

Atmospheric Chemistry of CO and NO_x

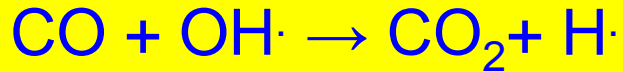


O(¹D) can have two routes:

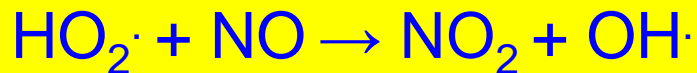


(hydroxyl radical)

This OH radical fundamental is responsible for the photo chemical/chemical reactions:



Or Simply combine:-



OH· radical regenerated.

} This is one more route for NO oxidation to NO₂

Finally, OH and NO₂ may react to form nitric acid,



All the reactions involved in the CO-NO_x chemistry are summarized in the following table:

Reaction	Rate Constant ^a
1. $\text{NO}_2 + h\nu \rightarrow \text{NO} + \text{O}$	Depends on light intensity
2. $\text{O} + \text{O}_2 + M \rightarrow \text{O}_3 + M$	$6.0 \times 10^{-34} (T/300)^{-2.3} \text{ cm}^6 \text{ molecule}^{-2} \text{ sec}^{-1}$
3. $\text{O}_3 + \text{NO} \rightarrow \text{NO}_2 + \text{O}_2$	$2.2 \times 10^{-12} \exp(-1430/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$
4. $\text{O}_3 + h\nu \rightarrow \text{O}({}^1\text{D}) + \text{O}_2$	$0.0028k_1$
5. $\text{O}({}^1\text{D}) + M \rightarrow \text{O} + M$	$2.9 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$
6. $\text{O}({}^1\text{D}) + \text{H}_2\text{O} \rightarrow 2\text{OH}\cdot$	$2.2 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$
7. $\text{CO} + \text{OH}\cdot \rightarrow \text{CO}_2 + \text{HO}_2\cdot$	$2.2 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1b}$
8. $\text{HO}_2\cdot + \text{NO} \rightarrow \text{NO}_2 + \text{OH}\cdot$	$3.7 \times 10^{-12} \exp(240/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$
9. $\text{OH}\cdot + \text{NO}_2 \rightarrow \text{HNO}_3$	$1.1 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$

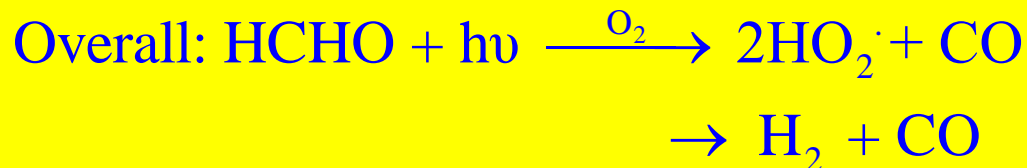
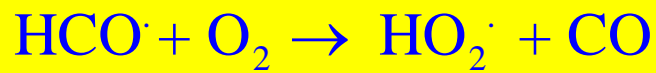
Summary

- The basic reaction mechanism of the CO/NO_x system exhibit many of the key features of those involving much more 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.
- It is useful to proceed to a molecule that is somewhat more complicated than CO to see how the similar NO_x mechanism develops.

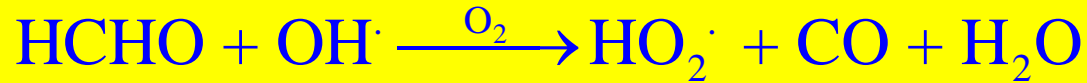
Atmospheric Chemistry of HCHO and NO_x

- Formaldehyde (HCHO) is a primary pollutant and also an oxidation product of hydrocarbons.
- These are basically emitted from automobiles.
- Formaldehyde undergoes two routes for the primary reactions in the atmosphere: (i) Photolysis and (ii) Ordinary chemistry

Route (i):



Route 2:



Summary

- All reactions are because of photochemistry and reaction with OH·
- HCHO/HC/CO → HO₂·
- HO₂ to oxidize NO to NO₂.
- NO_x removal from system is through OH· to HNO₃

All the reactions involved in the CO-NOx chemistry are summarized in the following table:

Reaction	Rate Constant
1. $\text{NO}_2 \xrightarrow{h\nu} \text{NO} + \text{O}$	Depends on light intensity
2. $\text{O} + \text{O}_2 + M \rightarrow \text{O}_3 + M$	See Table 4.2
3. $\text{O}_3 + \text{NO} \rightarrow \text{NO}_2 + \text{O}_2$	See Table 4.2
4. $\text{HCHO} + h\nu \xrightarrow{4a} 2\text{HO}_2\cdot + \text{CO}$	Depends on light intensity
$\xrightarrow{4b} \text{H}_2 + \text{CO}$	Depends on light intensity
5. $\text{HCHO} + \text{OH}\cdot \xrightarrow{5} \text{HO}_2\cdot + \text{CO} + \text{H}_2\text{O}$	$1.1 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$
6. $\text{HO}_2\cdot + \text{NO} \xrightarrow{6} \text{NO}_2 + \text{OH}\cdot$	See Table 4.2
7. $\text{OH}\cdot + \text{NO}_2 \xrightarrow{7} \text{HNO}_3$	See Table 4.2

Here the CO-OH reaction is omitted from the previous Table, as it is generally slower than those involving HCHO. Applying the PSSA, then:

$$[\text{O}_3]_{ss} = \frac{k_1[\text{NO}_2]}{k_3[\text{NO}]}$$

$$[\text{OH}]_{ss} = \frac{2k_{4a}[\text{HCHO}]}{k_7[\text{NO}_2]}$$

$$[\text{HO}_2]_{ss} = 2k_{4a} \left\{ 1 + \frac{k_5[\text{HCHO}]}{k_7[\text{NO}_2]} \right\} [\text{HCHO}] / k_6[\text{NO}]$$

rate equations for NO_2 , NO , and HCHO are, as a result,

$$\frac{d[\text{NO}_2]}{dt} = \frac{2k_{4a}k_5[\text{HCHO}]^2}{k_7[\text{NO}_2]}$$

$$\frac{d[\text{NO}]}{dt} = -2k_{4a} \left\{ 1 + \frac{k_5[\text{HCHO}]}{k_7[\text{NO}_2]} \right\} [\text{HCHO}]$$

$$\frac{d[\text{HCHO}]}{dt} = - \left\{ k_{4a} + k_{4b} + 2k_{4a} \frac{k_5[\text{HCHO}]}{k_7[\text{NO}_2]} \right\} [\text{HCHO}]$$

The behavior (concentration in ppm) of the system as a function of its initial conditions for HCHO and NO_x are calculated by using the models and explained in the figures

CASE 1: (Figure 1)

$[\text{NO}_2]_0 = 0.1$, $[\text{NO}]_0 = 0.01$,
 $[\text{HCHO}]_0 = 0.1$.

Then during first two minutes:

$[\text{NO}_2] = 0.069$, $[\text{NO}] = 0.0405$,
 $[\text{O}_3] = 0.032$

Over the 600 minute period, it can be observed that after the first 20 minutes NO_2 continually decreases, since even though NO is continually being converted to NO_2 by O_3 , there is such an excess of NO_2 that the $\text{NO}_2\text{-OH}$ reaction is removing NO_2 to HNO_3 at rate such that it dominates the NO_2

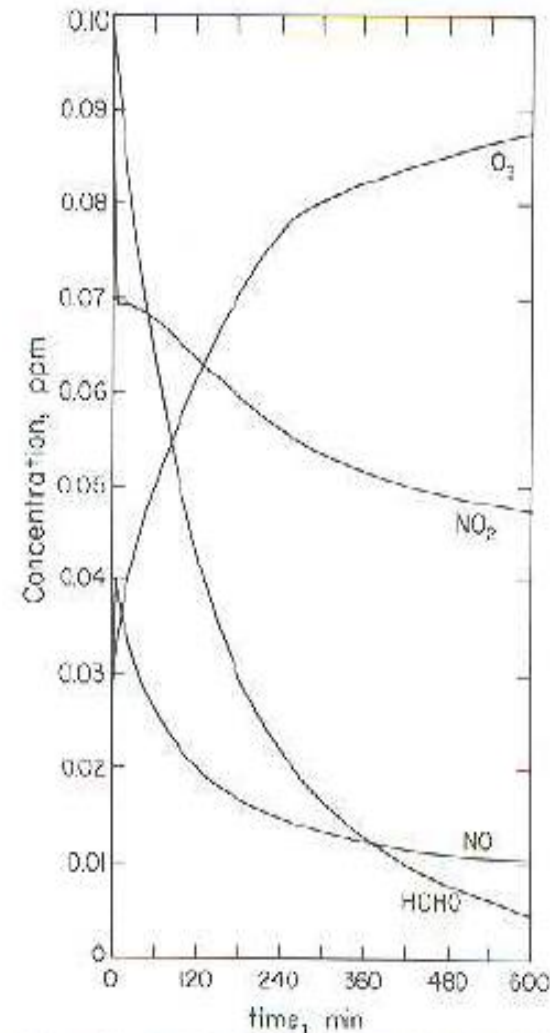


Figure 1 Photooxidation of formaldehyde in a mixture of NO , NO_2 , and air. Initial concentrations are $[\text{NO}_2]_0 = 0.1$ ppm, $[\text{NO}]_0 = 0.01$ ppm, and $[\text{HCHO}]_0 = 0.1$ ppm.

This figure shows the concentration versus time for the initial conditions: $[\text{NO}_2]_0 = 0.1$, $[\text{NO}]_0 = 0.1$, $[\text{HCHO}]_0 = 1.0$

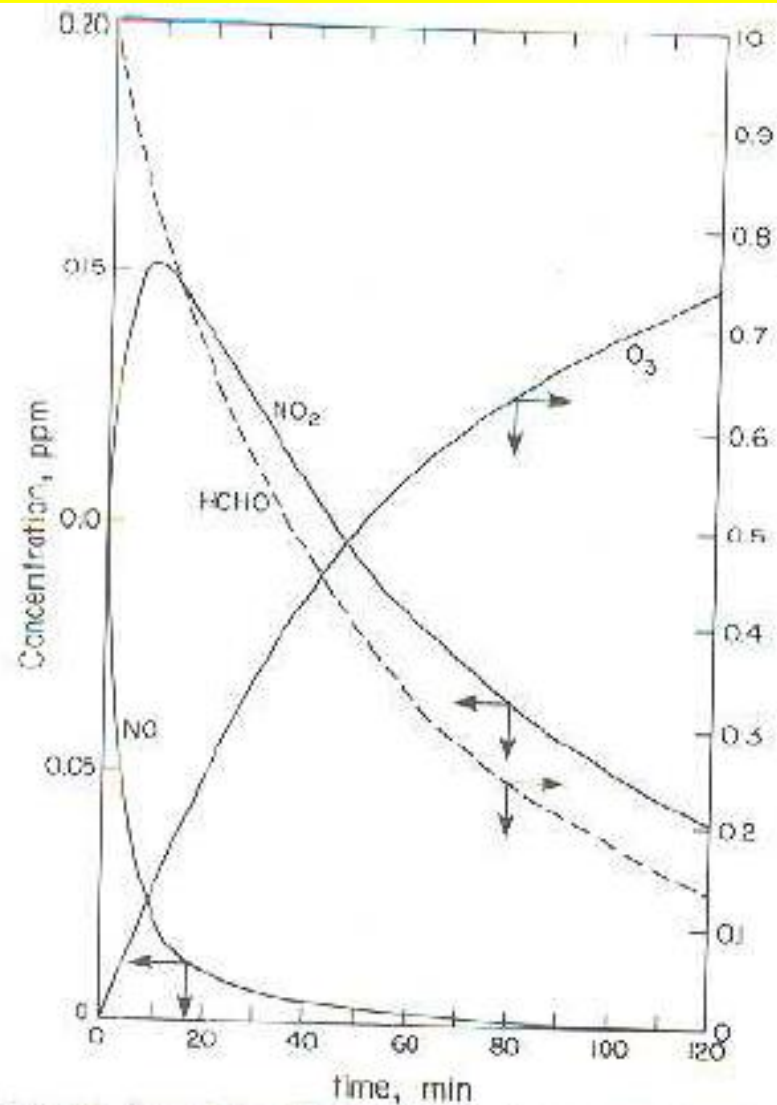


Figure Photooxidation of formaldehyde in a mixture of NO, NO₂, and air. Initial concentrations are $[\text{NO}_2]_0 = 0.1$ ppm, $[\text{NO}]_0 = 0.1$ ppm, and $[\text{HCHO}]_0 = 1.0$ ppm.

This figure shows the concentration versus time for the initial conditions: $[\text{NO}_2]_0=0.1$, $[\text{NO}]_0=1.0$, $[\text{HCHO}]_0=1.0$

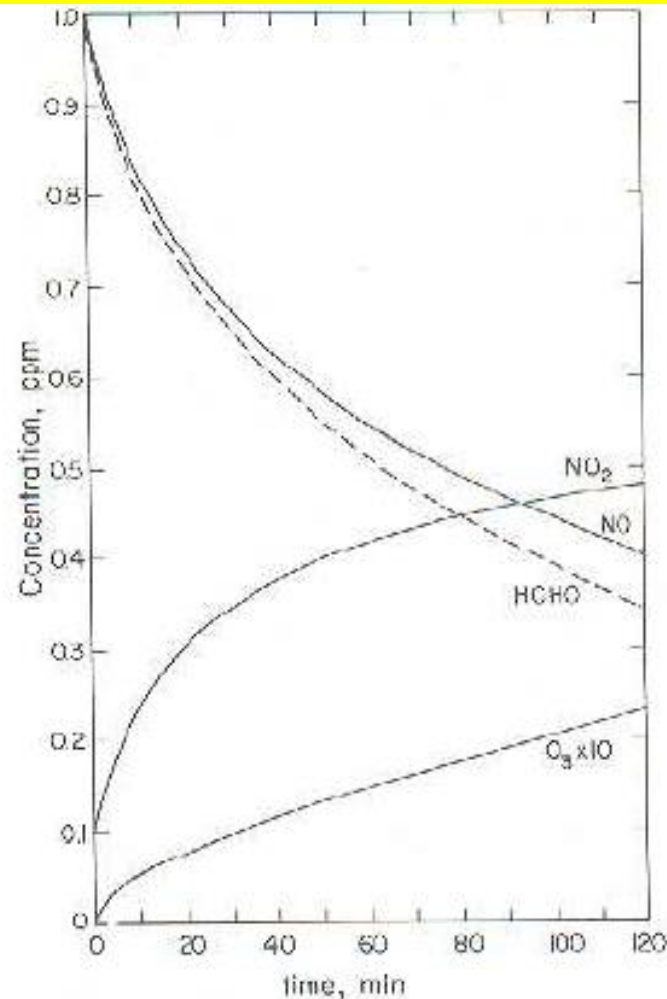


Figure Photooxidation of formaldehyde in a mixture of NO , NO_2 , and air. Initial concentrations are $[\text{NO}_2]_0 = 0.1$ ppm, $[\text{NO}]_0 = 1.0$ ppm, and $[\text{HCHO}]_0 = 1.0$ ppm.

- The conversion of NO to NO₂ and the formation of O₃ are therefore driven by HCHO through its production of HO₂. Thus, the theoretical maximum amount of O₃ that could be produced in this system is:

$$[O_3] = [HCHO]_0 + [NO_2]_0$$

- When all the NO_x is converted to HNO₃, the system ceases reacting. In a sense, a given system can be characterized by its ability to produce O₃.
- The effect of [HCHO]₀ on NO₂ dynamics is shown in the following figure.

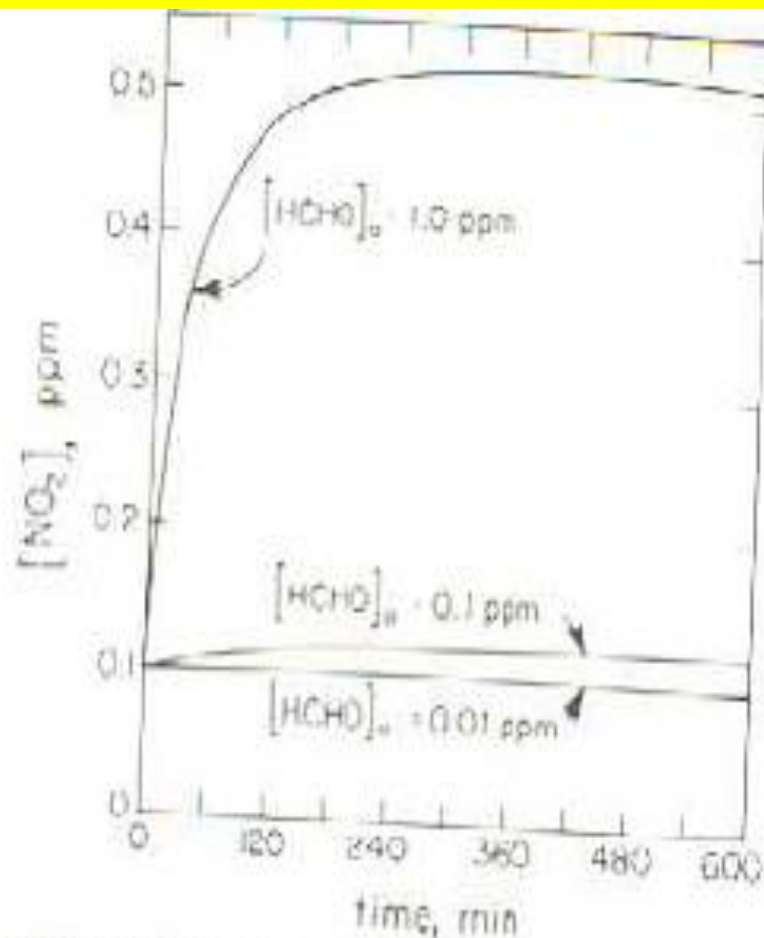
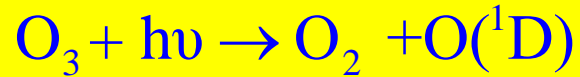
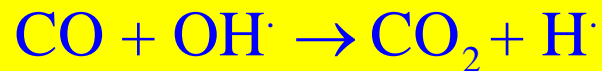
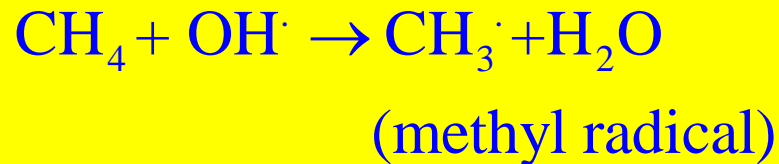


Figure 1 Effect of initial concentration of formaldehyde on the dynamics of NO_2 in the photooxidation of a mixture of HCHO , NO , and NO_2 in air. In the three cases shown, $[\text{NO}_2]_0 = 0.1 \text{ ppm}$ and $[\text{NO}]_0 = 1.0 \text{ ppm}$.

Oxidation of Methane



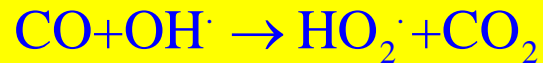
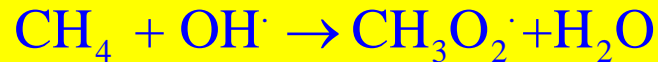
Then hydroxyl radicals react with CH_4 and CO present in the atmosphere.



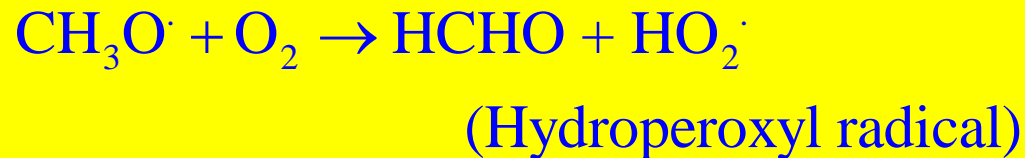
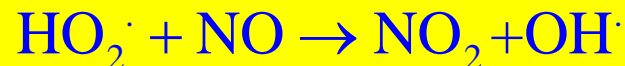
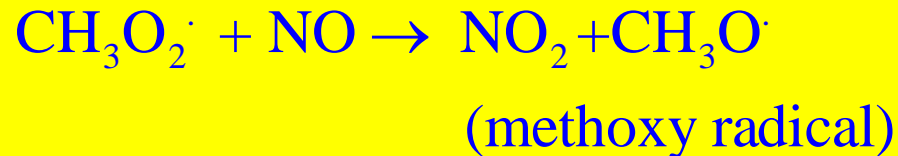
Then instantaneously the following reaction takes place



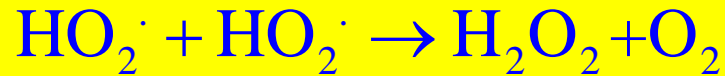
So that the CH_4 and CO-OH reactions may be written simply as:



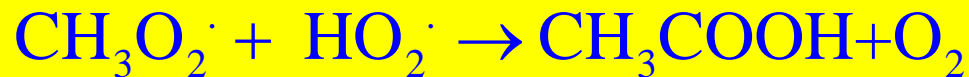
The peroxy radicals in turn, participate in a chain-propagating sequence that converts NO to NO_2 and in the process, produces additional OH and peroxy radical species:



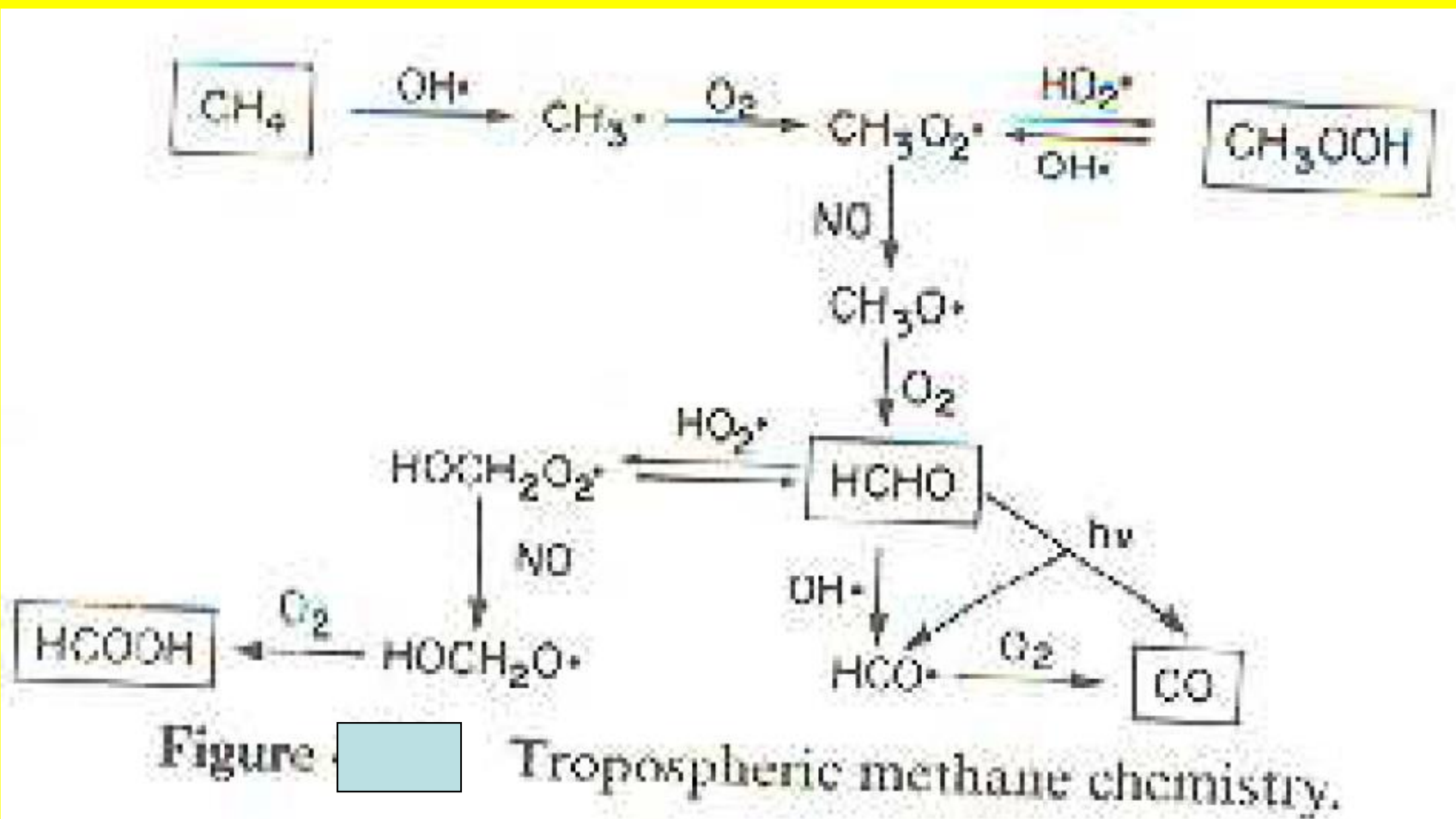
The major chain terminating steps include nitric acid and hydrogen peroxide formation,



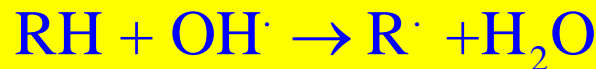
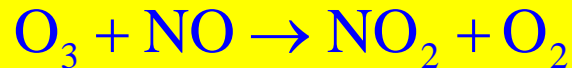
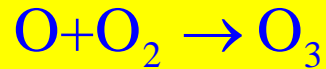
The CH_3O_2 radical can react with either NO or HO_2 , the later reaction being:



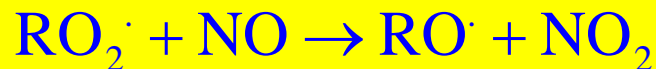
The following figure shows the atmospheric degradation path for methane.



Generalized –Chemistry for O₃ formation



(general HC)



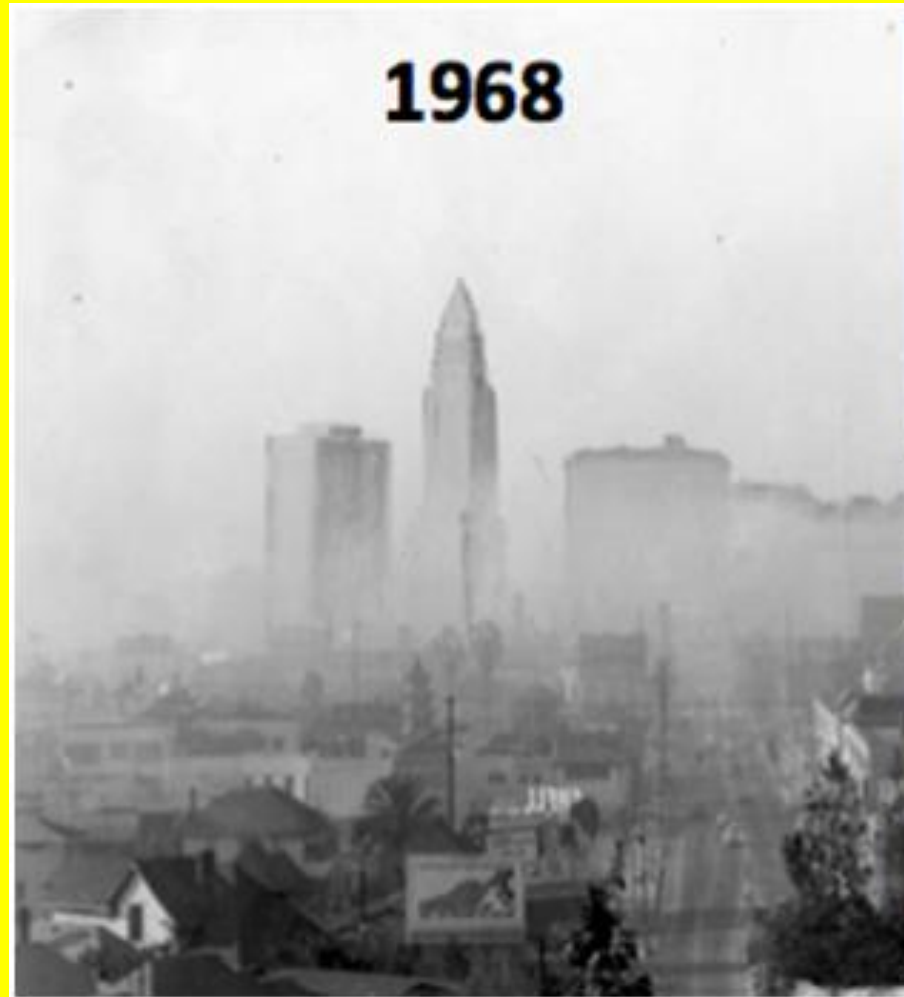
(It follows aldehyde chemistry)

→ Eventually will lead to CO₂

→ Stabilize NO₂ to HNO₃

→ Form H₂O₂ (highly oxidizing agent)

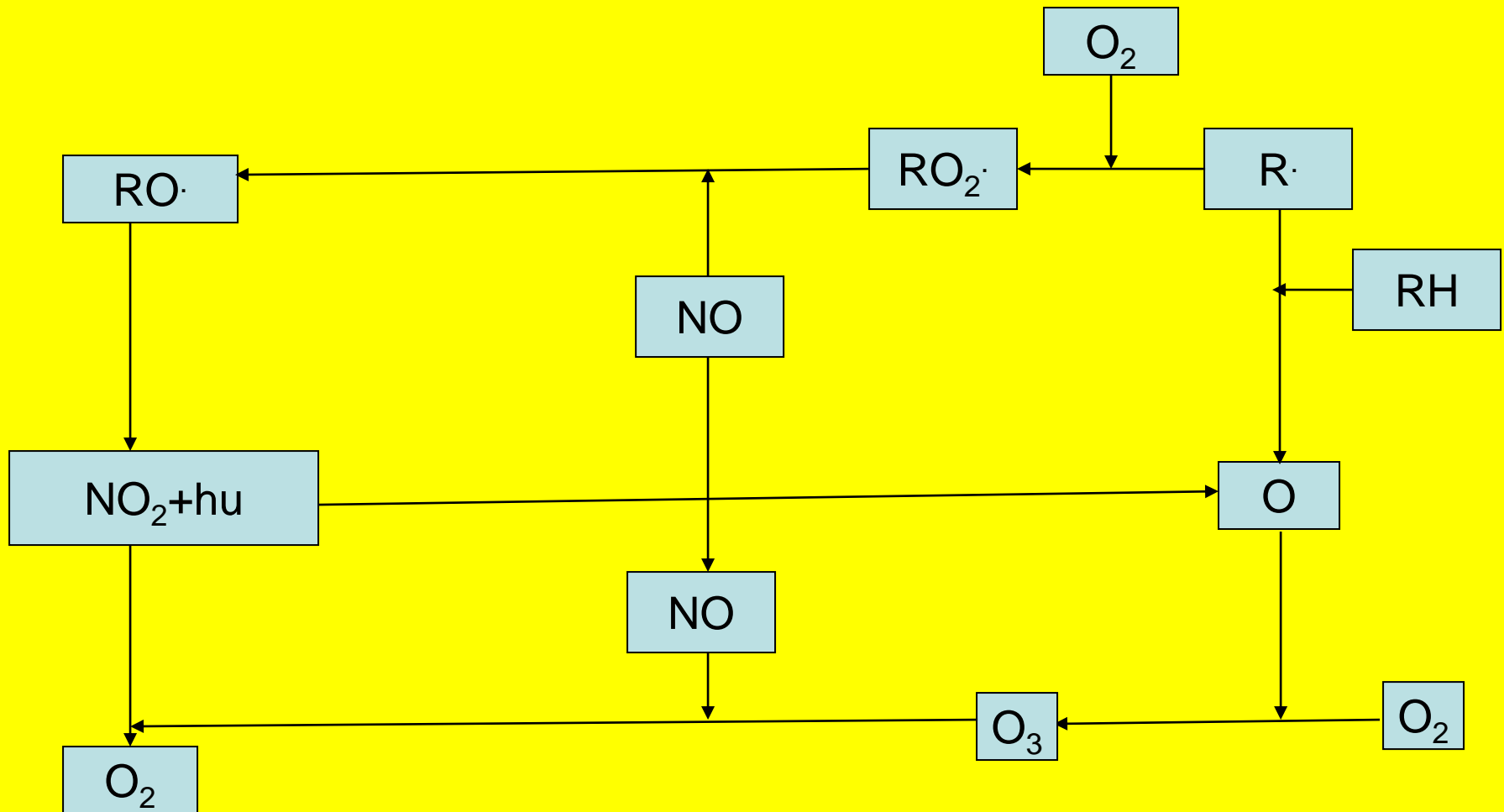
1968



2005



Figure: Formation of ozone



Aromatic Chemistry

Peroxyacetyl Nitrate (PAN): Consider Acetaldehyde (CH₃CHO)



(Acetyl radical)



(Acetyl peroxy radical)

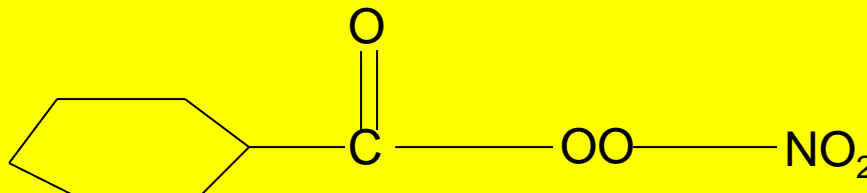


(Peroxyacetyl Nitrate)

Pungent smell,
Eye irritation,

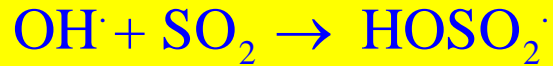
Decomposes very
quickly in the
atmosphere

Peroxybenzoyl- Nitrate (PBN)

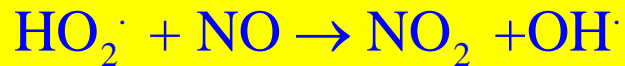


Chemistry of Sulfur Dioxide

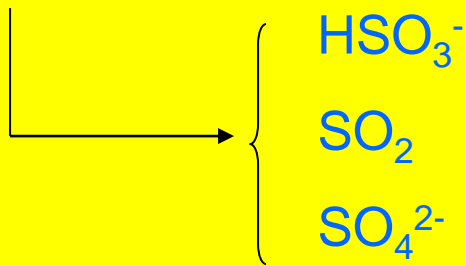
Gas-phase reaction



(Rate limiting step, does not happen so easily)



Aqueous-phase reaction



Through series of complex reactions, e.g. H_2O_2 , O_3 , $\text{O}_2 \rightarrow$ eventually oxidized to SO_4

Chemistry of Iron (Fe)

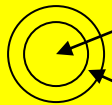
Fe:

0.19 – 0.51 $\mu\text{g}/\text{m}^3$

1.1 – 2.1 $\mu\text{g}/\text{m}^3$ (Urban)



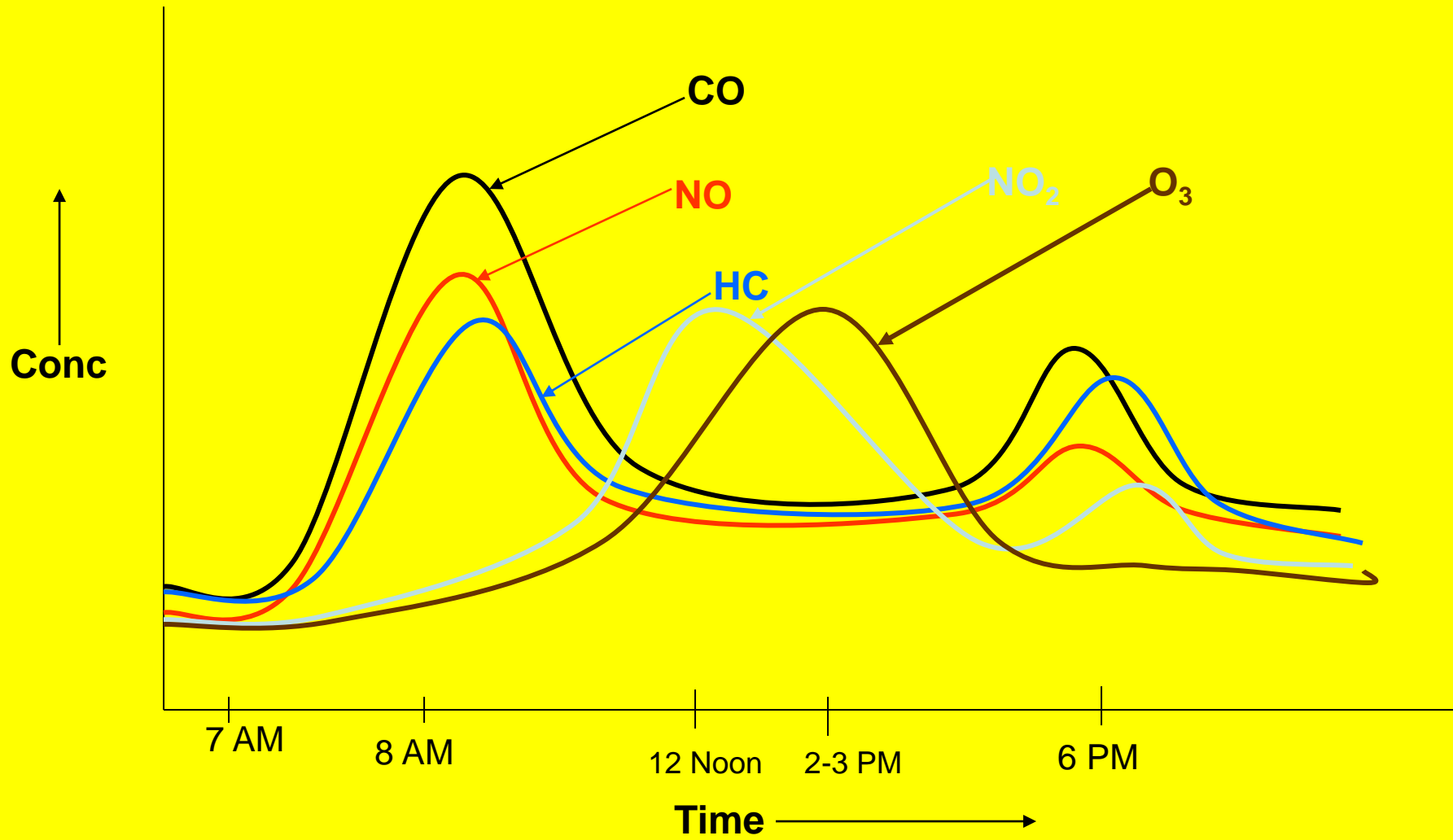
$\text{Fe}_2\text{O}_3 + \text{SO}_2 \rightarrow \text{SO}_4$ (Gas-solid phase interaction)



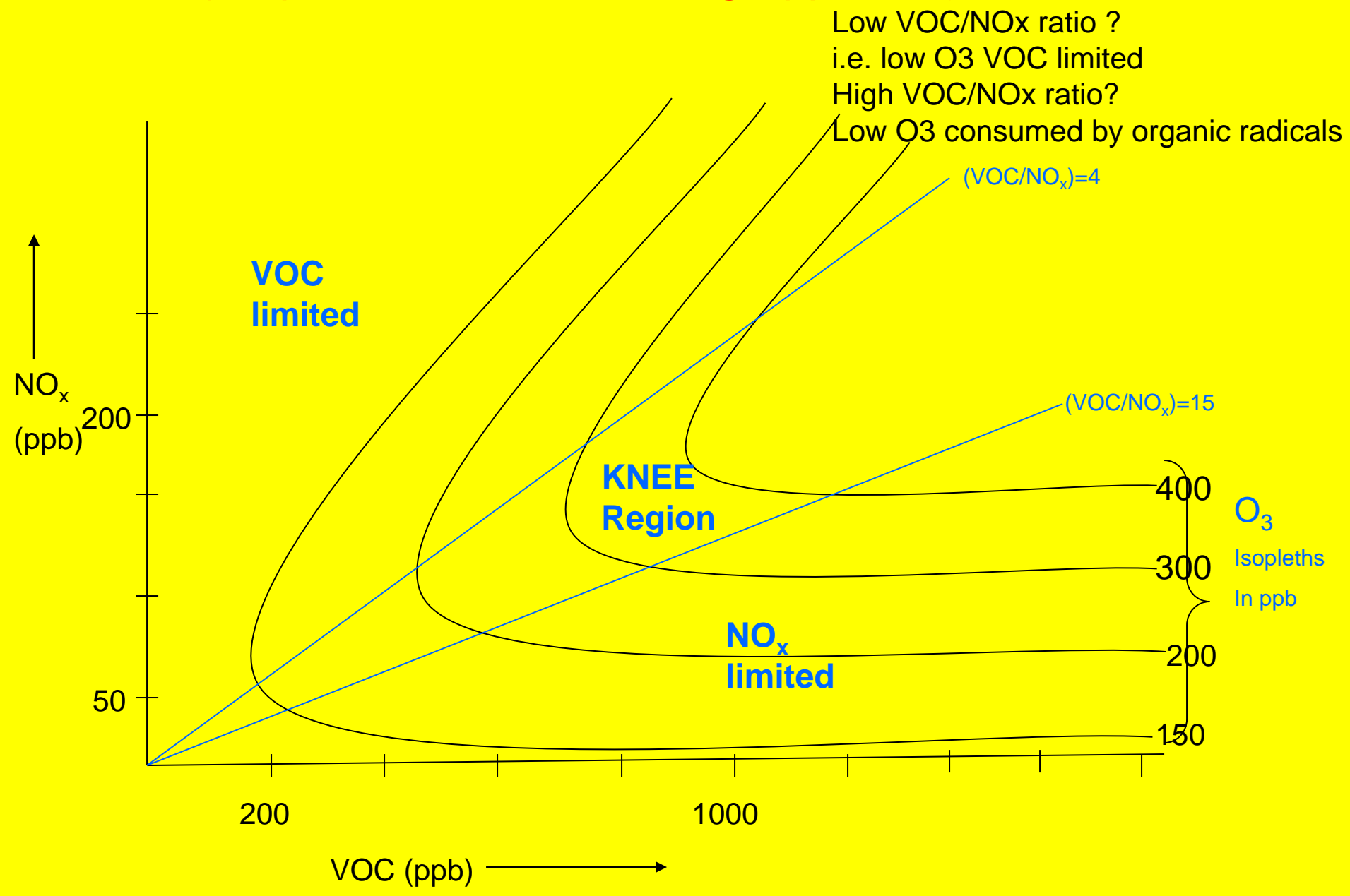
Solid particle with Fe

Aqueous phase

Dissolved O_2 can oxidize
the SO_2 in presence of Fe

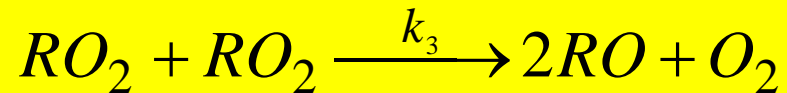
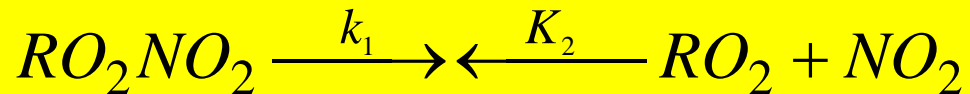


EKMA (Empirical Kinetic Modeling Approach)



Assignment/Example

Alkylperoxy nitrate decomposes in the following way



Assume that RO_2NO_2 are decomposing in a chamber and its decay is observed. We wish to estimate k_1 from the experiment. Assume RO_2 and NO_2 are at pseudo-steady state and $[RO_2]=[NO_2]$. Show that first order rate constant for RO_2NO_2 decay is related to fundamental rate constants of the system in the following way