Chemistry 471/671

Atmospheric Chemistry II:
Urban Smog

The Oxidation of Methane

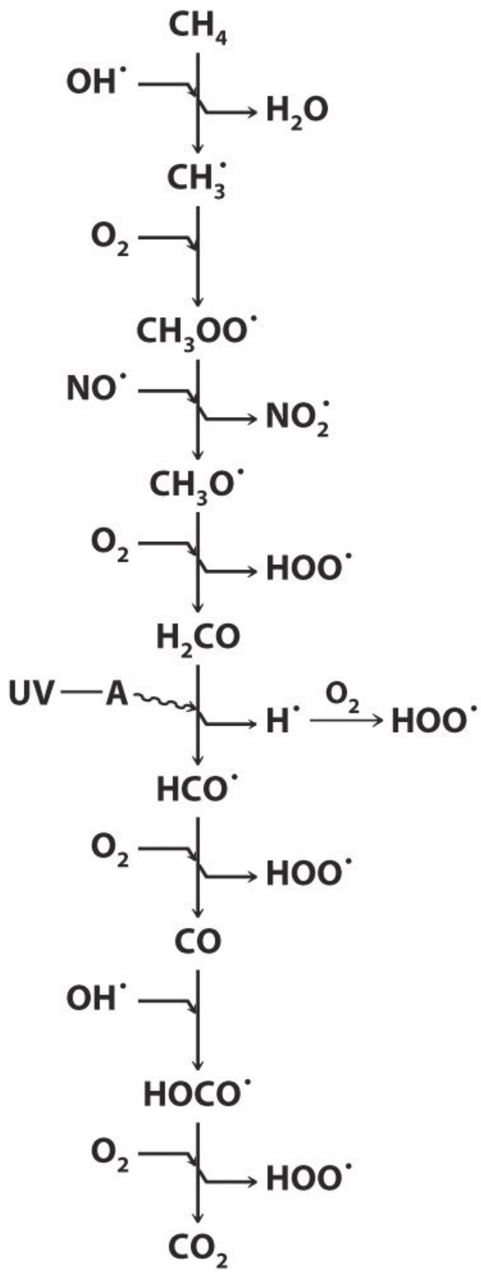


Figure 3-2
Environmental Chemistry, Third Edition

Does it have a peroxy bond?

Can I make an aldehyde by C-C cleavage?

Can I abstract an H to make a multiple bond to oxygen?

If no to all of the above, add O_2

Fate of VOCs

In reality, most oxidation schemes produce an array of products

How do we predict which of many reaction pathways are more likely to occur?

It makes sense to consider this as a function of transition states

Which transition states are lower in energy? The pathways regulated by these TS will have faster rates, and will generally account for more of the *reactive flux*

Fate of VOCs

Most of these TS involve the formation of radical species

Some radical species are more stable than others

Consider OH abstracting an H atom from propane:

$CH_3CH_2CH_3 + OH \rightarrow \bullet CH_2CH_2CH_3 + H_2O$

$\rightarrow CH_3\bullet CHCH_3 + H_2O$

Which is the more probable reaction?

Fate of VOCs

$CH_3CH_2CH_3 + OH \rightarrow \bullet CH_2CH_2CH_3 + H_2O$

$\rightarrow CH_3\bullet CHCH_3 + H_2O$

Which is the more probable reaction?

Trivial answer: the one with the lower activation barrier

More usefully: the one with the more stable radical being formed at the TS

Recall organic chemistry and the Markovnikov addition...

When forming a carbocation intermediate, the cation is located on the **most substituted** carbon

Markovnikov’s Rule

The more substituted centers are able to spread out the electron density through induction and hyperconjugation

The same reasoning applies to radical transition states: The **more substituted** radical is more stable

Similar arguments apply in the addition to double bonds – OH adds to the *less* substituted terminus (leaving the radical at the *more* substituted end)

Note: it’s actually a little more complicated…
Allylic and benzylic radicals are even more stable than tertiary ones, due to delocalization

phenyl < primary (1º) < secondary (2º) < tertiary (3º) < allyl ≈ benzyl

Fate of VOCs

If OH reacts with an alkene, does it abstract an H or add to the double bond?

Markovnikov's rule doesn't help us distinguish between two dissimilar products

$OH + CH_2{=}CH_2 \rightarrow \bullet CH{=}CH_2 + H_2O$?

$\rightarrow \bullet CH_2{-}CH_2OH$?

What if there's more than one double bond?

What if there's a cycle... or an aromatic ring?

What if OH and O_3 are both possible reagents?

In non-trivial systems, additional experimental and/or theoretical work is needed

Fate of VOCs – Radical Production

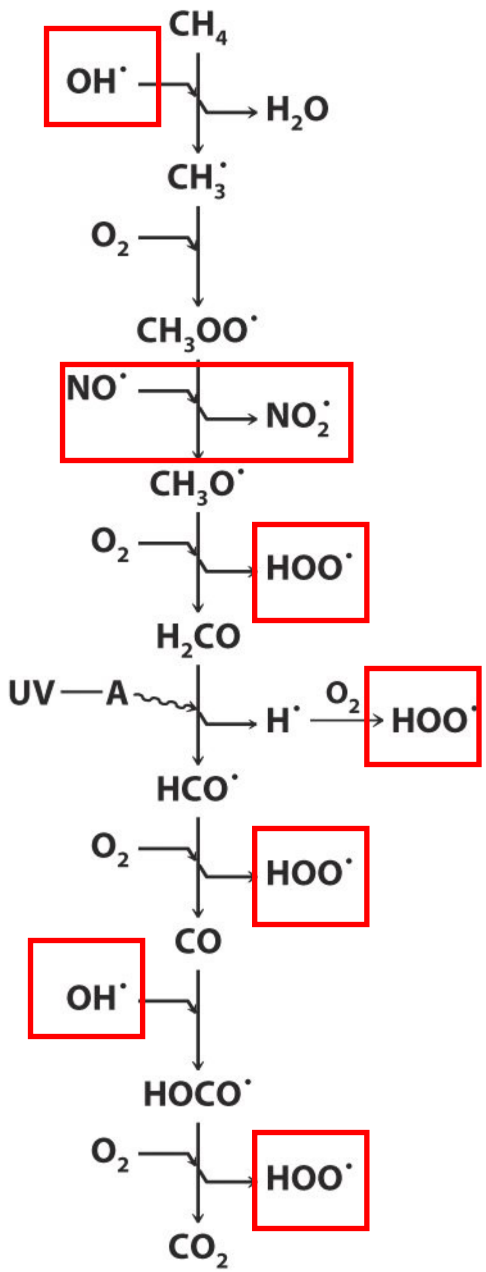


Figure 3-2
Environmental Chemistry, Third Edition

The oxidation of methane to CO_2 consumes 2 OH radicals… but produces 4 HO_2 radicals, and converts 1 NO radical into NO_2

Peroxy radicals drive more NO to NO_2:

$$HO_2 + NO \rightarrow OH + NO_2$$

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

So the net result of converting a ONE carbon species in to CO_2:

2 OH are generated

5 NO radicals are converted to NO_2

Fate of VOCs – Radical Production

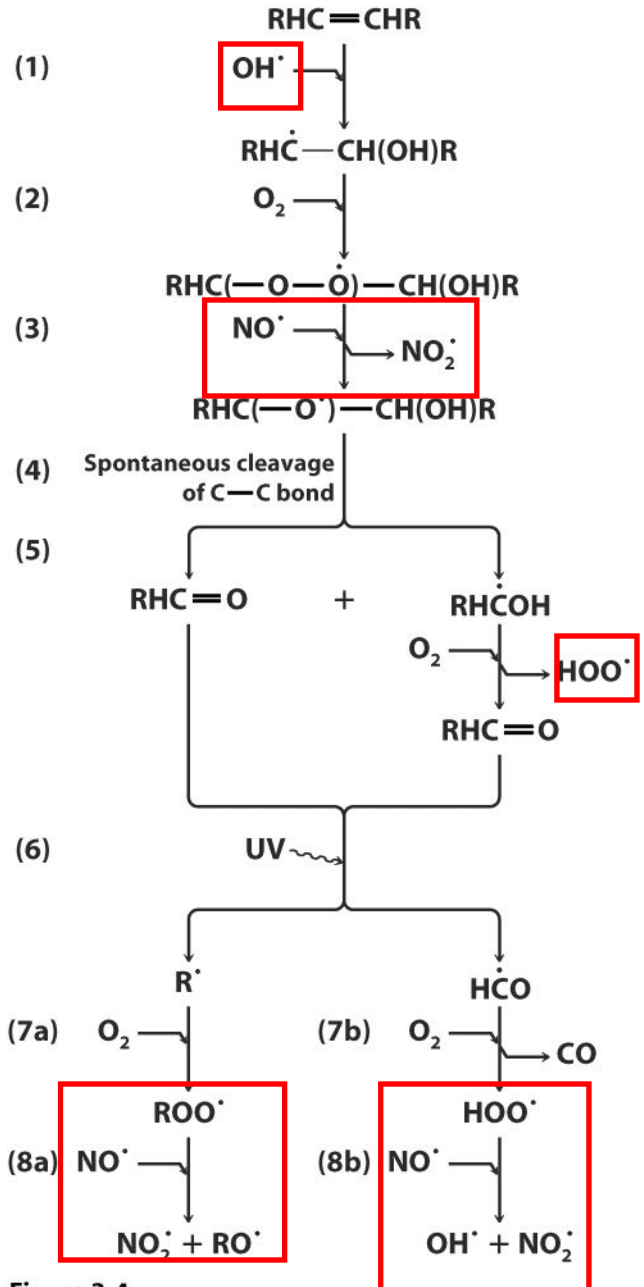


Figure 3-4
Environmental Chemistry, Third Edition

- The partial oxidation of our generic alkene consumes 1 OH radical, produces 2 HO_2 radicals (a net gain of 1 OH), and converts 4 NO radicals into NO_2
- And this pathway isn't finished – "RO" almost certainly contains more H and/or more double bonds.

Fate of VOCs – Radical Production

The reactions of most VOCs in the atmosphere are initiated by attack of the hydroxyl radical, but the radical chain reaction that follows produces many more OH radicals, and converts NO into NO_2

Radical “families”:

H, OH, HO_2 – “odd hydrogen”, HO_x

NO, NO_2, NO_3 – “odd nitrogen”, NO_x

The net result of the oxidation is a dramatic increase in radicals in the atmosphere the longer the chain propagates – and in many cases, “smog”.

Urban Air Pollution – "London" Smog

"London" smog:

- **fog**
- **soot particles**
- **sulfur dioxide**
- **tar**

This forms a highly acidic mist.

Some incidents of deaths associated with sulfurous smog:

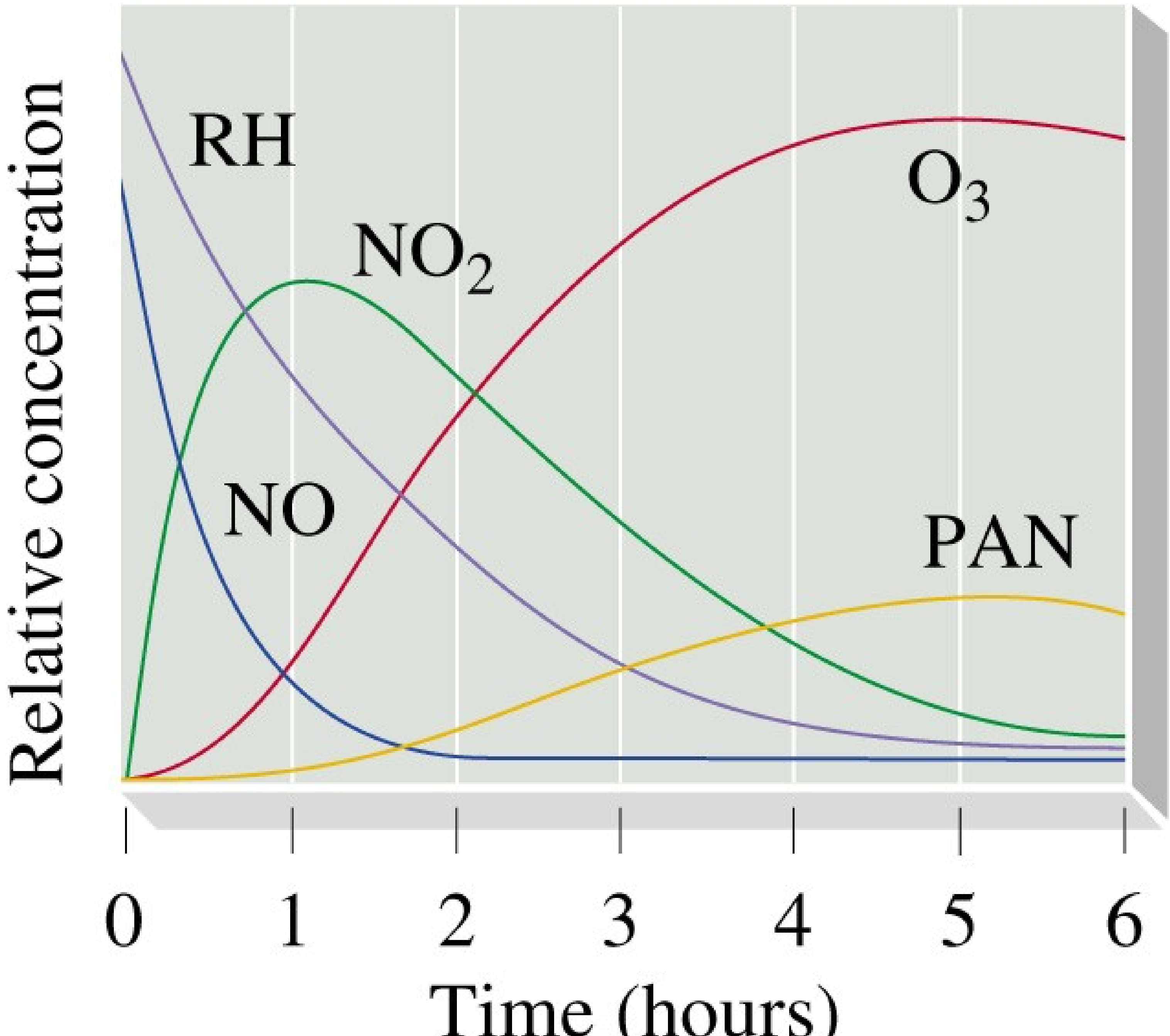
1930	Meuse Valley, Belgium	63
1948	Donora, Pennsylvania	20
1952	London (5 days)	4000
1962	London	700

These deaths lead to a reduction in coal consumption and an increase in alternative fuels, such as gasoline...

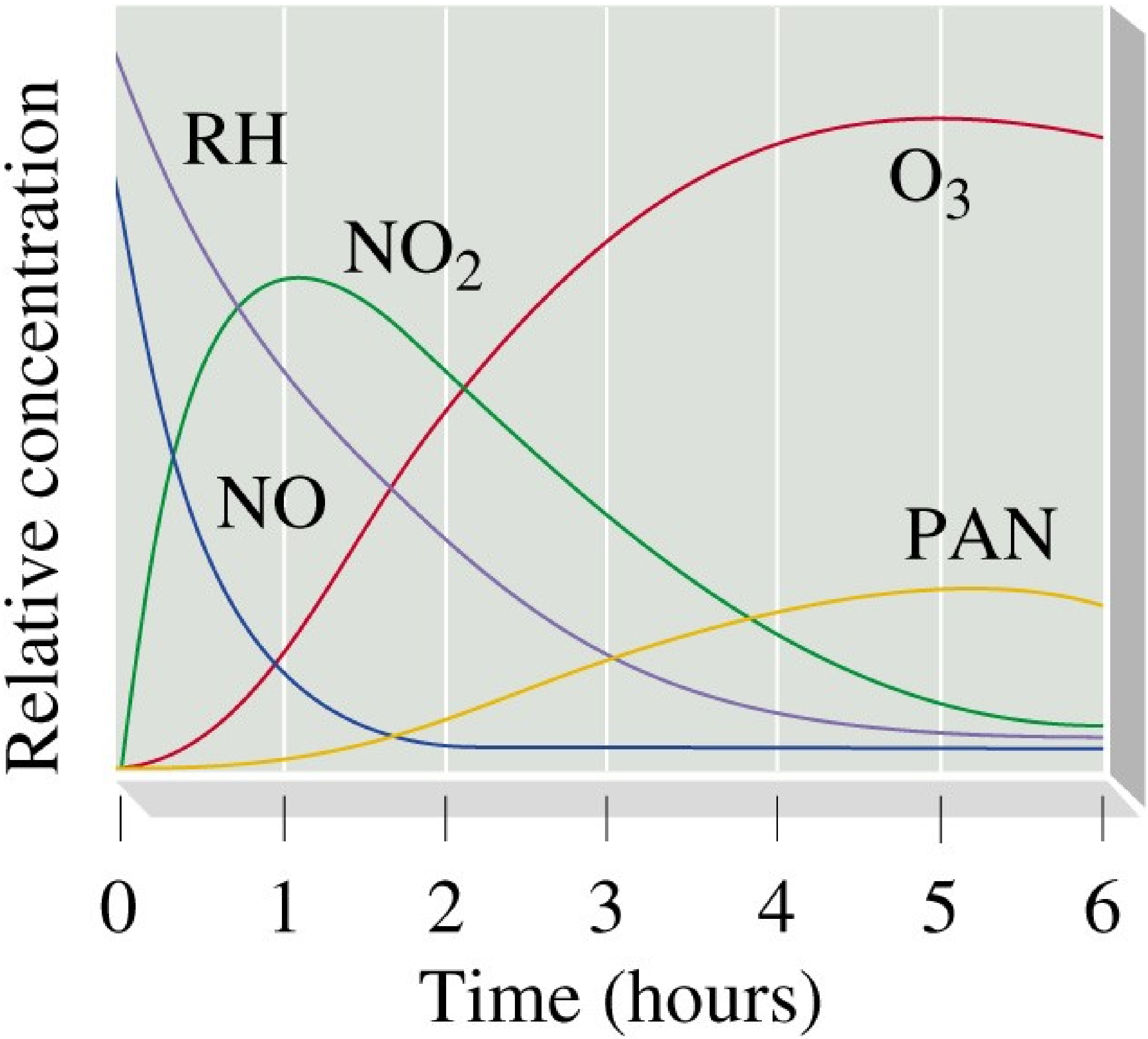
Urban Air Pollution – “Los Angeles” Smog


Los Angeles Smog: driven by the photochemistry of the volatile organic compounds (VOCs) and oxygenated nitrogen species (NO_x) contained in exhaust from combustion engines.

Photochemical smog is air saturated with ozone, VOCs and aerosol particles.



Relative concentration
RH
O_3
NO_2
NO
PAN
0
1
2
3
4
5
6
Time (hours)



Sources of ozone in the troposphere:

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

$$O + O_2 \rightarrow O_3$$

Sinks of ozone:

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

These reactions are a null cycle... But in urban areas, this balance is disrupted

As VOC oxidation converts NO into NO_2, the LOSS term for ozone diminishes and the SOURCE term grows

Timeline of a smog incident

1) Sunlight initiates photolysis of the NO_x **reservoir species** (HONO, $HONO_2$, PAN, NO_3)

2) VOCs from morning rush hour react with OH and NO to form aldehydes

3) Aldehydes are photolyzed to produce radicals (autocatalysis)

4) Radicals oxidize NO to NO_2, which photolyzes to produce O_3

5) As radical concentrations grow, PAN and H_2O_2 are produced

6) When the sun goes down, NO_3 continues some oxidation and the NO_x reservoir grows

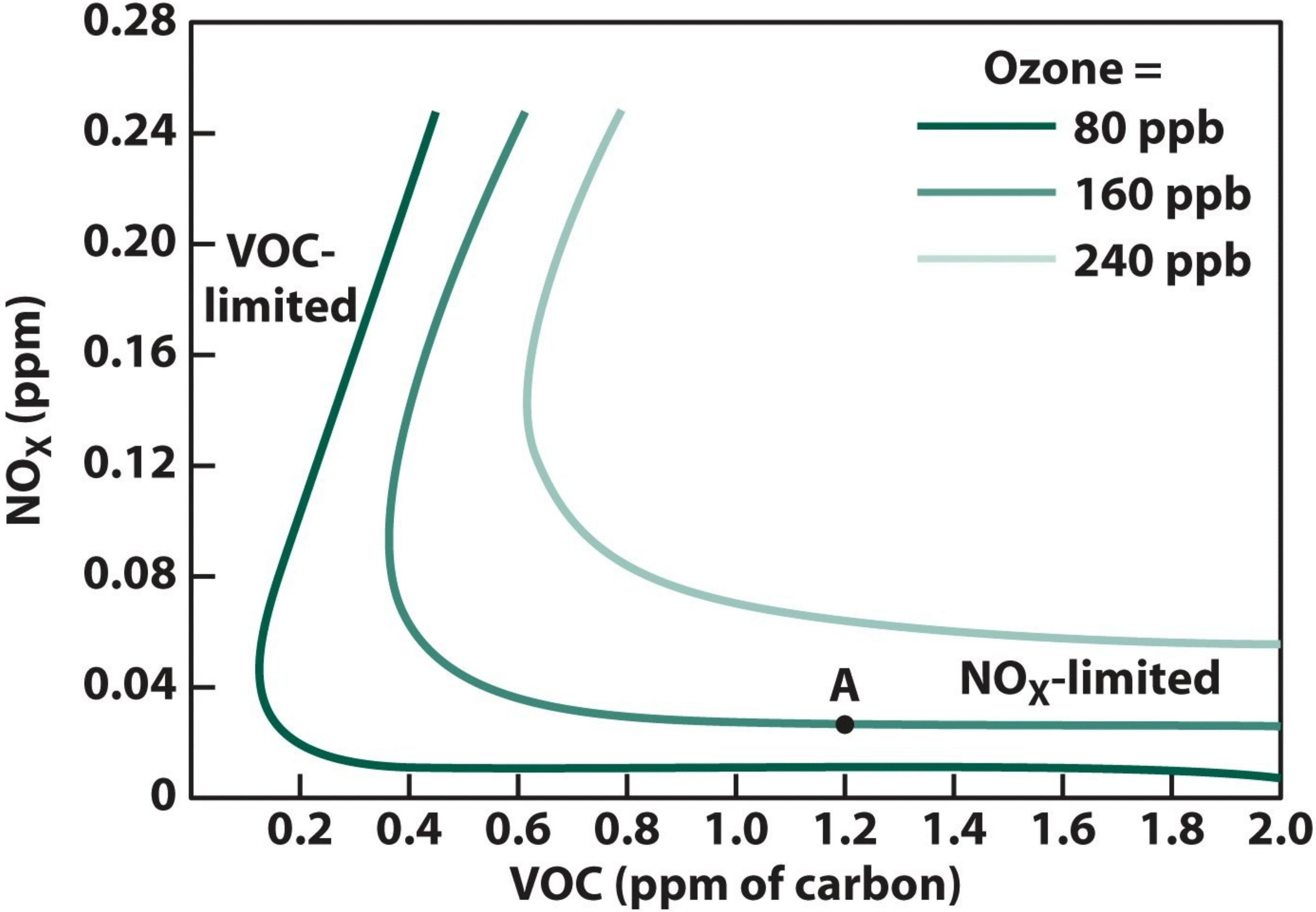


Figure 2-6
Environmental Chemistry, Third Edition

Particulates in the Atmosphere

Photochemical smog is air saturated with ozone, VOCs and aerosol particles.

Where does the aerosol come from?

- Condensation of hot gases from combustion exhaust
- Coagulation of VOC-based radicals
- Condensation of *secondary* pollutant species with low vapor pressures

Particulates in the Atmosphere

While it is convenient to ignore them in terms of chemistry, there are many other obvious sources of particulates in the atmosphere

Smoke, smog, mist, fog, dust, aerosols

To talk in generalities, we assume particles are spherical – even though very few are

We define particles by their diameter

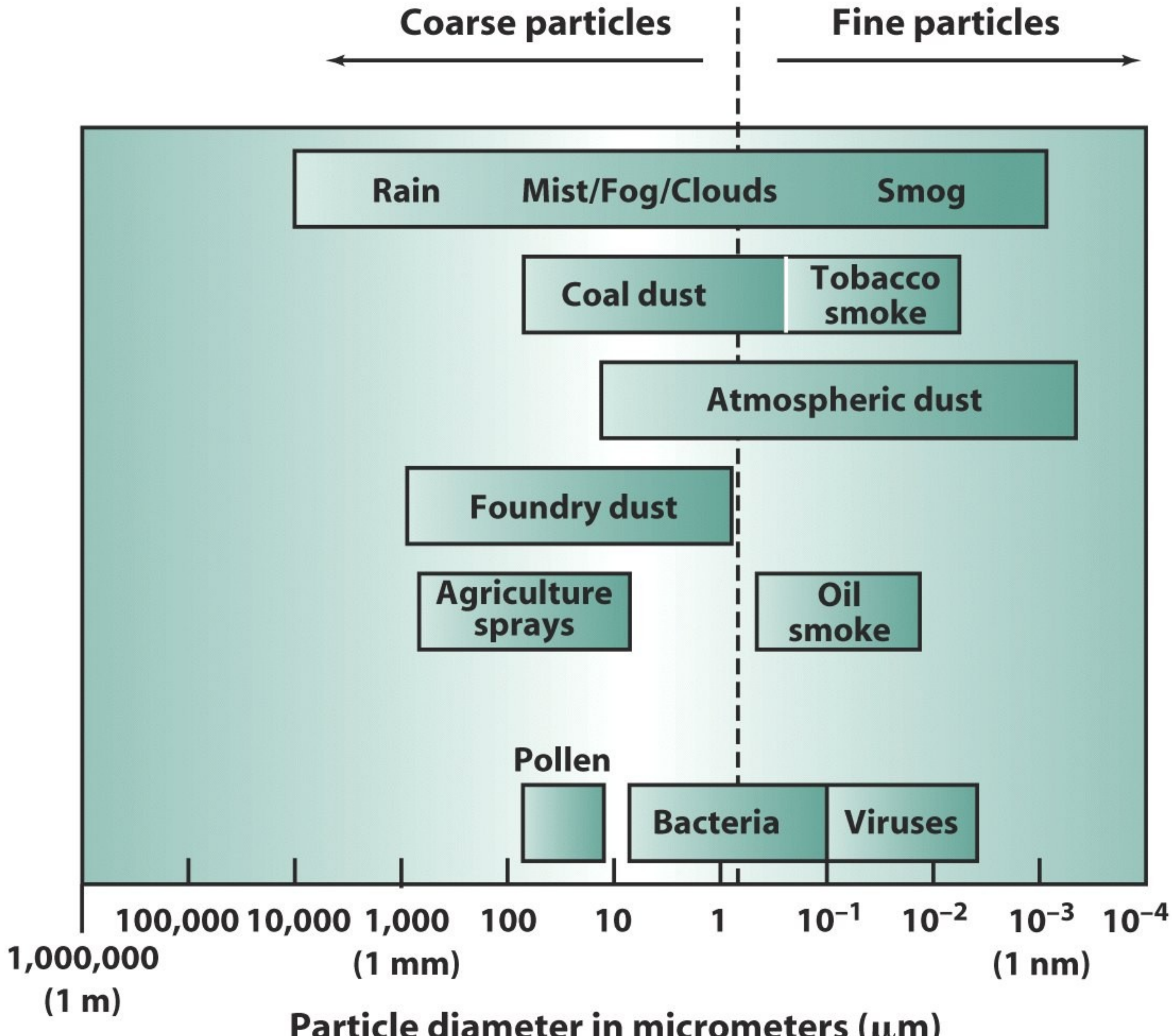


Figure 2-15
Environmental Chemistry, Third Edition

Particulates in the Atmosphere

PM indices:

Because the molecular composition varies, we use mass: $\mu g/m^3$

Generally, smaller particles are more hazardous (why?), and so measurements generally report the *largest* diameter included in the record:

PM_{10} – “inhalable”

$PM_{2.5}$ – “respirable”