

Example using methane.

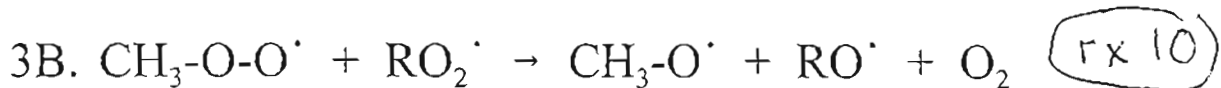
70³¹¹

Oxidation of Methane to Formaldehyde as a prototype

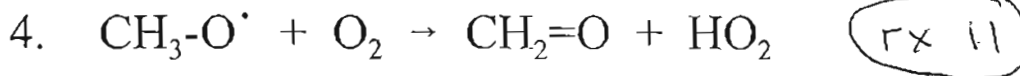
[only] VOC (oversimplified) (righthand side and bottom of cartoon p 69)



OH much more reactive than RO_2 , HO_2 , NO_3



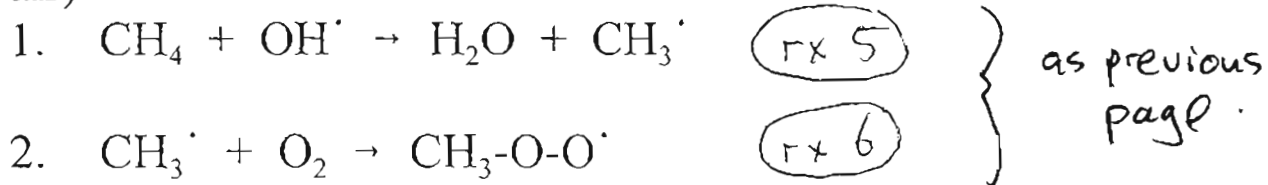
R = CH_3 or H



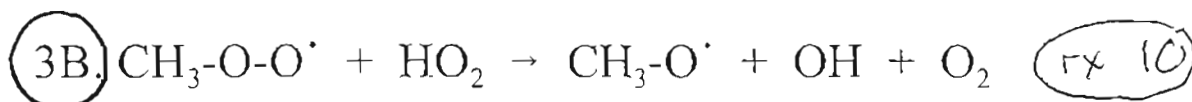
$\text{CH}_3\text{-O}^\cdot$ reacts much faster with O_2 than it abstracts H from CH_4

Reactions 3A and 3B are in competition – both always occur

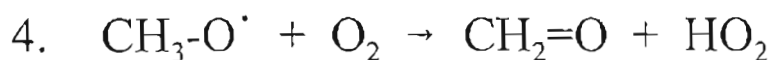
When Reaction **3B** predominates (low $[\text{NO}_x]$; unpolluted air)



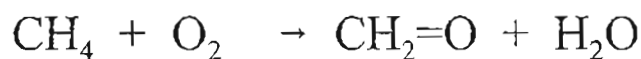
} as previous page.



peroxy radicals tend to self-annihilate rather than abstract hydrogen

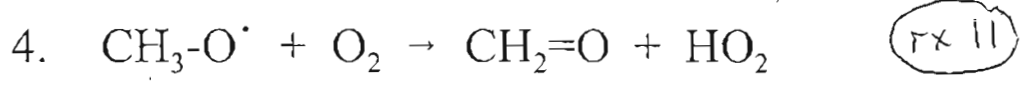
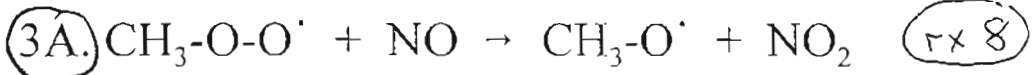
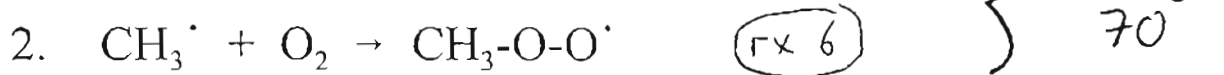


Net reaction I:

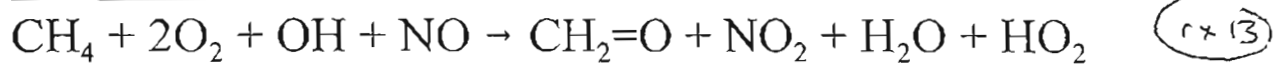


Under these conditions, methane ^{oxidation} ~~production~~ produces no ozone as a byproduct

When Reaction 3A predominates (high [NO_x], polluted air)



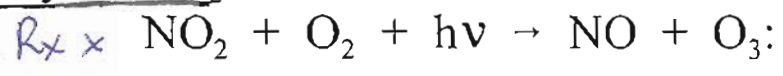
Net reaction



This is inconvenient, because of the reactive intermediates that are present in the equation → use of cycles in which the concentrations of reactive intermediates are eliminated.

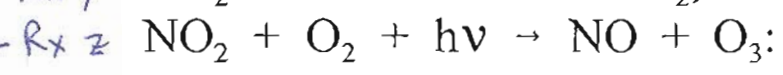
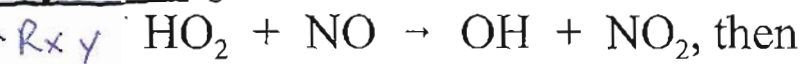
Note NO → NO₂; OH → HO₂

Recycle NO₂ → NO



(the pseudo-equilib. of page 65)

Recycle HO₂ → OH



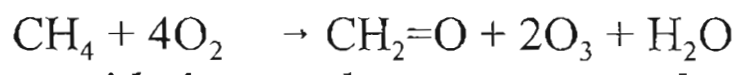
(rx 8)

(reverse of rx 7)

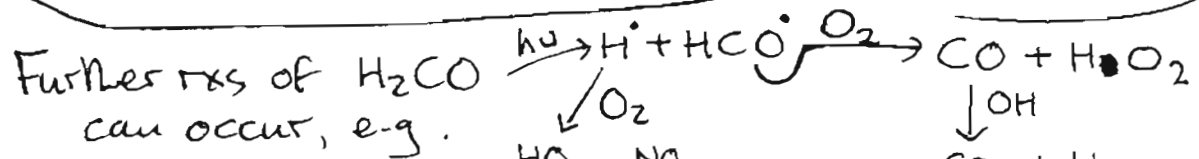
same rx.

Sum and add to rx 13

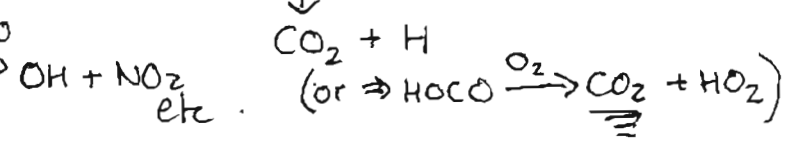
New net reaction II:



Methane oxidation produces ozone as a byproduct



* Final oxidn. product of CH₄ is CO₂ (note OH· net increase)



Are all VOCs created equal?

No!! The main issue is their reactivity with OH radicals. Fast reaction \rightarrow more tendency to form ozone locally, especially if $t_{1/2}$ is only a few hours.

Generally, alkenes and aromatics (OH reacts by addition) are more reactive than alkanes (OH reacts by H abstraction).

Biogenic hydrocarbons (alkenes) are highly reactive.

In general: alkenes > higher alkanes > aromatics

Photochemical Ozone Creation Potential (POCP) was developed by the Organization for Economic Cooperation and Development (OECD) as an approximate approach to rank VOCs in terms of ozone forming ability based on the emission of equal masses of the VOC and ethylene

$$\text{POCP} = \frac{k(\text{VOC})}{k(\text{C}_2\text{H}_4)} \times \frac{\text{M}(\text{C}_2\text{H}_4)}{\text{M}(\text{VOC})} \times 100$$

at 298 K, $k(\text{ethene}) = 8.5 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

Rate const.
for rx.
with
OH \cdot

Compound	k_{OH}	POCP	Compound	k_{OH}	POCP
ethylene	8.5×10^{-12}	100	propylene	2.6×10^{-11}	204
1-hexene	3.7×10^{-11}	145	toluene	6.0×10^{-12}	21
<i>p</i> -xylene	2.4×10^{-11}	74	styrene	5.5×10^{-11}	165
cyclohexane	7.5×10^{-12}	29	2-butanone	8.9×10^{-13}	4
isoprene	9×10^{-11}	1000	3-methylpentane	5.7×10^{-12}	22

Sources of nitrogen oxides in the troposphere from vehicles, power plants.

The *primary pollutant* is always NO:



Natural background of NO_x is < 1 ppbv (lightning). All combustion processes increase $[\text{NO}_x]$ above background

- US data: transportation 40-45%; power generation, 30-35%; industrial, 20%

Low $[\text{O}_3]$ in major cities at night

1. $\text{NO}_2 + h\nu (\lambda < 400 \text{ nm}) \rightarrow \text{NO} + \text{O}$ daytime only
2. $\text{O} + \text{O}_2 \rightarrow \text{O}_3$
3. $\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2$ day and night

NO formation continues, but ozone formation shuts down, \therefore the concentration of ozone declines

Low $[\text{O}_3]$ in major cities during pollution episodes

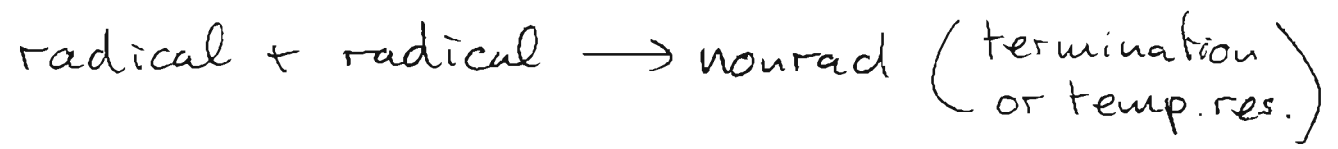
- High NO emissions “eat up” O_3

$$\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2$$
- NO_2 “eats up” OH

$$\text{NO}_2 + \text{OH} \rightarrow \text{HNO}_3(\text{g})$$
- Low OH means a low rate of VOC oxidation, hence low production of O_3 as a byproduct

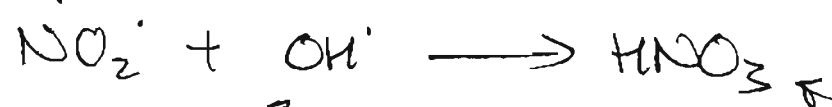
Highest O_3 occurs down-wind of city centre – in the suburbs

Later stages of photochemical smog ... the concn of radicals is high, so rxs. such as;



can occur.

An important example is the rx.

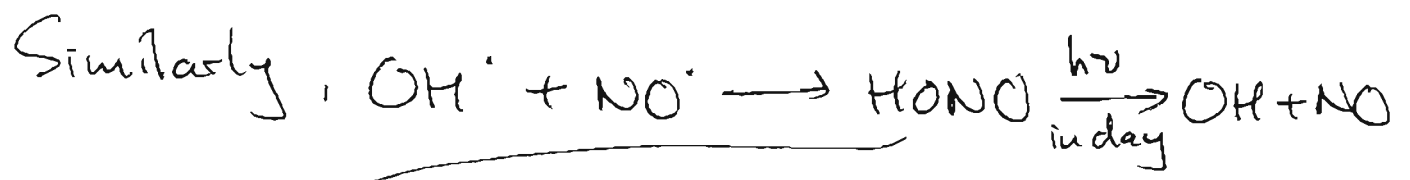


If both these concns are high we get

The average lifetime of HNO₃ is several days.

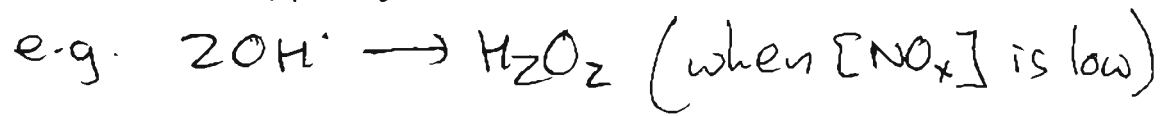
It can be photolysed back to NO₂ and OH or it can be removed (permanently) from the atmosphere by rain or deposition on particles.

Hence, a smog → acid rain linkage



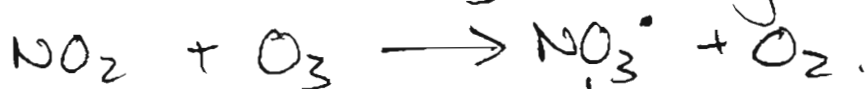
at night this concn increases, such that at sunrise, photolysis can contribute to [OH]

Other "termination" rxs.

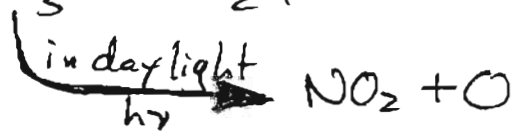


Hence the afternoon stage of a photochemical smog (see Fig, my p61) is characterised by a build-up of oxidising agents, e.g. H_2O_2 , HNO_3 , PAN (see my p69 and below) as well as O_3 .

Another late-day, but important species is NO_3^{\cdot} (nitrate radical) obtained when high concus of NO_2 and O_3 occur together.

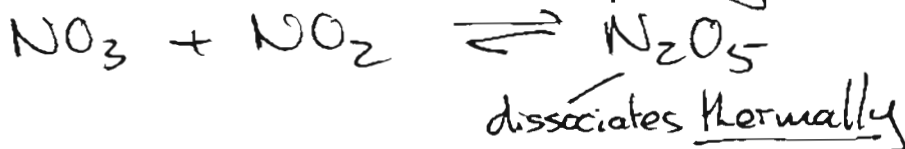


at night it prowls around and attacks HC's



So at night when $[OH] \longrightarrow$ almost zero, NO_3^{\cdot} initiates the oxidation of HC's (like OH[•] does)

NO_3^{\cdot} can also end up in a temporary reservoir.



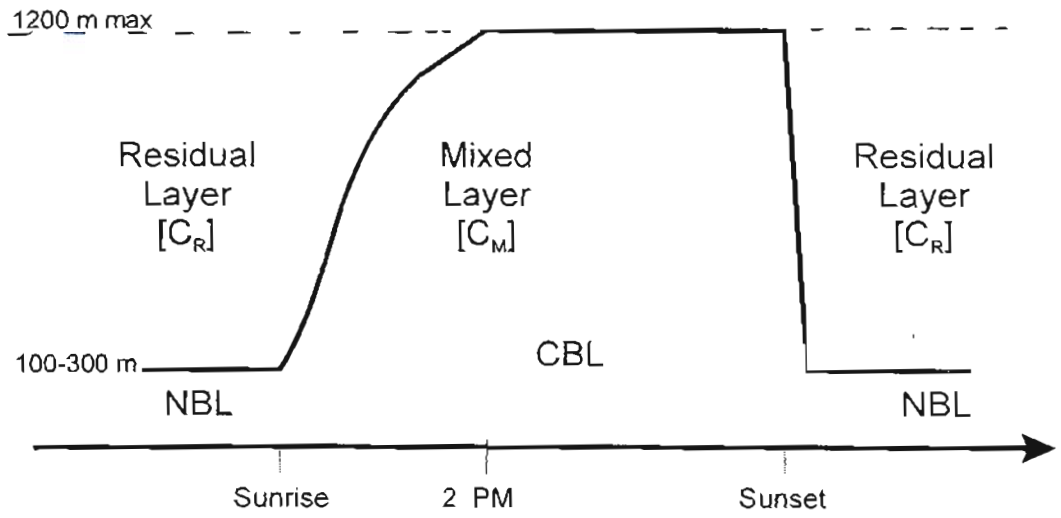
The problem of advection

← transport from 1 region to another

Vancouver or Los Angeles: due to westerly air flow, "up-wind" air is "clean". Excess ozone above the nocturnal boundary layer dissipates (because of winds) by morning, when mixing brings in clean air.

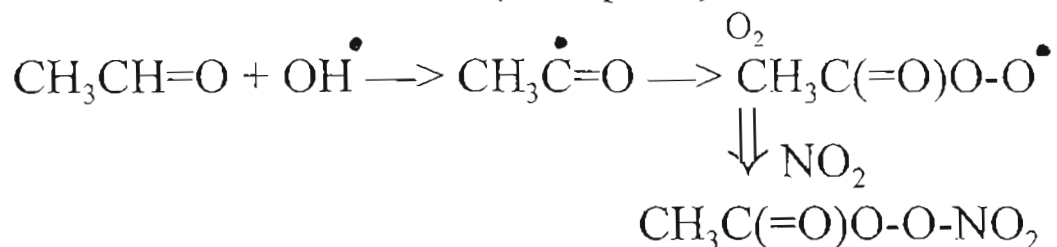
NBL [shallow (0-200m), stable layer of air (forms as ground cools in evening)]

Southern Ontario: upwind air brings high [O₃] from Detroit, Windsor, Ohio Valley. Air above the nocturnal boundary is ozone-rich. [O₃] at ground level falls at night due to NO + O₃ reaction, but morning mixing raises [O₃] because air aloft is still ozone-rich. Seen in data from CN Tower.

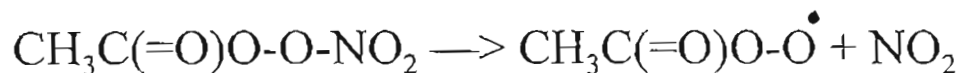


The effect of temperature

- Ozone episodes are promoted by high temperature
- The reason is that PAN (peroxyacetyl nitrate) and related congeners act as storage reservoirs for NO_x .
- Formation of PAN (text, p. 82)



- PAN has a large E_{act} for decomposition (113 kJ/mol)



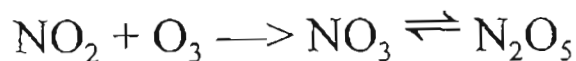
- Tying up NO_2 inhibits O_3 formation ($\text{NO}_2 =$ precursor); at high T, less NO_2 is tied up, so more O_3 forms

Tropospheric chemistry at night — see also ~~my~~ page 76

- NO_3^\bullet (nitrate radical) initiates chain reactions, but is much less reactive than OH



- NO_3^\bullet is indirectly made from NO_2

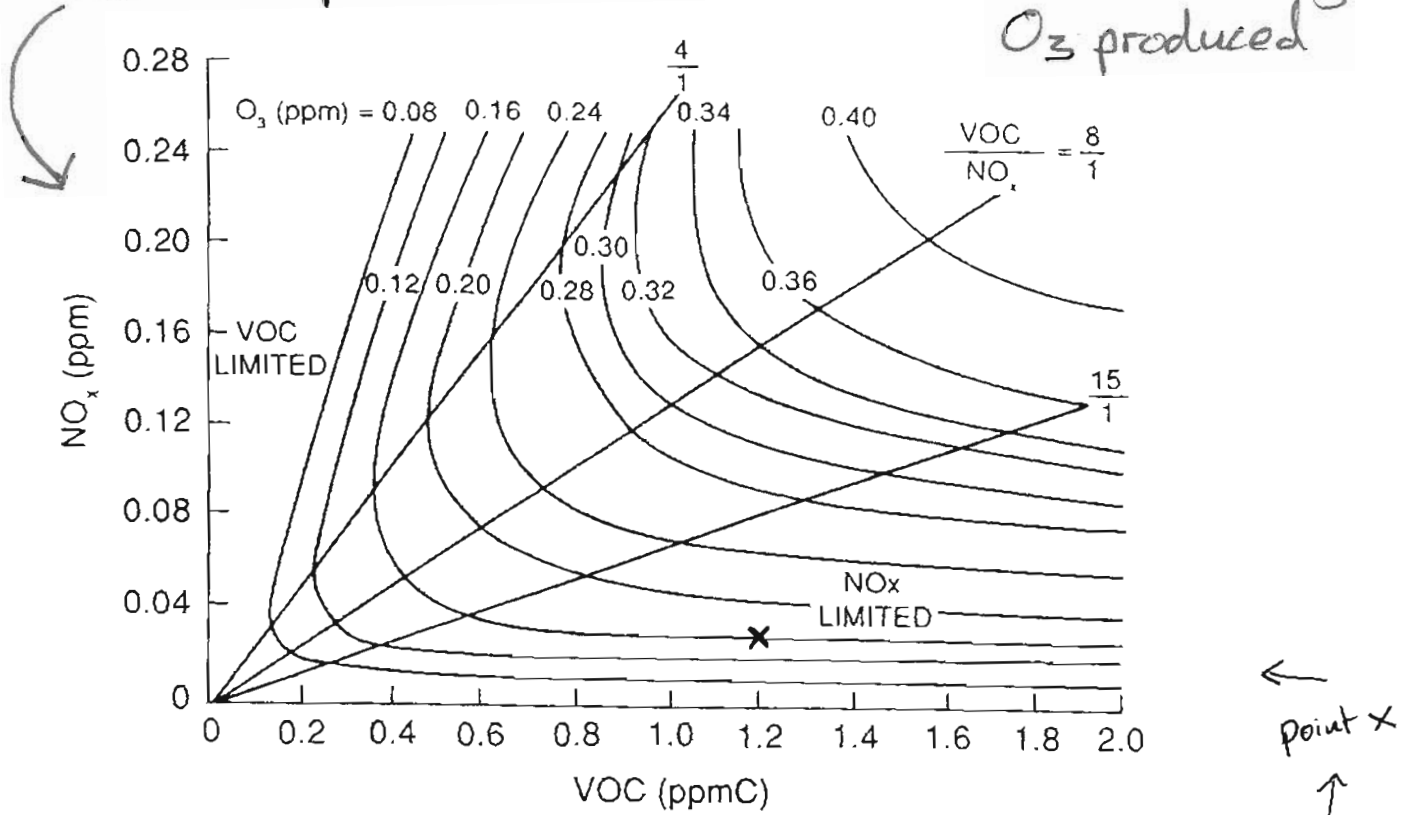


NO_3 is readily decomposed by sunlight, but N_2O_5 is not

Emission controls

- Concepts: lower emissions of NO_x and VOCs by adjusting air-fuel ratios and using catalytic converters (text, pp. 85-89)
- The failure to control ground level ozone (US National Research Council Report, 1991) due to underestimation of VOC inventories, notably biogenic hydrocarbons, e.g., isoprene, CH₂=C(CH₃)-CH=CH₂
- Concept: either NO_x or VOCs can be the limiting reactant

Relationship between VOC & NO_x concns and resulting O₃ produced



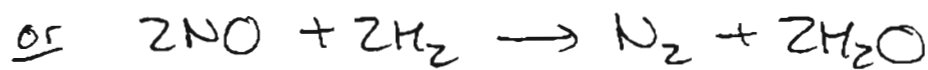
But suggests that NO_x reduction is more effective than VOC reduction. For example: reducing [VOC] from 1.2 to 0.8 ppm maintains the same [O₃] (0.16 ppm). However, reducing NO_x from say, 0.03 ppm (at x) to about $\frac{1}{2}$ of this value, brings the [O₃] down to ~0.08 ppm, i.e. factor of 2 decrease

Catalytic converters

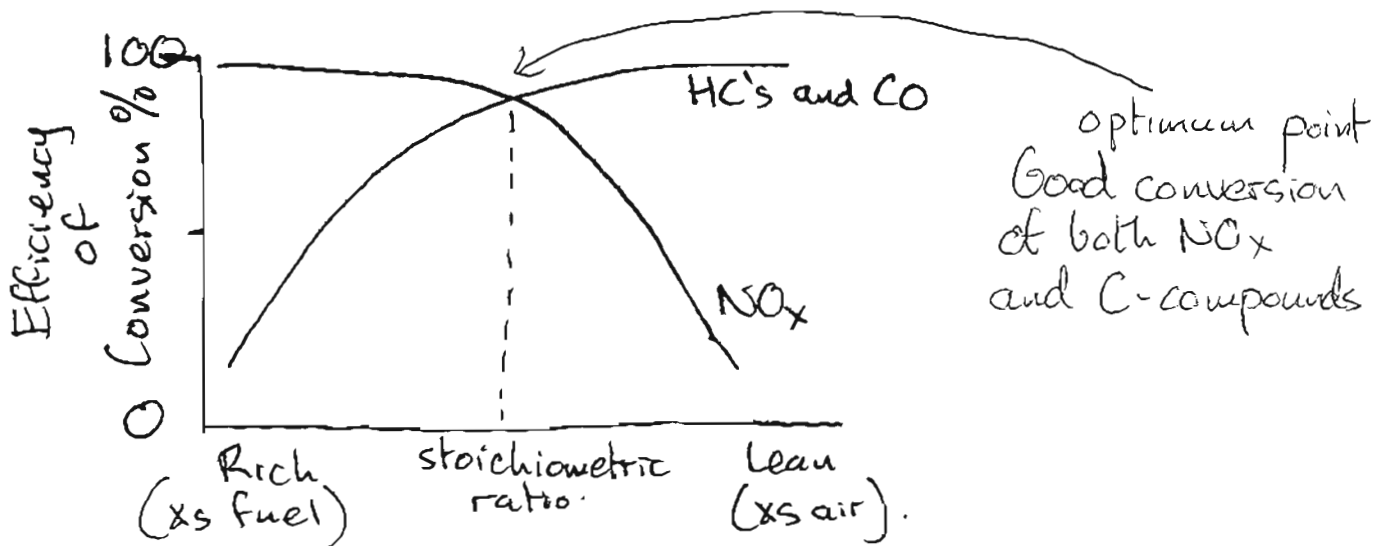
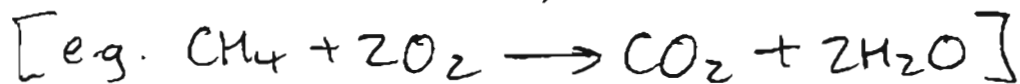
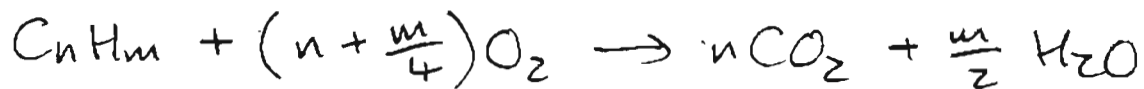
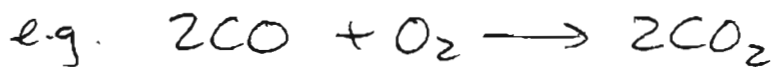
(80)

Matrix of inert oxides is impregnated with platinum - rhodium catalyst (crystallites, ~ 10 nm size).

Converts nitrogen oxides to N_2 and O_2 using unburned HC's and combustion intermediates CO and H_2 as reducing agents



Carbon-containing gases are oxidised almost completely to CO_2 and H_2O

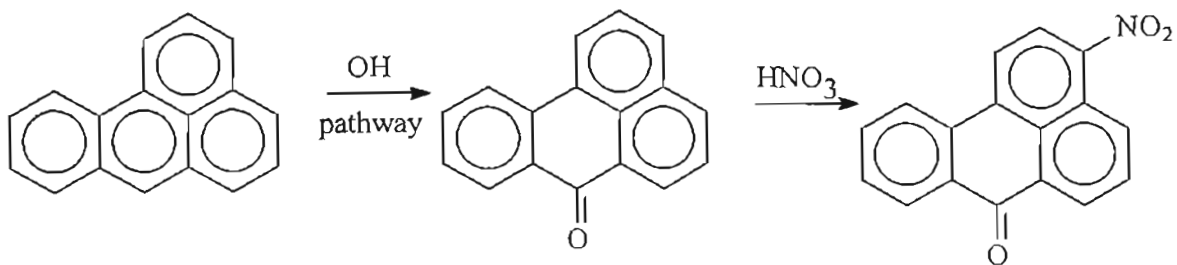
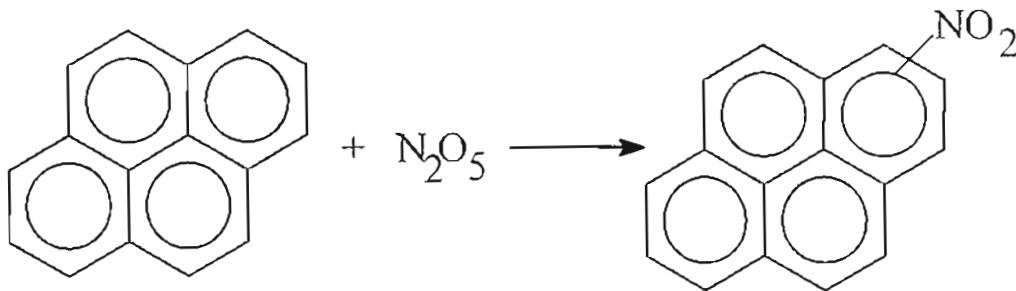


The kicker: converter does not work until warmed 

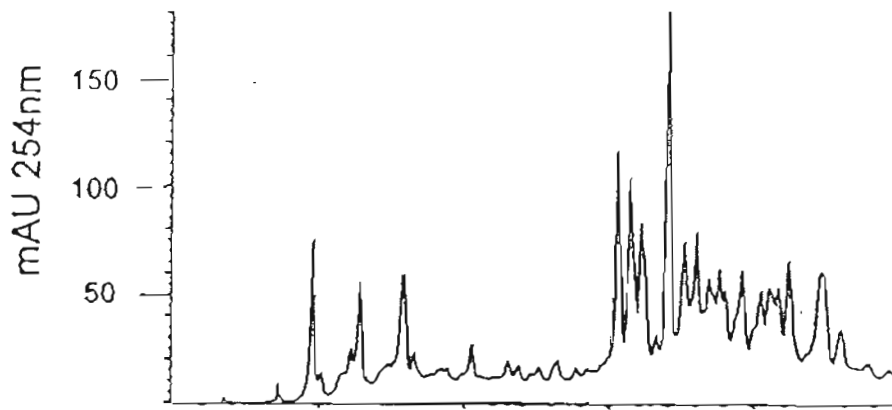
81

Problem compounds in urban/suburban air pollution

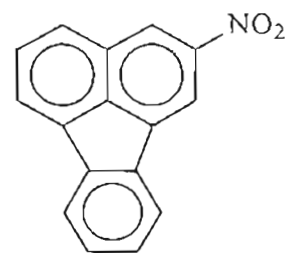
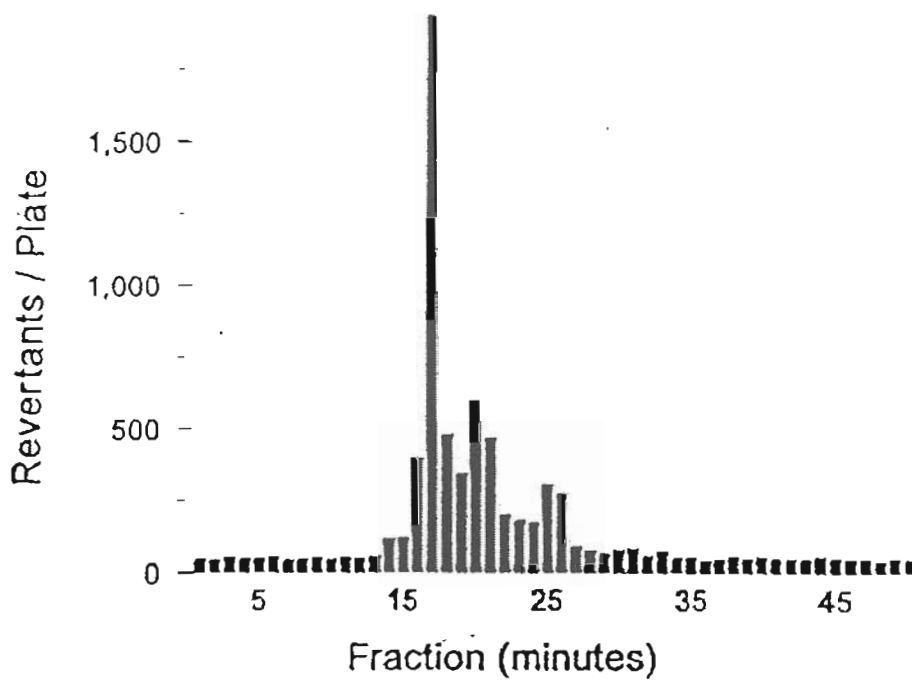
- Primary pollutants
 - VOCs, including polycyclic aromatic compounds
 - NO_x
 - CO , (SO_2 – see later)
 - Secondary pollutants
 - Ozone (powerful oxidant)
 - Aldehydes
 - Organic nitrates
 - Nitro-PAHs
- O_3 and PAN are toxic to people/animals and even more toxic to plants (reduces rate of photosynthesis).*



Mutagenic substances in urban air (Legzdins et al., 1994)



HPLC



Ames Assay