Tropospheric Chemistry – Basic Photochemical Cycles and Hydrogen Compounds

The troposphere contains a manifold of chemical species from which the most important ones are the OH-radical, ozone and the nitrogen oxides. The gas-phase chemistry involves the oxidation of organic substances in presence of sunlight. In fact the troposphere is overall an oxidizing medium and all reactions are driven to the highest oxidation states of the compounds.

**Governing reactions involving ozone, NO\(_x\), OH, OH\(_2\), HCHO, CH\(_4\)**

By presence of NO and NO\(_2\) in sunlight, ozone formation happens according to the following reaction:

\[
\text{(1) } \text{NO}_2 + \text{hv} \rightarrow \text{NO} + \text{O}
\]

\[
\text{(2) } \text{O} + \text{O}_2 + \text{M} \rightarrow \text{O}_3 + \text{M}
\]

Ozone can react with NO in the following way when no other species are present (side reaction):

\[
\text{(3) } \text{O}_3 + \text{NO} \rightarrow \text{NO}_2 + \text{O}_2
\]

In the stratosphere as well as in the troposphere ozone reacts in the following way:

\[
\text{(4) a } \text{O}_3 + \text{hv}(\text{<319nm) } \leftrightarrow \text{O} + \text{O}_2
\]

\[
\text{b } \rightarrow \text{O}^{(1)}\text{D}) + \text{O}_2
\]

Approximately 10% of the O\(^{(1)D}\) reacts to form hydroxyl radicals:

\[
\text{(5) } \text{O}^{(1)\text{D}} + \text{H}_2\text{O} \rightarrow 2\text{OH}•
\]
The hydroxyl radical is one of the key species in tropospheric chemistry and reacts with most of the trace compounds. With CO for instance it forms CO$_2$ and a hydrogen atom, which in turn reacts extremely fast with mol. oxygen gaining a peroxyradical:

\[
\begin{align*}
(6) \quad & CO + OH \rightarrow CO_2 + H \\
(7) \quad & H + O_2 + M \rightarrow HO_2 + M \text{ (fast)} \\
(8) \quad & CO + OH \rightarrow CO_2 + HO_2
\end{align*}
\]

Reaction (8) presents a summary of reaction (6) and (7). The peroxyradical is rather reactive and undergoes reaction (9):

\[
(9) \quad HO_2 + NO \rightarrow NO_2 + OH
\]

As net reaction of OH, CO and NO we can formulate:

\[
\text{Net: } CO + 2O_2 + h\nu \rightarrow CO_2 + O_3
\]

To terminate the catalytic cycle and remove OH from the system, OH can react with NO to form HNO$_3$:

\[
(10) \quad OH + NO_2 + M \rightarrow HNO_3 + M
\]

**Formaldehyde:**

Formaldehyde follows two main reactions – the photolysis with sunlight and reaction with the OH-radical:

\[
\begin{align*}
(11) \quad & HCHO + h\nu \rightarrow H + HCO \text{ (45% with reaction (13))} \\
& \quad \rightarrow H_2 + CO \text{ (55%)} \\
(12) \quad & HCHO + OH \rightarrow HCO + H_2O \\
(13) \quad & HCO + O_2 \rightarrow HO_2 + CO \text{ (fast)} \\
(14) \quad & HCHO + h\nu \rightarrow 2HO_2 + CO
\end{align*}
\]
(15) \[ \text{HCHO + OH} \rightarrow \text{HO}_2 + \text{CO} + \text{H}_2\text{O} \]

**Methane:**

Methane (CH\(_4\)) reacts with the hydroxyl radical to form the methyl radical, instantaneously reacting with oxygen to form a methyl peroxy radical:

(16) \[ \text{CH}_4 + \text{OH} \rightarrow \text{CH}_3 + \text{H}_2\text{O} \]

(17) \[ \text{CH}_3 + \text{O}_2 + \text{M} \rightarrow \text{CH}_3\text{O}_2 + \text{M} \]

(18) \[ \text{CH}_4 + \text{OH} \rightarrow \text{CH}_3\text{O}_2 + \text{H}_2\text{O} \]

The most important reactions of the methyl peroxy radical are with NO, NO\(_2\) and HO\(_2\) radicals:

(19) \[ \text{CH}_3\text{O}_2 + \text{NO} \rightarrow \text{CH}_3\text{O} + \text{NO}_2 \]

(20) \[ \text{CH}_3\text{O}_2 + \text{NO}_2 + \text{M} \leftrightarrow \text{CH}_3\text{OONO}_2 + \text{M} \]

(21) \[ \text{CH}_3\text{O}_2 + \text{HO}_2 \rightarrow \text{CH}_3\text{OOH} + \text{O}_2 \quad (\tau \sim 2\text{days}) \]

(22) \[ \text{CH}_3\text{OOH} + \text{hv} \rightarrow \text{CH}_3\text{O} + \text{OH} \]

(23) \[ \text{CH}_3\text{OOH} + \text{OH} \rightarrow \text{H}_2\text{O} + \text{CH}_3\text{O}_2 \quad (0.67) \]

\[ \rightarrow \text{H}_2\text{O} + \text{HCHO} + \text{OH} \quad (0.33) \]

The reaction of the methoxy radical with molecular oxygen leads to the only major product of methane oxidation with lifetimes longer than a few seconds – formaldehyde:

(24) \[ \text{CH}_3\text{O} + \text{O}_2 \rightarrow \text{HCHO} + \text{HO}_2 \quad (\tau \sim 3\text{hours}) \]

To terminate the chain reaction initiated by methane oxidation, the OH radical reacts with NO\(_2\) (10) and the HO\(_2\) radical combines to hydrogen peroxide and oxygen. Another termination mechanism for the hydroxyl peroxy radical is the reaction with ozone:

(25) \[ \text{HO}_2 + \text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2 \]

(26) \[ \text{HO}_2 + \text{O}_3 \rightarrow \text{OH} + 2\text{O}_2 \]
**Hydroxyl radical:**

The hydroxyl radical does not react with one of the major compounds of the atmosphere like N\textsubscript{2}, O\textsubscript{2}, but it does react easily with most of the trace constituents present. Direct measurements of OH concentrations are very difficult because of its high reactivity and lack of suitable instrumentation, therefore OH-levels are derived from indirect measurements of species known to be reacting or consuming OH. From this the following estimates were set:

- **daytime [OH] (summer)** \(5-10 \times 10^6\) molecules/cm\(^3\)
- **daytime [OH] (winter)** \(1-5 \times 10^6\) molecules/cm\(^3\)
- **nighttime [OH]** \(\leq 2 \times 10^5\) molecules/cm\(^3\)

The main pathways of OH-radical formation are:

a) **Photolytic destruction of ozone:**

\[ (4) \quad O_3 + h\nu \quad \rightarrow \quad O_2 + O(^1D) \]

\[ (5) \quad O(^1D) + H_2O \quad \rightarrow \quad 2OH \]

b) **Reaction between the peroxy radical and NO:**

\[ (9) \quad HO_2 + NO \quad \rightarrow \quad OH + NO_2 \]

b) **Photolysis of nitrous acid:**

\[ (27) \quad HONO + h\nu \quad \rightarrow \quad OH + NO \]

**Nitrate radical:**

Another strongly oxidizing constituent in the troposphere is the nitrate-radical NO\textsubscript{3}:

\[ (28) \quad NO_2 + O_2 \quad \rightarrow \quad NO_3 + O_2 \]

\[ (29) \quad NO_2 + NO_3 \quad \leftrightarrow \quad N_2O_5 \]

NO\textsubscript{3} is destroyed rapidly during daytime by the following two reactions:

\[ (30) \quad NO_3 + h\nu(700\text{nm}) \quad \rightarrow \quad NO + O_2 \]

\[ (31) \quad NO_3 + h\nu(580\text{nm}) \quad \rightarrow \quad NO_2 + O \]
and additionally reacts with NO:

\[(32) \quad \text{NO}_3 + \text{NO} \rightarrow 2\text{NO}_2\]

**Ozone in the Troposphere:**

The principal source of ozone in the troposphere is the photochemical production via the methane oxidation chain (see below), with NO concentration (reaction (9) for the production and (26) for the destruction) are the critical step dictating the fate of the HO\(_2\) radical.

**Methane oxidation chain:**

\[(16-18) \quad \text{CH}_4 + \text{OH} \rightarrow \text{CH}_3\text{O}_2 + \text{H}_2\text{O}\]
\[(19) \quad \text{CH}_3\text{O}_2 + \text{NO} \rightarrow \text{CH}_3\text{O} + \text{NO}_2\]
\[(24) \quad \text{CH}_3\text{O} + \text{O}_2 \rightarrow \text{HCHO} + \text{HO}_2\]
\[(9) \quad \text{HO}_2 + \text{NO} \rightarrow \text{OH} + \text{NO}_2\]
\[(1) \quad 2(\text{NO}_2 + \text{hv}) \rightarrow \text{NO} + \text{O}\]
\[(2) \quad 2(\text{O} + \text{O}_2 + \text{M}) \rightarrow \text{O}_3 + \text{M}\]

Net: \(\text{CH}_4 + 4\text{O}_2 + 2\text{hv} \rightarrow \text{HCHO} + 2\text{O}_3 + \text{H}_2\text{O}\)

Reaction (9) involving NO leads to the production of ozone, whereas reaction (26) destroys ozone:

\[(26) \quad \text{HO}_2 + \text{O}_3 \rightarrow \text{OH} + 2\text{O}_2\]

The so-called break-even concentration of NO, below which ozone is destroyed and above which it is produced, depends on the local ozone concentration, OH\(_2\) concentrations and other factors like NO\(_x\) mixing ratios. Ozone lifetimes vary depending on altitude, latitude and season. The life times are shorter in summer due to the higher solar fluxes and shorter near the surface due to higher water vapor mixing ratios.

Other principal sinks of ozone are besides reaction (26) the photochemical reactions (4) and (5).
The global ozone budget is comprised of the following parameters:

Production of ozone in the troposphere and transport of ozone downward from the stratosphere. Loss of ozone by dry deposition and in situ chemical destruction. The main problem of calculating the ozone budget lays in the uncertainty of the in situ tropospheric production. Thus downward transport and the loss rates are known by measurements of OH$_2$, CH$_4$ and CO rates. However, there is little doubt that production and loss of tropospheric ozone are dominated by in situ processes and not by downward transport.

Regional tropospheric ozone:

Major high concentrations of ozone are bound to slow-moving high-pressure systems in summer. Such systems are associated with pronounced inversion of the normal temperature profile trapping pollutants in a thin layer of the atmosphere. Increasing temperatures with height do not allow colder air from below to mix with air above. Additionally winds are in high pressure systems only light supporting the accumulation of precursor species in the boundary layer. Such events are highly favourable for the photochemical production of ozone. The situation can last for several days under extremely stable conditions, particularly in summer when solar radiation is high. It is resolved when low pressure systems pass through with increasing winds and clouds. Clouds play a major role in transporting pollutants from the boundary layer to the upper layers of the troposphere (venting).
Chemistry of Organic Compounds in the Troposphere

Alkanes:

Alkanes react in the troposphere with OH and NO₃ radicals via the following reactions:

\[(33)\] \( \text{RH} + \text{OH} \rightarrow \text{R} + \text{H}_2\text{O} \]

\[(34)\] \( \text{RH} + \text{NO}_3 \rightarrow \text{R} + \text{HNO}_3 \]

The resulting methyl radical reacts fast and exclusively with \( \text{O}_2 \) to yield a peroxyradical:

\[(35)\] \( \text{R} + \text{O}_2 + \text{M} \rightarrow \text{RO}_2 + \text{M} \]

The peroxyalkyl radical in turn reacts under tropospheric conditions with NO in two pathways:

\[(36)\] \( \text{RO}_2 + \text{NO} \rightarrow \text{RO} + \text{NO}_2 \]

\[\rightarrow \text{RONO}_2 \]

The second reaction is favoured with increasing pressure and decreasing temperature. By increased \( \text{NO}_2 \) concentrations in urban environments \( \text{RO}_2 \) reacts with \( \text{NO}_2 \) in the following way:

\[(37)\] \( \text{RO}_2 + \text{NO}_2 + \text{M} \rightarrow \text{ROONO}_2 + \text{M} \]

Other reactions of the peroxyalkyl radical appear to be with \( \text{HO}_2 \) and with other \( \text{RO}_2 \) radicals:

\[(38)\] \( \text{RO}_2 + \text{HO}_2 \rightarrow \text{ROOH} + \text{O}_2 \]

\[(39)\] \( \text{R}_1\text{R}_2\text{CHO}_2 + \text{R}_1\text{R}_2\text{CHO}_2 \rightarrow 2\text{R}_1\text{R}_2\text{CHO} + \text{O}_2 \) (major)

\[\rightarrow \text{R}_1\text{R}_2\text{CHOH} + \text{R}_1\text{R}_2\text{CO} + \text{O}_2 \]

\[\rightarrow \text{R}_1\text{R}_2\text{CHOOCR}_1\text{R}_2 + \text{O}_2 \]

The most important reaction of alkanes in the troposphere is reaction (36). The alkoxy radicals formed in reaction (36) determine at most the products resulting from atmospheric oxidation of VOC’s. Such alkoxy radicals undergo several different reactions in the troposphere:

Reactions with \( \text{O}_2 \) (preferred reaction for primary alkoxy radicals with chains of two or fewer C):
(40) \[ \text{RO} + \text{O}_2 \rightarrow \text{RCHO} + \text{HO}_2 \]

Unimolecular decomposition:

(41) \[ \text{RCH}_2\text{O} \rightarrow \text{R} + \text{HCHO} \]

(42) \[ \text{RR}_1\text{CHO} \rightarrow \text{R} + \text{R}_1\text{CHO} \]

(43) \[ \text{RR}_1\text{R}_2\text{CO} \rightarrow \text{R} + \text{R}_1\text{C(O)R}_2 \]

Isomerization (here of n-pentane) (44):

Alkenes:

Alkenes react with the hydroxyl radical, with ozone, with the NO\textsubscript{3} radical and atomic oxygen.

Ethene reaction with OH:

(45) \[ \text{C}_2\text{H}_4 + \text{OH} \rightarrow \text{HOCH}_2\text{CH}_2 \]
(46) \( \text{HOCH}_2\text{CH}_2 + \text{O}_2 \rightarrow \text{HOCH}_2\text{CH}_2\text{O}_2 \)

(47) \( \text{HOCH}_2\text{CH}_2\text{O}_2 + \text{NO} \rightarrow \text{NO}_2 + \text{HOCH}_2\text{CH}_2\text{O} \)

(48) \( \text{HOCH}_2\text{CH}_2\text{O} \rightarrow \text{HCHO} + \text{CH}_2\text{OH} \) (72%)

(49) \( \text{HOCH}_2\text{CH}_2\text{O} + \text{O}_2 \rightarrow \text{HOCH}_2\text{CHO} + \text{HO}_2 \) (28%)

(50) \( \text{CH}_2\text{OH} + \text{O}_2 \rightarrow \text{HCHO} + \text{HO}_2 \)

Overall reaction under assumption that (46) and (49 +50) are very fast and \( \text{HOCH}_2\text{CH}_2\text{O}_2 \) is produced in only these two ways:

(51) \( \text{C}_2\text{H}_4 + \text{OH} + 2\text{NO} \rightarrow 2\text{NO}_2 + 1.44\text{HCHO} + 0.28\text{HOCH}_2\text{CHO} + \text{OH} \)

Alkene reactions with OH proceed by addition of the OH radical to the double bound to form a \( \beta \)-hydroxyalkyl radical, followed by fast addition of \( \text{O}_2 \) to gain a \( \beta \)-hydroxyalkyl peroxy radical. In presence of NO the peroxy radical reacts with NO to form either a \( \beta \)-hydroxylalkoxy radical plus \( \text{NO}_2 \) or \( \beta \)-hydroxynitrate:

(52)
The $\beta$-hydroxyl alkoxy radicals can decompose, react with O$_2$ or isomerize like in the case of the alkanes. Except for ethene, alkenes choose the decomposition pathway to react:

(53)

Reaction of alkenes with NO$_3$:

As by reaction with OH alkenes react with NO$_3$ under addition of NO$_3$ to the double bond, followed by rapid O$_2$ addition to produce the $\beta$-nitroalkoxy peroxy radical. This in turn reacts with NO, NO$_2$ or O$_2$:

(54)
Alkene reaction with ozone:

Ozone is added to the olefinic double bond followed by rapid decomposition of the rather instable molozonide:

(55)

The formed so-called Criegee biradical can be stabilized by collision or undergo unimolecular decomposition (known for ethene and propene):

(56) ethene

(57) propene

Aromatic Compounds:
The two major pathways proposed are H-atom abstraction (58) – accounting for about 10% of the cases – and OH-radical addition (59) – accounting for about 90% of the cases.

Abstraction (58):

Addition (59):

The radical formed by addition of OH (59) can react further with O₂ (60) or NO₂ (61):

Reaction with O₂ (60):

Abstraction (~16%)

Addition (~84%)
Reaction with NO\textsubscript{2} (61):

**Aldehydes:**

Aldehydes undergo photolysis, react with OH and with NO\textsubscript{3} radicals with latter ones of minor importance.

Acetaldehyde photolyses by reaction (62):

\begin{align*}
(62) & \quad \text{CH}_3\text{CHO} + \text{hv} \rightarrow \text{CH}_4 + \text{CO} \\
& \quad \rightarrow \text{CH}_3 + \text{HCO}
\end{align*}

Aldehydes other than formaldehyde or acetaldehyde react after reaction (63), forming an acyl radical:

\begin{align*}
(63) & \quad \text{RCHO} + \text{OH} \rightarrow \text{RCO} + \text{H}_2\text{O} \\
(64) & \quad \text{RCO} + \text{O}_2 + \text{M} \rightarrow \text{RC(O)OO} + \text{M} \\
(65) & \quad \text{RC(O)OO} + \text{NO} \rightarrow \text{RC(O)O} + \text{NO}_2 \\
(65a) & \quad \text{RC(O)O} \rightarrow \text{R} + \text{CO}_2 \\
(66) & \quad \text{RC(O)OO} + \text{NO}_2 + \text{M} \leftrightarrow \text{RC(O)OONO}_2 + \text{M}
\end{align*}
with reaction pathway (65, 65a) of minor importance. Reaction (66) leads to PAN’s peroxyacyl nitrates.

**Peroxyacyl Nitrates (PAN’s):**

PANs are constituents of photochemical smog and are formed by reaction of OH with aldehydes (see above (66)):

\[
\begin{align*}
& (67) \quad \text{CH}_3\text{CHO} + \text{OH} \rightarrow \text{CH}_3\text{CO} + \text{H}_2\text{O} \\
& (68) \quad \text{CH}_3\text{CO} + \text{O}_2 \rightarrow \text{CH}_3\text{C(O)O}_2 \\
& (69) \quad \text{CH}_3\text{C(O)O}_2 + \text{NO}_2 + \text{M} \leftrightarrow \text{CH}_3\text{C(O)O}_2\text{NO}_2 + \text{M}
\end{align*}
\]

Reaction (69) competes with reaction (70):

\[
\begin{align*}
& (70) \quad \text{CH}_3\text{C(O)O}_2 + \text{NO} \rightarrow \text{NO}_2 + \text{CH}_3\text{C(O)O} \\
& (70a) \quad \text{CH}_3\text{C(O)O} + \text{O}_2 \rightarrow \text{CH}_3\text{O}_2 + \text{CO}_2
\end{align*}
\]

The principal loss mechanisms are the thermal decomposition via reaction (66) and/or (69) and depends on the NO and NO\textsubscript{2} concentration as well as on the temperature. Since the thermal decomposition is strictly depending on temperature, PAN’s have quite high lifetimes in the upper troposphere and can be transported over long distances.

**Ketones:**

Acetone is an omnipresent atmospheric species with mixing ratios of about 1ppb in rural sites. Global sources of acetone and ketones are secondary formation from atmospheric oxidation of precursor hydrocarbons (propane, isobutane, and isobutene) accounting for 51%, direct emission from biomass burning accounting for about 26%, and primary anthropogenic emission. Removal of acetone happens by photolysis (64%), reaction with OH (24%) and deposition (12%). Acetone photolysis produces the PAN precursor CH\textsubscript{3}CO are calculated to be responsible for about 50% of PAN. The average lifetime of acetone is about 16 days.
Atmospheric Chemistry of Biogenic Hydrocarbons

Biogenic hydrocarbons are highly reactive and undergo the same reactions as alkenes, they are essentially alkenes or cycloalkenes. The life times of these hydrocarbons are estimated to be rather short, compared to other organic species. Reactions with OH radicals and ozone are thought to be in the same range during the daytime, whereas NO3 radical reactions are important during the night.

Isoprene:

The most important and abundant species of biogenic hydrocarbons is isoprene (=2-methyl-1,3-butadiene):

Isoprene reacts with OH and NO3 radicals as well as ozone. The isoprene-OH reaction proceeds almost entirely by addition of the OH radical to the double bonds. The major products are formaldehyde (HCHO), methacrolein (CH2=C(CH3)CHO) and methyl vinyl ketone (CH=CHC(O)CH3). The isoprene-ozone reaction follows basically the same mechanism as the OH radical by addition of O3 to the double bonds. A primary ozonide is later decomposed to carbonyl and biradical products to form ultimately formaldehyde, methacrolein and methyl vinyl ketone. Like in the two cases above also the isoprene-NO3 radical reaction proceeds in the way of addition to the double bonds, with addition to the 1-position dominating the 4-position. The major products of OH-, O3-, and NO3- isoprene reactions are themselves reactive to OH and O3 and might even photolyze as methacrolein and methyl vinyl ketone do.
Reduced Nitrogen Compounds

Amines:

The major gas-phase reactions involve the OH-radical and gaseous nitric acid:

*Reactions with the OH-radical:*

\[
\begin{align*}
(71) \quad & \text{NH}_3 + \text{OH} \rightarrow \text{H}_2\text{O} + \text{NH}_2 \\
(72) \quad & \text{CH}_3\text{NH}_2 + \text{OH} \rightarrow \text{H}_2\text{O} + \text{CH}_3\text{NH} \\
(73) \quad & (\text{CH}_3)_2\text{NH} + \text{OH} \rightarrow \text{H}_2\text{O} + (\text{CH}_3)_2\text{N} \\
(74) \quad & \rightarrow \text{H}_2\text{O} + \text{CH}_2\text{NHCH}_3 \\
\end{align*}
\]

*Reaction with nitric acid (g):*

\[
(75) \quad \text{NH}_3 + \text{HNO}_3 \rightarrow \text{NH}_4\text{NO}_3(s)
\]

Ammonia is highly soluble in water and acids and its primary removal way is the reaction with this compounds rather than with OH, which is slow.

Nitriles:

Experimental data suggest that nitriles mainly react with OH radicals:

\[
(76) \quad \text{CH}_3\text{CN} + \text{OH} \rightarrow \text{H}_2\text{O} + \text{CH}_2\text{CN}
\]

Nitrites:

For nitrites the only major loss process in the troposphere is photolysis:

\[
(77) \quad \text{CH}_3\text{ONO} + \text{hv} \rightarrow \text{CH}_3\text{O} + \text{NO} \quad (\tau=10-15\text{min at noon})
\]
Atmospheric Gas Phase Chemistry of Sulfur Compounds

Sulfur oxides:

For the gas phase chemistry the OH reaction with SO$_2$ is the most important pathway:

\begin{align*}
(78) \quad & \text{SO}_2 + \text{OH} + \text{M} \rightarrow \text{HOSO}_2 + \text{M} \\
(79) \quad & \text{HOSO}_2 + \text{O}_2 \rightarrow \text{HO}_2 + \text{SO}_3 \\
\end{align*}

By presence of water vapor SO$_3$ readily reacts with water vapor to form sulfuric acid:

\begin{align*}
(80) \quad & \text{SO}_3 + \text{H}_2\text{O} + \text{M} \rightarrow \text{H}_2\text{SO}_4 + \text{M} \\
\end{align*}

Dimethyl Sulfide (DMS):

DMS reacts with OH and NO$_3$ radicals in the following way:

\textit{Abstraction} at higher temperatures (298K~80%; 285K~50%):

\begin{align*}
(81) \quad & \text{CH}_3\text{SCH}_3 + \text{OH} \rightarrow \text{CH}_3\text{SCH}_2 + \text{H}_2\text{O} \\
(82) \quad & \text{CH}_3\text{SCH}_2 + \text{O}_2 + \text{M} \rightarrow \text{CH}_3\text{SCH}_2\text{O}_2 + \text{M} \\
(83) \quad & \text{CH}_3\text{SCH}_2\text{O}_2 + \text{NO} \rightarrow \text{CH}_3\text{SCH}_2\text{O} + \text{NO}_2 \\
(84) \quad & \text{CH}_3\text{SCH}_2\text{O} \rightarrow \text{CH}_3\text{S} + \text{HCHO} \text{ (fast)} \\
\end{align*}

marine boundary layer (low NO$_3$):

\begin{align*}
(85) \quad & \text{CH}_3\text{SCH}_2\text{O}_2 + \text{HO}_2 \rightarrow \text{CH}_3\text{SCH}_2\text{OOH} + \text{O}_2 \\
\quad & \quad \rightarrow \text{CH}_3\text{SCHO} + \text{H}_2\text{O} + \text{O}_2 \\
(86) \quad & \text{CH}_3\text{S} + \text{O}_2 \rightarrow \text{CH}_3\text{SO}_2 \\
(87) \quad & \rightarrow \text{CH}_2\text{S} + \text{HO}_2 \\
\end{align*}
Addition at lower temperatures (285K~50%):

\[(88) \quad \text{CH}_3\text{SCH}_3 + \text{OH} \leftrightarrow \text{CH}_3\text{S(OH)}\text{CH}_3\]

\[(89) \quad \text{CH}_3\text{S(OH)}\text{CH}_3 + \text{O}_2 \rightarrow \text{CH}_3\text{S(O)}\text{CH}_3 + \text{HO}_2\]

**Tropospheric Chemistry of Halogen compounds:**

**Cycles of halogen species:**

Organic halogen molecules are attacked in the atmosphere by sun light or OH-radicals and release atomic halogens.

**Reaction with OH:**

\[(90) \quad \text{CH}_3\text{Cl} + \text{OH} \rightarrow \text{CH}_2\text{Cl} + \text{H}_2\text{O}\]

\[(91) \quad \text{CH}_2\text{Cl} + \text{O}_2 + \text{M} \rightarrow \text{CH}_2\text{ClO}_2 + \text{M}\]

\[(92) \quad \text{CH}_2\text{ClO}_2 + \text{NO} \rightarrow \text{NO}_2 + \text{HCHO} + \text{Cl}\]

\[(93) \quad \text{Cl} + \text{RH} \rightarrow \text{HCl} + \text{R}\]

Reaction (93) proceeds readily for F and Cl, whereas Br, and I react preferably in the following way:

\[(100) \quad \text{X} + \text{O}_3 \rightarrow \text{XO} + \text{O}_2\]

\[(101) \quad \text{HX} + \text{OH} \rightarrow \text{X} + \text{H}_2\text{O}\]

\[(102) \quad \text{XO} + \text{hv} \rightarrow \text{X} + \text{O}\]

\[(103) \quad \text{XO} + \text{NO} \rightarrow \text{X} + \text{NO}_2\]

\[(104) \quad \text{XO} + \text{HO}_2 \rightarrow \text{HOX} + \text{O}_2\]

Hydrogen halides can be also liberated from sea salt aerosol by reaction of strong acids like H\(_2\)SO\(_4\) and HNO\(_3\):

\[(105) \quad \text{H}_2\text{SO}_4 + 2\text{NaX(s)} \rightarrow 2\text{HX} + \text{Na}_2\text{SO}_4(s)\]