyoxal and methylglyoxal are of central importance in the chemical reaction scheme of the troposphere. These two compounds have three photolysis channels [14]:

$$\mathrm{RCOCHO} + h\nu \rightarrow \begin{cases} \mathrm{RH} + 2\ \mathrm{CO}, \\ \mathrm{RCO} + \mathrm{HCO}, \\ \mathrm{RCHO} + \mathrm{CO}. \end{cases} \tag{35}$$

The important atmospheric reactions of glyoxal and methylglyoxal are their interactions with HO and O_2. Glyoxal and methylglyoxal react with HO forming oxy radicals:

$$\mathrm{RCOCHO} + \mathrm{HO} \rightarrow \mathrm{RCO\dot{C}O} + \mathrm{H_2O}. \tag{36}$$

For glyoxal, the oxy radical formed can either decompose to $\mathrm{H\dot{C}O}$ or react with O_2:

$$\mathrm{HCO\dot{C}O} \begin{cases} \rightarrow \mathrm{H\dot{C}O} + \mathrm{CO}, \\ \overset{O_2}{\rightarrow} \mathrm{HCOC(O)O\dot{O}}, \\ \overset{O_2}{\rightarrow} \mathrm{HO_2} + 2\ \mathrm{CO}. \end{cases} \tag{37}$$

Under atmospheric conditions, methylglyoxal does not react with O_2, it only decomposes to $\mathrm{CH_3\dot{C}O}$ and CO.

3.4. Organic Nitrate and Nitrite Chemistry

Due to anthropogenic emissions of NO_x, a large variety of nitrogen containing organic compounds can be formed in the troposphere. Alkyl nitrates are primarily formed by photooxidation of alkanes by NO_x. The reactions of alkyl nitrates with NO_3 and O_3 are expected to be so slow that they have no importance in the atmosphere. Thus, the loss of alkyl nitrates takes place via a H-abstraction reaction between HO and alkyl nitrates:

$$\mathrm{RONO_2} + \mathrm{HO} \rightarrow \mathrm{\dot{R}[\text{-}H]ONO_2} + \mathrm{H_2O}. \tag{38}$$

These alkyl nitrate radicals undergo reactions with NO and O_2 forming alkyl nitrate oxy radicals which either decompose, isomerize or react with O_2:

$$\mathrm{R^1\dot{C}HR^2CH(ONO_2)R^3} + \mathrm{O_2} + \mathrm{NO} \rightarrow \mathrm{R^1C\dot{O}HR^2CH(ONO_2)R^3} + \mathrm{NO_2} \tag{39}$$

and

$$\mathrm{R^1C\dot{O}HR^2CH(ONO_2)R^3} \begin{cases} \rightarrow \mathrm{R^1CH\dot{O}} + \mathrm{\dot{R}^2CH(ONO_2)R^3}, \\ \overset{O_2}{\rightarrow} \mathrm{R^1COR^2CH(ONO_2)R^3} + \mathrm{HO_2}, \\ \rightarrow \text{isomerization}. \end{cases} \tag{40}$$

Alkyl nitrates and nitriles can be photolysed to alkoxy radicals:

$$\begin{aligned} \mathrm{RONO_2} + h\nu &\rightarrow \mathrm{R\dot{O}} + \mathrm{NO_2}, \\ \mathrm{RONO} + h\nu &\rightarrow \mathrm{R\dot{O}} + \mathrm{NO}. \end{aligned} \tag{41}$$

The chemistry of alkoxy radicals is described in section *Alkane Chemistry*. The photolysis of alkyl nitrites occurs very rapidly and therefore its reaction with HO is negligible under atmospheric conditions.

Presently, the only studied peroxyacyl nitrate is PAN. PAN's interaction with HO is slow in the lower troposphere. It is not expected to photodissociate in the troposphere and it is not highly water soluble. This enables PAN to be transported over long distances. Instead, the dominant loss of PAN is the unimolecular thermal decomposition reaction:

$$\mathrm{PAN}\ (+\mathrm{M}) \rightarrow \mathrm{CH_3C(O)O\dot{O}} + \mathrm{NO_2}\ (+\mathrm{M}), \tag{42}$$

which is the reverse of reaction 31. The peroxy radical formed can decompose further according to reaction 30. Therefore, PAN acts as a reservoir for NO_x [1].

3.5. Aromatic Chemistry

Two groups of aromatic compounds are important to consider in tropospheric chemistry: Mono- and Polycyclic Aromatic Hydrocarbons (MAHs, PAHs). The chemistry of aromatic compounds either involves the substituent groups or the aromatic ring. Anthropogenic aromatic compounds react primarily with HO [2, 11, 13], and in this case the addition of HO to the aromatic ring is the dominant reaction [2, 11, 13]. In the Regional Atmospheric Chemistry Mechanism (RACM) [12] ≈90 % is considered to be addition of HO and ≈10 % a reaction with the substituent groups on the aromatic ring. The reaction of HO with aromatic compounds (aro–$\mathrm{(CH)_6}$ symbolise benzene) can be illustrated as

$$aro\text{–}\mathrm{(CH)_5(CHR)} + \mathrm{HO} \begin{cases} \rightarrow aro\text{–}\mathrm{(CH)_5\dot{C}R} + \mathrm{H_2O}, \\ \overset{\mathrm{M}}{\rightleftharpoons} aro\text{–}\mathrm{(\dot{C}H)_4(CHR)(CH(HO))} + \text{other isomers.} \end{cases} \tag{43}$$

The chemistry of the substituent groups on the aromatic compound is identical to that described in the sections concerning the chemistry of alkane, alkene, alkyne, carbonyl, organic nitrates or organic nitrites chemistry, depending on which functional group CHR belongs to [11].

Even though HO addition to the aromatic ring is the most important channel, the product radical has a limited lifetime of ≈0.3 s at 298 K and 1 atm. before it breaks into the reactants again. A comparison of the rate constants between the aromatic radicals formed in reaction 43 and possible atmospheric compounds shows that, at 298 K and 1 atm., the important reactions are the reactions with $\mathrm{O_2}$ and $\mathrm{NO_2}$ [13]. Presently, there are still many uncertainties related to the chemistry of the aromatic radicals and the product yields [1, 12, 13], but the following possible reaction pathways are assumed; the reactions with $\mathrm{NO_2}$ can add $\mathrm{NO_2}$ to the aromatic ring (with $\mathrm{H_2O}$ as a residue product) and/or from cresol (with HONO as a residue product). The reaction with $\mathrm{O_2}$ forms peroxy radicals, where $\text{–}\mathrm{(O\dot{O})}$ is directly attached to the aromatic ring. We will in this context not go into further detail since this chemistry still is uncertain. For further information consult Refs [1, 12, 13].

4. Chemistry of the Troposphere, Future Challenges

Tropospheric inorganic chemistry is relatively well known. Even though the knowledge of organic atmospheric chemistry has grown significantly since 1980s there are still many uncertainties related to many aspects of our understanding. Some examples are:

— chemistry of high molecular weight organic compounds (e. g. aromatic and biogenic);
— radical reactions (e.g. peroxy — peroxy radical reactions);
— photo-oxidation processes (quantum yields and absorption cross sections);
— heterogeneous processes.

ACMs have over the years been based on measured rate constants and mechanistic studies from laboratory experiments. Due to experimental limitations ACMs today represents best the atmosphere at temperatures near 298 K [6, 14]. While an ACM shall be valid from 200 to 300 K in order to represent the troposphere and stratosphere. Furthermore, the uncertainty in rate parameters are usually greater for the more reactive organic compounds. In the following we will outline the areas of atmospheric chemistry which we find have the highest uncertainties.

4.1. Uncertainties in Aromatic Atmospheric Chemistry

The chemistry if aromatics is still highly uncertain. The uncertainties are related both to the rate constants the of aromatic chemistry and the yields of the formed products. As indicated by fig. 2 the first oxidation step of emitted hydrocarbons is its reaction with HO. Of these kinds of reactions only 23 with MAHs and 16 with PAHs have been studied. In tables 1 and 2 a list of some of the laboratory studies of this type of reactions is presented. Table 1 presents the systems which only have been studied by one laboratory. Table 2 describes some systems which have been studied by more than one laboratory. Two things can be concluded from these tables. First — most of the rate constants of HO with aromatic compounds are still highly uncertain, even for one of the most abundant and important PAH anthracene. Second — results from only one laboratory are insufficient for estimating the rate constant. Furthermore, rate constants for only 20 of the many aromatic products of the oxidation of MAHs have been determined (14 are single studies). For the non-aromatic products, from the oxidation of the aromatic compounds, only 25 studies have been performed and 19 of those are single studies.

Perhaps the highest uncertainty related to the oxidation of MAHs and PAHs is the nature and yields of the compounds formed, especially the HO initiated reactions. The reason is that product studies of HO + aromatics from chamber experiments show carbon mass losses of more than 30 %, typically more than 50 %. The current understanding of the first two steps

Table 1

Studies of reactions between aromatic compounds and HO which only have been performed by one laboratory

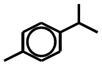
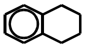
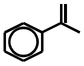
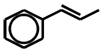
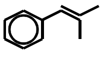
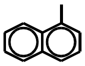
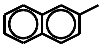
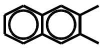
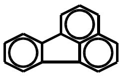
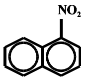
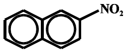
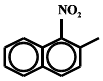
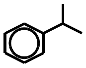
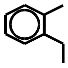
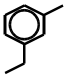
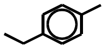
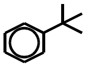
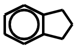
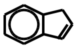
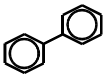
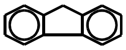
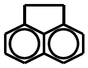
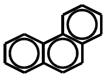
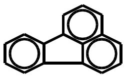
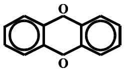
Name	**Structure**	**Name**	**Structure**
p-cymene		tetralin	
α-methyl-styrene		β-methyl-styrene	
β-β-dimethyl-styrene		1-methyl-naphthalene	
2-methyl-naphthalene		2,3-dimethyl-naphthalene	
acenaphthalene		flouranthene	
1-nitro-naphthalene		2-nitro-naphthalene	
2-methyl-1-nitro-naphthalene			

Table 2

Rate constant uncertainties for the reactions between aromatic compounds and HO which have been performed by more than one laboratory

Name	**Structure**	**Uncertainty**	**Name**	**Structure**	**Uncertainty**
iso-propyl-benzene		< 30%	*o*-ethyl-toluene		< 30%
m-ethyl-toluene		< 30%	*p*-ethyl-toluene		< 30%
tert-butyl-benzene		< 30%	indane		< 30%
indene		< 30%	biphenyl		30%
flourene		factor of 1.5	acenaphtene		factor of 2
phenanthrene		factor of 2	dibenzo-*p*-dioxin		factor of 1.5
dibenzofuran		30%	anthracene		$[18; 289]\times10^{-12}\mathrm{cm}^3$

in the oxidation mechanism of aromatics (aromat+HO→adduct, followed by adduct+O_2) is understood. However, the subsequent reaction mechanisms are not, and the relative importance of the many possible radical species and reaction pathways is unclear. Hence, the knowledge of the overall atmospheric oxidation mechanisms of the aromatic compounds are at present rather limit. Therefore, it is quite possible that some yet unidentified reactions pathways exists. Highest priority — a study of the products from the oxidation of most important aromatics: toluene, xylenes and trimethyl-substituted benzenes.

For many simple atmospheric important carbonyl molecules (e.g. HCHO, $CH_3C(O)CH_3$, CH_3CHO, CH_3CH_2CHO, CHOCHO and CH_3COCHO) and NO_2 the photochemistry has been determined. That means the cross-section and quantum yields. These quantities are therefore also included in most of the developed lumped ACMs. It is therefore reasonable to believe that the photolysis of MAHs and PAHs with carbonyl groups could have an important impact on atmospheric chemistry. Gas-phase spectra of some MAHs have been measured, e.g. benzaldehyde. But gas-phase spectra of nitrobenzaldehyde, nitrobenzene, nitronaphthalenes and their methyl-substituted derivatives should be determined. On the other hand, the photochemistry of phenols and cresols appears to be relatively unimportant within the troposphere. For PAHs, the photodissociation of the HO-substituted (e. g. hydroxynaphthalenes and hydroxyphenanthrenes) and nitrophenolic compounds (e. g. the nitro- and polynitrophenols) could perhaps be significant in the troposphere.

4.2. Uncertainties in Non-Aromatic Atmospheric Chemistry

Rate coefficients for HO + alkene, for most of the alkenes which have been studied, appears to be reasonably accurate. The database for peroxy radical + peroxy radical reactions, and peroxy radical reactions with HO_2 are very limited. Only rate constants of 19 peroxy radical self-reactions have been reported [7, 8]. Only for 10 of these reactions the temperature dependence have been determined. For the cross-reactions the number of investigated reactions is even more sparse, only 18 reactions have been investigated, for 6 of these the temperature dependence has been determined. Compared with the description in *Section 3*, fig. 2, and the fact that approximately 68 different VOC emitants are assumed to be important to include in ACATMs in Europe [9, 10], we can conclude that this chemistry is very roughly described in ACATMs.

If we assume that each peroxy radical can react with every other peroxy radical in an ACM, and assume that each reaction has three different reaction channels, then

$$\text{the total number of reactions} = \mathrm{n} \times \frac{3\,\mathrm{n}\ +\ 1}{2}, \tag{44}$$

where n is the number of peroxy radicals. Thus for only 10 peroxy radicals there can easy be up to 165 reactions, but only 15 product studies have been reported. The problem become even more complex, since the decomposition of the alkoxy radicals is important and it is expected to be sensitive to both temperature and pressure.

The alkene reaction with NO_3 44 different systems and rate constants have been investigated. However, only 21 of these studies involve more than one laboratory group. As described in *Section 4.1* it is important that several independent groups derive additional measurements of the 23 other alkene + NO_3 reactions. The problem with these types of reactions, compared with HO + alkene, is that the rates extend over several orders of magnitude.

Probably the reactions of greatest uncertainties are that of O_3 + alkene. The mechanism described by reactions 22 and 23 is reasonable well established, since primary ozonides have been directly detected at low temperatures in the condensed phase [15]. The main problem for these reactions which need to be solved can be summarised as follows:
— direct determination of the rate coefficients;
— which products are formed from the reactions?
— determination of rates of the stabilised Criegee biradical with NO, NO_2, H_2O and SO_2;
— can the stabilised Criegee biradical react with NO_xs?
— to what extent are HO-radicals generated by the O_3–alkene reactions?
Ozonolysis of alkenes are mainly important in urban polluted areas.

4.2.1. Uncertainties in Aromatic Chemistry Related to Alkene-like Substituents on the Aromatic Ring and Non-Aromatic Products from Aromatic Oxidation

NO_3 + aromatics appear to be unimportant in the atmosphere unless a group attached to the aromatic ring has a double bound (ex. indene, styrene), or have an -OH group attached to the aromatic ring (ex. phenols, cresols). However, very few studies have been performed: NO_3 + phenol, *o*-, *m*-, *p*-cresol or *m*-nitro-phenol, and these studies in most cases give rates with uncertainty factors larger then 1.5.

Reactions of aromatics with O_3 are only important if the MAHs have substituents with carbon double or triple bounds, see discussion above. However, in view of the relative unimportance of O_3 with aromatics it has a low priority.

During the oxidation of aromatics ring-opening mechanisms are active forming unsaturated dicarbonyls. Three classes of dicarbonyls are formed in this oxidation: 1,2-, 1,4- and 1,6-dicarbonyls. However, the nature and yields of many of these products remain uncertain often unknown.

5. Current State of Lumped Atmospheric Chemistry Mechanisms

In order to understand the effects of emissions from anthropogenic and biogenic sources on the air quality ACATMs are used. It is recognised that one of the central parts in ACATMs is the ACM [4, 5] if realistic concentrations of surface ozone and other air pollutants shall be predicted. It is therefore important that the ACM includes all the important atmospheric chemical reactions and that the utilised rate constants and product yields for the gas-phase reactions, and the quantum yields and absorption cross sections for the photolysis reactions are of high accuracy. This is not an easy task and because the chemical reactivity of the organic compounds in the polluted troposphere is extremely complicated and many uncertainties are still related to atmospheric chemistry, see *Section 4*. There have been developed highly detailed atmospheric chemical mechanism, e.g. the Master Chemical Mechanism (MCM) [16, 17]. The MCM includes more than 2400 chemical species and more than 7100 chemical reactions. Due to computational demands on processor time and memory it is not possible to incorporate such a complex chemical mechanism in ACATMs today.

A large variety of lumped ACMs have been developed during the last couple of decades for use in ACATMs. Examples of such mechanisms are given in table 3. Even though some of these mechanisms are rather old and therefore do not have the newest chemistry included they are still used in ACATMs, and it is not easy/possible to update the mechanism with the newest rate constant and emission information since knowledge to how the mechanism is lumped together is needed. However, the most used ACMs in Europe today are CBM-IV, EMEP and RACM. The important impact of atmospheric chemical mechanisms in ACATMs have given rise to several comparison studies of ACMs over the years. A presentation and the main conclusions

Table 3

Overview of the most frequently used Lumped ACMs in ACATMs

Mechanism Abbreviation	**Developed**	**Number of**		Ref.
		Species	**Reactions**	
ADOM-II	USA, 1986	47	114	[18]
CBM-IV	USA, 1989	27	63	[19]
RADM2	USA, 1990	63	158	[20]
SAPRC-90	USA, 1990	60	155	[21]
IVL	Europe, 1997	715	1640	[22]
EMEP	Europe, 1997	79	141	[23]
RACM	USA, 1997	77	237	[12]
SAPRC-99	USA, 1999	74	211	[24]

Acronyms:

ADOM-II: Acid Deposition and Oxidant Model II.
CBM-IV: Carbon Bond Mechanism IV.
RADM2: second generation Regional Acid Deposition Model.
SAPRC-90: Statewide Air Pollution Research Center-90.
IVL: Swedish Environmental Research Institute.
EMEP: European Monitoring and Evaluations Program Meteorological Synthesizing Centre-West.
RACM: Regional Atmospheric Chemistry Mechanism.
SAPRC-99: Statewide Air Pollution Research Center-99.

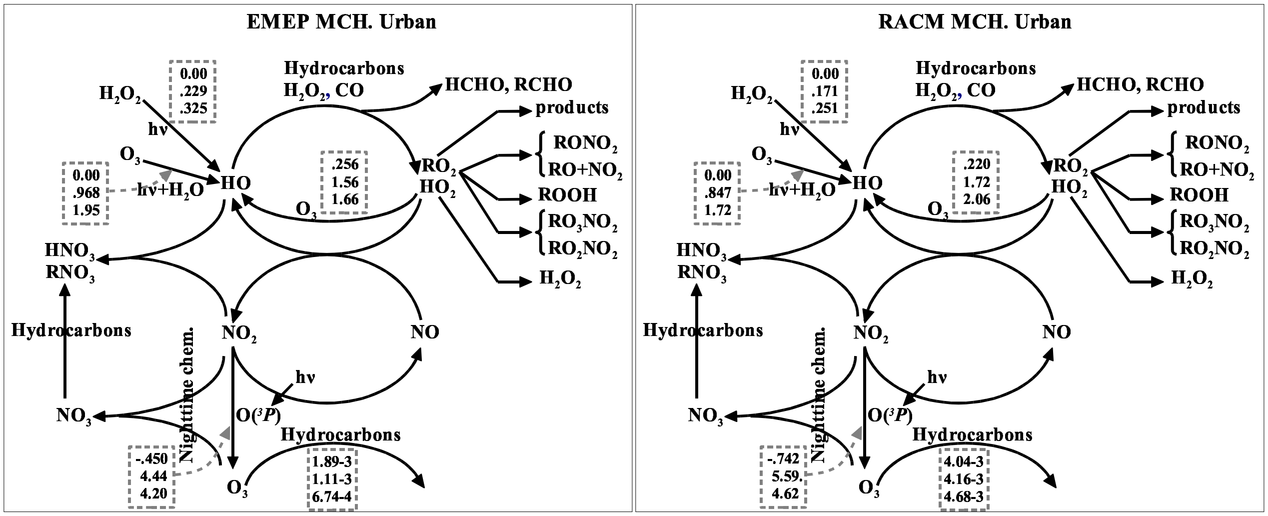


Fig. 4. Simplified illustration of the chemistry of the polluted atmosphere (description see *Section 4*) with the results of a simulation from EMEP and RACM of chemical production and loss of O_3. The numbers in the figure are the production (the arrow in the lower left corner that goes to O_3) and losses (the rest of the numbers) in ppbV/hour of O_3 for a typical polluted European location. The numbers correspond to: upper — midnight after 2.5 days simulation, lower — noon after 3 days simulation, and in between — 9 o'clock in the morning after 2.875 days simulation. Notation: 1.18-6 mean $1.18 \cdot 10^{-6}$.

from these comparison studies are described by Gross and Stockwell [25].

Due to the frequent use of EMEP and RACM in European ACATMs Gross and Stockwell [25] performed a comprehensive comparison of these two mechanisms based on typical atmospheric boundary layer conditions ranging from rather rural to rather polluted (231 box model simulations for each mechanism). All the simulations were started at local noon and run for three days and a summertime location in France. The mechanism comparison showed that concentrations predicted by the two mechanisms in general were very close to each other. This can also been seen in fig. 4 where the chemical production/loss for O_3 formation simulated by EMEP and RACM is rather similar after the mechanisms have reacher equilibrium. However, both mechanisms are based on the same guessed rates and reactions, i.e. the same amount of uncertainty. Nevertheless, few of the simulated scenarios gave very different results for the two mechanisms. This shows that only one "typical" scenario (which often has been considered to be sufficient) is not enough in order to make a proper mechanism comparison.

5.1. Deficiencies in Lumped Atmospheric Gas-Phase Chemistry Mechanisms

Besides the uncertainties in the atmospheric organic chemistry described in *Section 4* lumped ACMs have also some other deficiencies. Many of the chemical compounds emitted from the continent and marine biosphere have an impact on the chemical composition, aerosol formation and aerosol growth. In table 4 typical annual biogenic VOC and sulfur emissions from different natural sources are presented.

The importance of BVOCs and sulfur emissions on the regional air quality is not completely quantified, since it is extremely difficult to estimate these compounds emissions and chemistry.

5.1.1. Uncertainties in the Treatment of Biogenic Compounds

Several hundreds different BVOCs have been identified, most well known are ethene, isoprene and monoterpenes, see table 4. BVOC emissions depends highly on the vegetation type, therefore BVOC emission inventories are calculated from land-use data. However, BVOC emissions from plants are usually only given for isoprene and monoterpenes, as shown in table 4 these are also the most important BVOCs. BVOC emission inventories are still extremely uncertain (uncertainty factor from 2.5 to 9), furthermore the following questions need to be answered:

- How shall the emissions of monoterpenes be split into specific species? (α-pinene, β-pinene, limonene etc.).
- How good are the land-use data bases to describe the current BVOC emissions?
- How good are seasonal changes of vegetation described in the land-use data bases?
- How good are human changes of vegetation described in the land-use data bases?

The understanding of biogenic chemistry is very incomplete. Today only one lumped ACM treat other biogenic emitted species than isoprene, that is RACM. RACM has to other biogenic species than isoprene: API (α-pinene and other cyclic terpenes with more than one double bound) and LIM (d-limonene and other cyclic diene-terpenes).

Commonly used lumped mechanisms (CBM-IV, RADM2, EMEP and RACM) use the photooxidation mechanism of isoprene from Paulson et al. [28, 29]. Resent results from Ruppert [30] showed that using this mechanism e.g. destroy O_3 too rapid. That means the isoprene chemistry in these ACMs needs to be improved.

Table 4 (*a*)

Estimated global annual biogenic and sulfur emissions in Tg/year. The biogenic emissions are from Guenther et al. [26] and the sulfur emissions are from Berresheim et al. [27]:
a — excluding sea-salt contributions; *b* — excluding soil dust contributions

Global Biogenic VOC Emission Estimates (Tg/yr)

Source	**Isoprene**	**Monoterpene**	**Other VOCs**	**Total**
Woods	372	95	177	821
Crops	24	6	45	120
Shrub	103	25	33	194
Ocean	0	0	2.5	5
Other	4	1	2	9
Total	503	127	260	1150

Table 4 (*b*)

Global Sulfur Emission Estimates (Tg/yr)

Source	**H_2S**	**DMS**	**CS_2**	**OCS**	**SO_2**	**SO_4**	**Total**
Fossil-fuel combustion + industry					70	2.2	71–77
Biomass burning	<0.01		<0.01	0.08	2.8	0.1	15–25
Oceans	<0.3	15–25	0.08	0.17		40–320	15–25^a
Wetlands	0.006–1.1	0.003–0.68	0.0003–0.06	0.0006–0.12			0.01–2
Plants + soils	0.17–0.53	0.05–0.16	0.02–0.05	0.01–0.03		2–4	0.25–0.78^b
Volcanos	0.5–1.5			0.01	7–8	2–4	9.3–11.8
Anthropogenic (total)							73–80
Natural (total, without sea salt and soil dust)							25–40

5.1.2. Uncertainties in the Treatment of Sulphur Compounds

DiMethyl Sulphide (DMS) is a product of biological processes involving marine phytoplankton. According to Table 4 DMS accounts for 12.5 to 26 % to the total sulfur emitted into the atmosphere, the high interval indicating the high uncertainty of DMS emissions. DMS can be transfered into aqueous-phase aerosols or oxidised to several other gas-phase species which can contribute to aerosol formation and growth, e.g. SO_2, H_2SO_4, dimethyl sulphoxide and methane sulphinic acid. Therefore, it has been postulated that emission of DMS from the oceans can contribute to production of new condensation nuclei and eventually cloud condensation nuclei. Thus, DMS may have a significant influence on the Earth's radiation budget.

It is not an easy task to make a DMS gas-phase mechanism since many problems related to the gas- and liquid-phase mechanism are still not solved. For example the gas-phase mechanism developed during the ELCID project [31] included 30 sulphur species and 72 reactions; 49 of these reactions were guessed rate constants and 23 experimental determined rate constants.

A study by Gross and Baklanov [32] showed that it is important to include DMS in ACATMs if large ocean areas are included in the model domain, since DMS in the marine boundary layer can roughly contribute:

- from 13–27 % (summer) and 3–13 % (winter) to the formation of non sea salt aerosols;
- from 10–18 % (summer) and 1–10 % to the total aerosol formation.

Furthermore, too simplified DMS chemistry [$DMS(g)+HO(g) \rightarrow SO_2(g) \rightarrow H_2SO_4(l)$] mechanism used by Pandis et al. [33], Russel et al. [34], and Yoon and Brimblecombe [35] create too many new accumulation mode particles [36]. However, not only the DMS chemistry is uncertain many parameters used to described the mass transport of DMS and its oxidation products to the aerosols and their aerosol physics are still uncertain/unknown.

6. Discussion

In this overview of atmospheric chemistry we have focused on the gas-phase chemistry of the background troposphere and the polluted atmosphere. Other reactions exists in the nitrogen-oxygen chemical system described in *Section 2* and the chemistry of alcohols, ethers, carboxylic acids, unsaturated carbonyls and unsaturated dicarbonyls has been omitted since it would be too comprehensive to include in this context. For further information consult Refs. [1, 2, 6, 8, 12, 13, 14, 37].

We found that NO_2 and peroxy radicals are a product in many of the presented atmospheric reactions. NO_2 is important since it is an ozone formation agent. Peroxy radicals are important in many regions of the atmospheric boundary layer. Under marine conditions peroxy radical–peroxy radical reactions are important removal processes for peroxy radicals under low nitric oxide conditions and influence the concentrations of HO_2, H_2O_2, PAN, species with carbonyl groups, alcohols and organic acids. In relatively polluted and rural areas, peroxy radical reactions have a strong effect on the PAN concentrations and therefore also on the total concentration of odd nitrogen. In a polluted urban area, peroxy radicals react with NO under the production of NO_2 and alkoxy radicals.

Due to the complexity of the organic chemistry of the atmosphere a complete mechanism would require tens of thousands of chemical species and reactions. The reaction mechanisms and rates are not known for many of these. In *Sections 4* and *5* some uncertainties of atmospheric chemistry were outlined. The mentioned uncertainties were:

- the reactions between MAHs and PAHs with HO and the fate of the products;

— the reactions between O_3 and alkenes and the fate of the products;
— the overall atmospheric oxidation mechanism of aromatics and peroxide reactions;
— the isoprene chemistry in the lumped ACMs;
— the description of BVOC emissions;
— the DMS chemistry both with respect to rate constants and the product mechanism.

Atmospheric chemistry of organic and inorganic compounds absorbed on particles (heterogeneous reactions) and its reactions in aerosols are even more uncertain. Furthermore, many parameters which are needed to described the mass transport of gas-phase species to aerosols, the absorption of gas-phase species on particles and the mechanism of secondary aerosol generation are also important and to some extent unexplored.

Correlation methods [7, 38] have been frequently used to obtain new rate constants from existing rate constants. Gross et al. [39, 40] and Galvert et al. [8] have shown that these methods can be dangerous to use, because they can introduce errors with are a factor up to 10^4. Simple statistical methods such as transition state or phase-space theory will give more reliable results.

Experimental methods available to study the kinetics of reactive species and computer resources have improved dramatically since 1970s. Today, the various spectroscopic techniques applied to kinetic studies of the alkenes allow direct observation of reactive species. That results in increased precision in the determination of the rate coefficients and reaction mechanism. Moreover, high-level ab intio quantum mechanical calculations have provided valuable insight and are likely to play an important role in the future advances in the area of atmospheric chemistry.

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Received for publication June 2, 2005