Week 5 – Introduction to Atmospheric Photochemistry

Kinetics – we are mainly in Chapter 3, but examples are taken from Chapter 5 (see Text, pages 15, 321-322, 330-332, 97-99, 116-119)
What is the fate of an organic compound in an oxidizing atmosphere?

Let's consider methane, \( \text{CH}_4 \)

Naively, we would expect slow “combustion” of methane in an atmosphere loaded with oxygen.

\[
\text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2 \text{H}_2\text{O}
\]

The problem is that oxygen doesn’t really react with methane in a single step – combustion is a process that involves multiple ‘intermediate’ reactions that eventually will oxidize methane to \( \text{CO}_2 \) and water, but there are some interesting products that pop up along the way, and these can have important implications – for health, visibility, and the chemical state of the atmosphere.
So what does the ‘oxidation’ of methane look like, and what are the important intermediates? First, we note that methane is a fairly stable molecule, so it doesn’t react with just any old molecules. In fact, it reacts only with radicals (atoms or molecules with an unpaired electron). The hydroxyl (OH) is the most important species that initiates the oxidation of methane (and most other organic compounds in the atmosphere):

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

\[
\text{CH}_3 + \text{O}_2 + \text{M} \rightarrow \text{CH}_3\text{O}_2 + \text{M} \quad \text{(recombination reaction)}
\]

\[
\text{CH}_3\text{O}_2 + \text{NO} \rightarrow \text{CH}_3\text{O} + \text{NO}_2 \quad \text{(extraction reaction)}
\]

\[
\text{CH}_3\text{O} + \text{O}_2 \rightarrow \text{CH}_2\text{O} + \text{HO}_2
\]

\[
\text{HO}_2 + \text{NO} \rightarrow \text{OH} + \text{NO}_2 \quad \text{(reformation of OH)}
\]
Let’s take a closer look – note that some reactions produce species that are consumed in the next step – we call these ‘intermediates’. The aqua color below tracks the evolution of the hydrocarbon intermediates as they are progressively oxidized. Note, even after four steps, we are still a few steps away from carbon dioxide!

\[
\begin{align*}
\text{CH}_4 + \text{OH} & \rightarrow \text{CH}_3 + \text{H}_2\text{O} \\
\text{CH}_3 + \text{O}_2 + \text{M} & \rightarrow \text{CH}_3\text{O}_2 + \text{M} \\
\text{CH}_3\text{O}_2 + \text{NO} & \rightarrow \text{CH}_3\text{O} + \text{NO}_2 \\
\text{CH}_3\text{O} + \text{O}_2 & \rightarrow \text{CH}_2\text{O} + \text{HO}_2 \\
\text{HO}_2 + \text{NO} & \rightarrow \text{OH} + \text{NO}_2
\end{align*}
\]
Red colors below identify species that are critical to the reaction scheme, but are themselves not consumed. We call these species “catalysts,” since they are important for the overall reaction cycle to continue, but are themselves not consumed, so they are present for the next round of reactions. Notice our ‘friend’ M. This is simply “air” (mainly N\textsubscript{2} and O\textsubscript{2}). We will see that M is a bit different than the other catalysts OH and HO\textsubscript{2} because it doesn’t ever change forms.

\[
\begin{align*}
\text{CH}_4 + \text{OH} & \rightarrow \text{CH}_3 + \text{H}_2\text{O} \\
\text{CH}_3 + \text{O}_2 + \text{M} & \rightarrow \text{CH}_3\text{O}_2 + \text{M} \\
\text{CH}_3\text{O}_2 + \text{NO} & \rightarrow \text{CH}_3\text{O} + \text{NO}_2 \\
\text{CH}_3\text{O} + \text{O}_2 & \rightarrow \text{CH}_2\text{O} + \text{HO}_2 \\
\text{HO}_2 + \text{NO} & \rightarrow \text{OH} + \text{NO}_2
\end{align*}
\]
To determine the over ‘net’ result of these five reactions, we can cancel out species that appear on both sides of the overall reaction.

\[
\begin{align*}
\text{CH}_4 + \text{OH} &\rightarrow \text{CH}_3 + \text{H}_2\text{O} \\
\text{CH}_3 + \text{O}_2 + \text{M} &\rightarrow \text{CH}_3\text{O}_2 + \text{M} \\
\text{CH}_3\text{O}_2 + \text{NO} &\rightarrow \text{CH}_3\text{O} + \text{NO}_2 \\
\text{CH}_3\text{O} + \text{O}_2 &\rightarrow \text{CH}_2\text{O} + \text{HO}_2 \\
\text{HO}_2 + \text{NO} &\rightarrow \text{OH} + \text{NO}_2
\end{align*}
\]

\[
\text{CH}_4 + 2\text{O}_2 + 2\text{NO} \rightarrow \text{CH}_2\text{O} + \text{H}_2\text{O} + 2\text{NO}_2
\]
**CH₄ + 2O₂ + 2NO → CH₂O + H₂O + 2NO₂**

This net reaction is a bit more interesting than the simple formation of CO₂ and H₂O. It leaves behind a new hydrocarbon, formaldehyde, which is more toxic than methane and one that survives long enough in the atmosphere to be of concern for air quality. However, perhaps even worse, it converts two molecules of nitric oxide (NO) into nitrogen dioxide (NO₂). Nitrogen dioxide itself is highly toxic (although so is NO!), but what NO₂ does next is highly problematic:

**NO₂ + hv → NO + O**

**O + O₂ + M → O₃ + M**
The photolysis of NO\(_2\) (a process that can only take place in sunlight) thus rereleases NO so that it can participate in another series of reactions with other hydrocarbons (and essentially converts it into a catalyst for additional oxidation reactions).

\[
\text{CH}_4 + 4\text{O}_2 + 2\text{hv} \rightarrow \text{CH}_2\text{O} + \text{H}_2\text{O} + 2\text{O}_3
\]

We now have the makings of photochemical smog! Nature has taken a single – mainly harmless – molecule of methane and turned it into formaldehyde, a toxic molecule, and two ozone molecules. Ozone is very harmful for living things (as a molecule, it is toxic, but it’s also important for absorbing ultraviolet light, so we like ozone to stay put in the stratosphere where it is too far from the surface to be harmful, but provides a shield to protect us from harmful UV radiation).
Bimolecular Reactions

Typically, there are two types of reactions between molecules in the atmosphere that concern us. These are called 2nd order (bimolecular) and 3rd order (termolecular) reactions. We write a generic bimolecular reaction as:

\[ A + B \rightarrow C + D \]

The rate of this reaction can be written as:

\[ \frac{d[A]}{dt} = -k^{II} [A] [B] \]

where \( k^{II} \) is referred to as the “bimolecular rate coefficient” (or more usually, “rate constant”). Note that the sign of the term on the right is negative. This means that \([A]\) is decreasing with time, as it should (it is reacting away).

We can also say the following:

\[ -\frac{d[A]}{dt} = -\frac{d[B]}{dt} = \frac{d[C]}{dt} = \frac{d[D]}{dt} \]
Termolecular Reactions

Some reactions require three species to react in order for new products to form. This is generally the case for reactions that involve the recombination of two species into a new single species, for example, the formation of nitric acid from hydroxyl (OH) and nitrogen dioxide (NO₂):

\[
\text{OH} + \text{NO}_2 + \text{M} \rightarrow \text{HNO}_3 + \text{M}
\]

These reactions, called “termolecular”, have rate laws that can be written as the following for the general reaction between A, B, and C:

\[
\text{Rate} = -d[A]/dt = k^\text{III} [A] [B] [C]
\]

For the reaction above, this becomes:

\[
\text{Rate} = d[H\text{NO}_3]/dt = k^\text{III} [\text{OH}] [\text{NO}_2] [\text{M}]
\]

Air, or M, is our usual ‘third body’, as nitrogen and oxygen are very efficient at carrying away the energy of the reactants A and B when they stick together.
What are the units for $k^{II}$ and $k^{III}$?

The left hand side of the equation, the change in concentration with time ($d[A]/dt$), is usually expressed in molecules cm$^{-3}$ s$^{-1}$, so the right hand must also be in molecules cm$^{-3}$ s$^{-1}$. Ignoring the + and – sign,

$$k^{II} \text{ (cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}) \times [A] \text{ (molecule cm}^{-3}) \times [B] \text{ (molecule cm}^{-3})$$
$$= d[A]/dt \text{ (molecules cm}^{-3} \text{ s}^{-1})$$

$$k^{III} \text{ (cm}^6 \text{ molec}^{-2} \text{ s}^{-1}) \times [A] \text{ (molec cm}^{-3}) \times [B] \text{ (molec cm}^{-3}) \times [C] \text{ (molec cm}^{-3})$$
$$= d[A]/dt \text{ (molec cm}^{-3} \text{ s}^{-1})$$

So $k^{II}$ is in $cm^3$ molecule$^{-1}$ s$^{-1}$ and $k^{III}$ is in $cm^6$ molecule$^{-2}$ s$^{-1}$. It’s a little tricky getting used to units that are inverse concentration, but realize that they don’t represent anything physical, other than the fact that if the bimolecular rate coefficient for one reaction is larger than that for another, it means that the reaction with the larger rate constant is more likely to occur when two molecules collide. So, basically, the rate constant is just a number that tells us the likelihood that two molecules, when they collide, will react to form products.
Let’s go back to the oxidation of methane (CH$_4$). If the reaction with OH is the one that starts the whole reaction scheme going, then it will be the one that controls the rate at which the overall cycle will proceed. We’ll call this the “rate determining step.” What does it actually look like when we put real numbers in for the mixing ratios of CH$_4$ and OH?

\[-d[\text{CH}_4]/dt = k^\text{II} [\text{CH}_4] [\text{OH}]\]
\[\sim (1 \times 10^{-14} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}) \times (2 \text{ ppm}) \times (0.1 \text{ ppt})\]

We need to convert from mixing ratios to concentrations. Let’s assume we are at sea level ([M] = 2.45 x 10$^{19}$ molec cm$^{-3}$). So

[CH$_4$] = (2 x 10$^{-6}$) x (2.45 x 10$^{19}$ molec cm$^{-3}$) \sim 5 x 10$^{13}$ molec cm$^{-3}$

[OH] = (0.1 x 10$^{-12}$) x (2.45 x 10$^{19}$ molec cm$^{-3}$) \sim 2.5 x 10$^{6}$ molec cm$^{-3}$

\[-d[\text{CH}_4]/dt \sim (1 \times 10^{-14} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}) \times (5 \times 10^{13} \text{ molec cm}^{-3}) \times (2.5 \times 10^{6} \text{ molec cm}^{-3})\]

\[= 1.25 \times 10^6 \text{ molec cm}^{-3} \text{ s}^{-1}\]
Let’s take a quick look at what this ‘rate’ is telling us. If this rate were to remain the same with time, it would say that CH$_4$, at a concentration of 5x $10^{13}$ molec cm$^{-3}$ would be consumed by reaction of OH in a time, $\tau$, of 4x$10^6$ s.

That is,

$$\tau = \frac{5 \times 10^{13} \text{ molec cm}^{-3}}{1.25 \times 10^6 \text{ molec cm}^{-3} \text{ s}^{-1}}$$

Consequently, we call $\tau$ the lifetime of methane with respect to reaction with OH. Note that 1 day = 86400 s, so this represents a lifetime of 92 days. Because this value is longer than one day, to do this problem more correctly, we really should be using the amount of OH averaged over the time and space (i.e., location) of the air parcel that is in question, and an average value for the rate coefficient that takes variations in temperature into account as the air mixes throughout the troposphere. How do we do that?
In practice, rate constants such as $k^{II}$ above are specific to a particular reaction, and they must be measured separately for every reaction. They are then tabulated in a form called the Arrhenius expression.

$$k^{II} = A \exp (-E_a/RT).$$

"A" is called the pre-exponential; it is determined by such things as the size of the molecules that are reacting, the way they come together to form a new bond, and the way old bonds break. "$E_a$" is often called the activation energy; it is related to the overall energy of the reaction. The more energy the reactants have (I.e. the warmer the temperature) usually the more likely they are to react. This isn’t necessarily the case, however, as some reactions actually get slower at higher temperatures. However, the majority of reactions are faster at higher temperatures.
More General Rate Law

A rate law describes how the disappearance of reactant or appearance of product varies with time.

For a generic reaction that allows for more than one mole of a reactant or product to be consumed or produced:

\[ aA + bB \rightarrow cC + dD \]

\[
\text{rate} = -\frac{1}{a} \frac{d[A]}{dt} = -\frac{1}{b} \frac{d[B]}{dt} = \frac{1}{c} \frac{d[C]}{dt} = \frac{1}{d} \frac{d[D]}{dt}
\]
Another real example of a termolecular reaction

\[ 2 \text{NO} + \text{O}_2 \rightarrow 2 \text{NO}_2 \]

The rate of the reaction is then:

\[
\text{rate} = -\frac{1}{2} \frac{d[\text{NO}]}{dt} = -\frac{d[\text{O}_2]}{dt} = \frac{1}{2} \frac{d[\text{NO}_2]}{dt}
\]

So, \( \text{rate} = k \ [\text{NO}]^2 \ [\text{O}_2] \)
How large are rate constants for reactions?

Reactions between charged species ("ion-ion" reactions) are incredibly fast if the charges are opposite.

Reactions between charged species and neutral species ("ion-molecule" reactions) are also pretty fast, as the neutral species becomes polarized (i.e. charge within the molecule begins to separate and the molecules looks somewhat charged) as the ion approaches.

Reactions between two radicals ("radical-radical" reactions) can also be very fast because the two unpaired electrons would like to form a new covalent bond. Usually, these reactions occur on every collision. However, these reactions are not as fast as those involving ions, because the ions actually attract each other or other molecules, whereas radicals act more ‘neutral’ – they react IF they hit each other, but they don’t tend to pull other species towards them.

Reactions between radicals and molecules ("radical-molecule" reactions) can be fast, but usually less so than reactions between two radicals. They don’t typically occur on every collision – maybe only in one-in-ten or one-in-100 collisions.
A Note on Lifetimes

Recall that we defined the lifetime of a compound or substance in the atmosphere as the ratio of the amount of the substance (usually in units of concentration) to the rate at which the substance is being reacted away by some other chemical. Let’s take a look at what this means for a bimolecular reaction between A and B:

\[
A + B \rightarrow C + D \quad \text{rate} = k[A][B]
\]

The lifetime of A can be written as:

\[
\tau = \frac{[A]}{\text{rate}} = \frac{[A]}{(k[A][B])}
\]

\[
\tau = \frac{1}{k[B]}
\]
Molecules rarely react with each other (i.e. “molecule-molecule” reactions are the slowest of them all).

We call the fastest rates for any two reactants "gas kinetic”, meaning that a reaction occurs on every collision. Ion reactions have larger gas-kinetic rate coefficients. We don’t worry about these in the lower atmosphere, since there are so few ionic species present in the gas phase.

For a radical-radical or radical-molecule reaction, a ‘gas-kinetic’ rate coefficient will be no larger than about

\[ k \sim 1 \times 10^{-10} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1} \]

Most bimolecular reactions have rates between \( 10^{-11} \) and \( 10^{-14} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1} \)
Steady-State Approximation

Very often in atmospheric chemistry, we are not interested in a single reaction, but rather in a coupled set of reactions, where the products of one reaction are the reactants in the next. We make the assumption that these gases are in "steady-state"; that is, that their concentrations do not change with time.

For example:

\[
\begin{align*}
\text{rate of reaction} \\
\text{HO}_2 + \text{NO} &\rightarrow \text{OH} + \text{NO}_2 \quad k_1 [\text{HO}_2] [\text{NO}] \\
\text{OH} + \text{O}_3 &\rightarrow \text{HO}_2 + \text{O}_2 \quad k_2 [\text{OH}] [\text{O}_3]
\end{align*}
\]

In this pair of reactions, we need to consider what is causing OH and HO\(_2\) to change.
First, let's look at OH. It is produced by the first reaction and consumed by the second one. The rate of the first reaction is

\[ \text{Rate}_1 = k_1[\text{HO}_2][\text{NO}] \]

and the rate of the second is

\[ \text{Rate}_2 = k_2[\text{OH}][\text{O}_3]. \]

If the concentration of OH is not changing, it must be produced as fast as it is consumed. Thus:

\[ \frac{d[\text{OH}]}{dt} = 0 = k_1[\text{HO}_2][\text{NO}] - k_2[\text{OH}][\text{O}_3] \]

We can make the same argument for \( \text{HO}_2 \):

\[ \frac{d[\text{HO}_2]}{dt} = 0 = k_2[\text{OH}][\text{O}_3] - k_1[\text{HO}_2][\text{NO}] \]
In the not-too-distant past, accurate measurements of OH and HO$_2$ were not possible in the atmosphere. People would use relationships like these to assess both their observations and chemical models.

It is easy to rearrange either of the above expressions:

\[ 0 = k_1[\text{HO}_2][\text{NO}] - k_2[\text{OH}][\text{O}_3] \]

\[ k_1[\text{HO}_2][\text{NO}] = k_2[\text{OH}][\text{O}_3] \]

\[ [\text{OH}]/[\text{HO}_2] = k_1[\text{NO}]/k_2[\text{O}_3] \]

Thus, with measurements of ozone and nitric oxide (which are both relatively easy) and temperature (to get the rate constants right), one can estimate the ratio of OH to HO$_2$. 
**Sample Problem:** The production of ozone in the troposphere requires the photolysis of NO$_2$, followed by reaction of an oxygen atom with molecular oxygen:

\[
\text{NO}_2 + \text{hv} \rightarrow \text{NO} + \text{O} \quad \text{J} = 1 \times 10^{-2} \text{ s}^{-1}
\]

\[
\text{O} + \text{O}_2 + \text{M} \rightarrow \text{O}_3 + \text{M} \quad \text{k} = 6.1 \times 10^{-34} \text{ cm}^6 \text{ molec}^{-2} \text{ s}^{-1}
\]

If the NO$_2$ concentration is $2.46 \times 10^{10}$ molec cm$^{-3}$ and the density, [M], is $2.46 \times 10^{19}$ molec cm$^{-3}$, what is the steady-state production rate of ozone?

The only species that we can create a steady-state approximation for here is O, as it is the only one with both production and loss processes.

\[
d[O]/dt = J[\text{NO}_2] - k[O][\text{O}_2][\text{M}] = 0
\]

The production rate of ozone is:

\[
d[O_3]/dt = k[O][\text{O}_2][\text{M}]
\]

But, we don't know [O].

However, we can substitute from the steady-state expression for [O]:

\[
d[O_3]/dt = J[\text{NO}_2] = 1 \times 10^{-2} \text{ s}^{-1} \times 2.46 \times 10^{10} \text{ molec cm}^{-3}
\]

\[
= 2.46 \times 10^{8} \text{ molec cm}^{-3} \text{ s}^{-1}
\]
How do equilibrium constants relate to rate coefficients? We’ll come back to this when we deal with acid rain.

We write an equilibrium expression, with equilibrium constant $K_{eq}$, as:

$$A + B \leftrightarrow C + D \quad K_{eq} = \frac{[C][D]}{[A][B]}$$

We can break this into a forward reaction and reverse reaction:

$$A + B \rightarrow C + D \quad \text{rate of forward reaction} = k_f [A][B]$$
$$C + D \rightarrow A + B \quad \text{rate of reverse reaction} = k_r [C][D]$$

At equilibrium, the rates of forward and reverse reactions are equal (or else the concentrations of the species would change). So

$$k_f [A][B] = k_r [C][D]$$

Rearranging:

$$\frac{[C][D]}{[A][B]} = \frac{k_f}{k_r} = K_{eq}$$

So $K_{eq} = \frac{k_f}{k_r}$, the ratio of two reaction rate coefficients!