

Lecture 8. Fundamentals of atmospheric chemistry:

Part 3. Basic gas-phase chemical reactions in the troposphere and in the stratosphere.

Objectives:

1. Atmospheric species of interest.
2. Summary of basic gas-phase chemical reactions in the troposphere.
3. Summary of basic gas-phase chemical reactions in the stratosphere.

Readings: Turco: p.77-83 ; Brimblecombe: p. 49-54

1. Atmospheric species of interest.

Table 8.1 below lists some inorganic and organic gases that are important in the atmosphere.

Inorganic gases in the table are all those that contain either oxygen, nitrogen, sulfur, chlorine, bromine, and possibly either hydrogen or carbon, but not both hydrogen and carbon.

Organic gases are those that contain both hydrogen and carbon, but may also contain other atoms.

Hydrocarbons are organic gases that contains only hydrogen and carbon.

Hydrocarbons are divided primarily into *alkanes, cycloalkanes, alkenes, alkynes, aromatics, and terpenes.*

Non-methane hydrocarbons (NMHCs) are all hydrocarbons excluding methane.

Oxygenated hydrocarbons are *hydrocarbons plus oxygenated functional groups,* such as aldehydes, ketones, alcohols, acids, and nitrates.

Reactive organic gases (ROG) or volatile organic carbon (VOC) are *non-methane hydrocarbons* plus *oxygenated hydrocarbons*.

Non-methane organic carbon (NMOC) is *non-methane hydrocarbons* plus **carbonyls** (aldehydes and ketones).

Total organic gases (TOG) are methane plus ROGs or VOGs.

- Because the number of *organic gases* is VERY large, individual organics are often lumped into surrogate carbon bond groups, and the groups, instead of the gases, are used in chemical reactions.

Some examples of grouping:

Alkanes are those hydrocarbon molecules in which all the carbon bonds are shared with hydrogen atoms except for minimum number required for carbon-carbon bonds.

For instance, ethane $\text{CH}_3\text{-CH}_3$

Cycloalkanes are *alkanes* which have a ring structure.

NOTE: *Alkanes* generally react by replacement of a hydrogen atom. Once a hydrogen atom is removed from an alkane, the involved carbon atom has an unpaired electron and the molecule becomes a free radical, in this case an **alkyl radical** (often denoted as **R[•]**)

For instance, ethyl $\text{CH}_3\text{-CH}_2\cdot$

Alkenes are those hydrocarbon molecules in which two neighboring carbon atoms share a pair of electrons, a so-called *double bond*.

For instance, ethene $\text{CH}_2=\text{CH}_2$

Alkynes are those hydrocarbon molecules in which have *triple bond*.

For instance, acetylene **HC---CH**

Table 8.1

Some atmospheric inorganic and organic gases.

For convenience, organic sulfur, chlorine, and bromine-containing species are listed with inorganic species.

Chemical formula	Chemical name	Chemical formula	Chemical name
INORGANICS			
Oxygen			
O(1D)	atomic oxygen (singlet)	O ₂	molecular oxygen
O or O(3P)	atomic oxygen (triplet)	O ₃	ozone
Hydrogen			
H	atomic hydrogen	H ₂	molecular hydrogen
Oxygen / Hydrogen			
OH [·]	hydroxyl radical	HO ₂ [·]	hydroperoxy radical
H ₂ O	water vapor	H ₂ O ₂	hydrogen peroxide
Nitrogen/Oxygen/Hydrogen			
N ₂	molecular nitrogen	NO ₃ [·]	nitrate radical
NO	nitric oxide	N ₂ O ₅	dinitrogen pentoxide
NO ₂	nitrogen dioxide	N ₂ O	nitrous oxide
HONO (HNO ₂)	nitrous acid	HO ₂ NO ₂	peroxynitric acid
HNO ₃	nitric acid		
Sulfur/Oxygen/Hydrogen/Carbon			
S	atomic sulfur	OCS	carbonyl sulfide
SO	sulfur oxide	CS	carbon monosulfide
SO ₂	sulfur dioxide	CS ₂	carbon disulfide
SO ₃	sulfur trioxide	CH ₃ SH	methyl sulfide
HSO ₃	bisulfite	CH ₃ S [·]	methyl sulfide radical
HS [·]	hydrogen sulfide radical	CH ₃ SCH ₃	dimethyl sulfide (DMS)
H ₂ S	hydrogen sulfide	CH ₃ SCH ₂ [·]	dimethyl sulfide radical
H ₂ SO ₄	sulfuric acid	CH ₃ SSCH ₃	methyl disulfide
		CH ₃ SO ₃ H	methane sulfonic acid MSA

Chlorine/Oxygen/Hydrogen/ Nitrogen /Fluorine/Carbon			
HCl	hydrochloric acid	Cl ₂ O ₂	dichlorine dioxide
Cl	atomic chlorine	CH ₃ Cl	methyl chloride
ClO	chlorine monoxide	CH ₃ CCl ₃	methyl chloroform
OCIO·	chlorine peroxy radical	CCl ₄	carbon tetrachloride
ClOO·	chlorine peroxy radical	CFCl ₃	trichlorofluoromethane (CFC-11)
HOCl	hydrochlorous acid	CF ₂ Cl ₂	dichlorofluoromethane (CFC-12)
ClONO ₂	chlorine nitrate	CFCl ₂ CF ₂ Cl	1-fluorodichloro, 2-difluorochloroethane (CFC-113)
ClNO ₂	chlorine nitrite	CF ₂ ClH	chlorodifluoromethane (HCFC-22)
Cl ₂	chlorine gas		
Bromine/Oxygen/Hydrogen/ Nitrogen /Carbon			
HBr	hydrobromic acid	BrONO ₂	bromine nitrate
Br	atomic bromine	CH ₂ Br	methyl bromide
BrO	bromine monoxide	Br ₂	molecular bromine
HOBr	hypobromous acid	BrCl	bromine chloride
Carbon/Oxygen			
CO	carbon monoxide	CO ₂	carbon dioxide
ORGANICS			
Alkanes (single bond)			
CH ₄	methane	CH ₃ (CH ₂) ₅ CH ₃	heptane
CH ₃ CH ₃	ethane	CH ₃ (CH ₂) ₆ CH ₃	octane
CH ₃ CH ₂ CH ₃	propane	CH ₃ (CH ₂) ₇ CH ₃	nonane
CH ₃ (CH ₂) ₂ CH ₃	n-butane	CH ₃ (CH ₂) ₁₃ CH ₃	pentadecane
CH ₃ (CH ₂) ₃ CH ₃	pentane	C ₄ H ₁₀	2-methylpropane
CH ₃ (CH ₂) ₄ CH ₃	hexane	C ₄ H ₉ C(CH ₃) ₃	2,2-dmethyl hexane
Cyclo Alkanes			
CH ₂ CH ₂ CH ₂	cyclopropane	CH ₃ C ₅ H ₉	methylcyclopentane
CH ₂ (CH ₂ CH ₂) ₂	cyclopentane	CH ₃ C ₆ H ₁₁	methylcyclohexane
Alkenes (double bond)			
CH ₂ CH ₂	ethene (ethylene)	CH ₃ CHCHCH ₃	trans 2-butene
CH ₂ CHCH ₂	propene (propylene)	CH ₃ CH ₂ CHCH ₂	1-butene
Cyclo Alkenes			
C ₅ H ₈	cyclopentene	C ₆ H ₁₀	cyclohexene

Alkynes (triple bond)			
C_2H_2	acetylene		
Aromatics (double bond, with a 'benzene' ring structure)			
C_6H_6	benzene	$C_6H_5CH_3$	toluene
$C_6H_5C_2H_5$	ethylbenzene	$C_6H_4(CH_3)_2$	o-xylene
$(CH_3)_3C_6H_3$	1,2,3-trimethylbenzene	$C_6H_4(CH_3)_2$	m-xylene
Terpenes			
C_5H_8	isoprene	$C_{10}H_{16}$	α -pinene
Aldehydes (double bond between carbon and oxygen)			
CH_2O	formaldehyde	CH_3CH_2CHO	propionaldehyde
CH_3CHO	acetaldehyde	C_6H_5CHO	benzaldehyde
$HOCH_2CHO$	glycol aldehyde		
Ketones (double bond between carbon and oxygen)			
$CH_3C(O)CH_3$	acetone	$CH_3CH_2COCH_3$	methylethylketone
Alcohols			
CH_3OH	methanol (methyl alcohol)	CH_3CH_2OH	ethanol
C_6H_5OH	phenol		
Carboxylic Acid			
$HC(O)OH$	formic acid	$CH_3C(O)OH$	acetic acid
Nitrates/Nitrites/Nitric Acids			
CH_3ONO_2	methyl nitrate	$CH_3C(O)OONO_2$	peroxyacyl nitrate (PAN)
CH_3ONO	methyl nitrite	$CH_3O_2NO_2$	methylperoxy nitric acid
$C_6H_5CH_3ONO_2$	benzyl nitrate	$C_6H_3(CH_3)(OH)NO_2$	nitroresol
Alkyl Radicals			
$CH_3\cdot$	methyl radical	$CH_3CH_2\cdot$	ethyl radical
Alkoxy Radicals			
$CH_3O\cdot$	methoxy radical	$CH_3CH_2O\cdot$	ethoxy radical
Alkylperoxy Radicals			
$CH_3O_2\cdot$	methoxyperoxy radical	$CH_3CH_2O_2\cdot$	ethylperoxy radical
Acyl Radicals			
$HCO\cdot$	formyl radical	$CH_3CO\cdot$	acyl radical
Acyloxy Radicals			
$CH_3C(O)O\cdot$	acyloxy radical		
Acylperoxy Radicals			
$CH_3C(O)OO\cdot$	peroxyacyl radical	$CH_2CCH_3C(O)OO\cdot$	methyl peroxyacyl radical

2. Summary of basic gas-phase chemical reactions in the troposphere.

The troposphere behaves as a chemical reservoir distinct from the stratosphere. Some differences important for chemistry between the troposphere and the stratosphere are:

1. In general, the troposphere has warmer temperature and higher pressure; and higher concentration of atmospheric gases (including water vapor);
2. Less UV radiation is reaching the troposphere;
3. In general, clouds and aerosols are more abundant in the troposphere;

Therefore, it is common to distinguish between the chemistry of the troposphere and the chemistry of the stratosphere. In turn, the chemistry of the troposphere depends on tropospheric conditions: such as clean (background) troposphere or polluted troposphere.

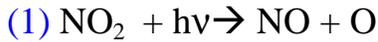
NOTE: the chemistry of the stratosphere focuses on the reactions that form and destroy ozone (it will be discussed in Lecture 35-38)

The gas-phase chemistry of the troposphere:

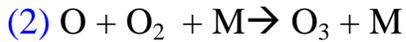
- The troposphere is an oxidative medium, the tendency is for species to be moved to a more oxidized state. For instance,
Hydrocarbons \rightarrow oxygenated hydrocarbons \rightarrow acids \rightarrow CO_2 ;
Reduced sulfur compounds (e.g., H_2S , CH_3SCH_3) \rightarrow SO_2 \rightarrow H_2SO_4 ;
 $\text{NO} \rightarrow \text{NO}_2 \rightarrow \text{HNO}_3$;
- The oxidation of organic species proceeds in the presence of oxides of nitrogen under the action of light. The predominant hydrocarbon in the troposphere is methane.

- In simple term one can say that hydroxyl radical controls daytime chemistry and the nitrate radical controls chemistry at night.

Basic photochemical cycle of NO_x (NO₂+NO), and O₃.

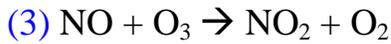


NO₂ absorbs at wavelengths < 424 nm



M represents O₂ or N₂ that absorbs the excess of energy

NOTE: This reaction is the main source of O₃



(1), (2) and (3) are strongly coupled.

If J₁, k₂, and k₃ are the reaction rate coefficients, then the rate equation for NO₂ is :

$$d[\text{NO}_2] / dt = k_3 [\text{NO}] [\text{O}_3] - J_1[\text{NO}_2]$$

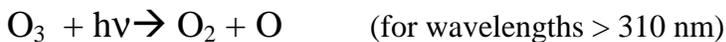
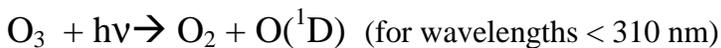
If this equation is considered steady-state, then it set to zero and the concentration of O₃ can be determined

$$[\text{O}_3] = J_1[\text{NO}_2] / (k_3 [\text{NO}])$$

which is known as **photostationary state relationship.**

However, the mixing ratio of O₃ measured in urban and regional troposphere are often greater than those calculated from the photostationary state relationship. It implies that other reactions than (1)-(3) are important.

Moreover, in the troposphere O₃ is destroyed by photolysis



Produced excited atomic oxygen can react with water vapor to form the hydroxyl radical:



- The hydroxyl radical is extremely important in the tropospheric chemistry. It converts NO_2 to HNO_3 , oxidizes carbon monoxide and reduced sulfur compounds, etc.

Basic chemistry of carbon monoxide and NO_x .

Oxidation of CO results in additional O_3 production.

It can be summarized as follows:



Note: that net formation of O_3 occurs because the conversion of NO to NO_2 is accomplished by the HO_2 radical rather than by O_3 itself.

Note: neither OH nor HO_2 radical is consumed in this reaction, which can be viewed as a **catalytic** oxidation of CO to CO_2

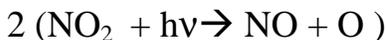
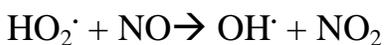
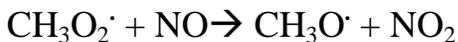
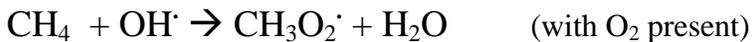
- **Catalysts** are substances which alter the rate of a chemical reaction without themselves appearing in the end products. Catalysts act by changing the mechanism of a reaction, so to allow progression via a transition state of lower energy, hence causing a lowering of the *activation energy* of the reaction.

Note: the basic reaction mechanism of the CO/NO_x system exhibits many of the key features of those involving complex organic molecules. In particular, the role of OH as the oxidizing species and the NO to NO₂ conversion by HO₂ are central to virtually every atmospheric organic/NO_x mechanism.

Basic chemistry of methane.

Oxidation of CH₄ (which the most abundant organic gas) results in additional O₃ production.

It can be summarized as follows:

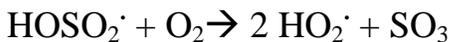
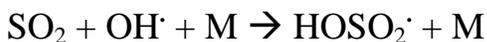


Basic chemistry of sulfur.

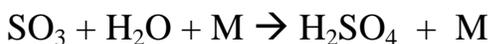
Sulfur oxides:

$2 \text{SO}_2 + \text{O}_2 \rightarrow 2 \text{SO}_3$ this reaction is very slow under catalyst-free conditions in the gas phase, that it can be totally neglected as a source of SO₃

Dominant reaction for SO₂:

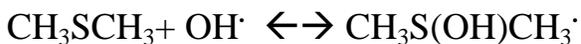


in the presence of water vapor



Reduced sulfur compounds (such as H₂S, CH₃SH, CH₃SCH₃, CS₂, OCS): react with OH[·] and NO₃[·]

The DMS-OH reaction proceeds via H-atom abstraction or OH addition to the sulfur atom in the DMS molecule:



then a complex chain of reactions take place leading to production of SO₂ → SO₃ → H₂SO₄

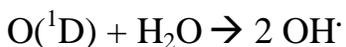
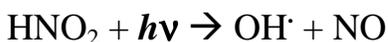
The DMS-NO₃ reaction proceeds initially via H-atom abstraction:



NOTE: the DMS oxidation chemistry is very complex, and is not completely understood at the moment

Hydroxyl radical, OH[·] is extremely important in day-time atmospheric chemistry.

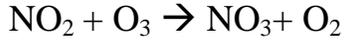
There are many formation mechanisms for OH[·] such as:



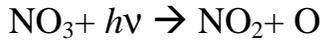
Nitrate radical, NO₃[·] is extremely important in night-time atmospheric chemistry.

At night the NO₃[·] can act as a hydrogen atom abstractor in the same way as OH[·]

It forms as :



NO_3 has low day-time concentration because of photolysis ($\lambda < 633\text{nm}$):

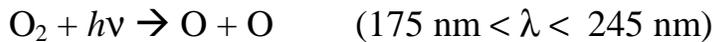
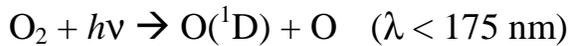


3. Summary of basic gas-phase chemical reactions in the stratosphere.

NOTE: detailed discussion of stratospheric chemistry is given in Lectures 35-38.

Background stratospheric condition (no chlorine and other halogens):

Ozone production:



then



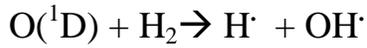
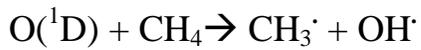
NO catalytic ozone destruction:



OH catalytic ozone destruction:

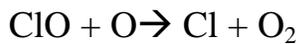
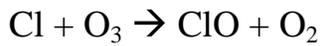


OH[·] is produced in the stratosphere by one of the several mechanisms:



Polluted stratospheric conditions: chlorine and bromine both affect ozone concentrations in the stratosphere.

Cl catalytic ozone destruction:



Br catalytic ozone destruction:

