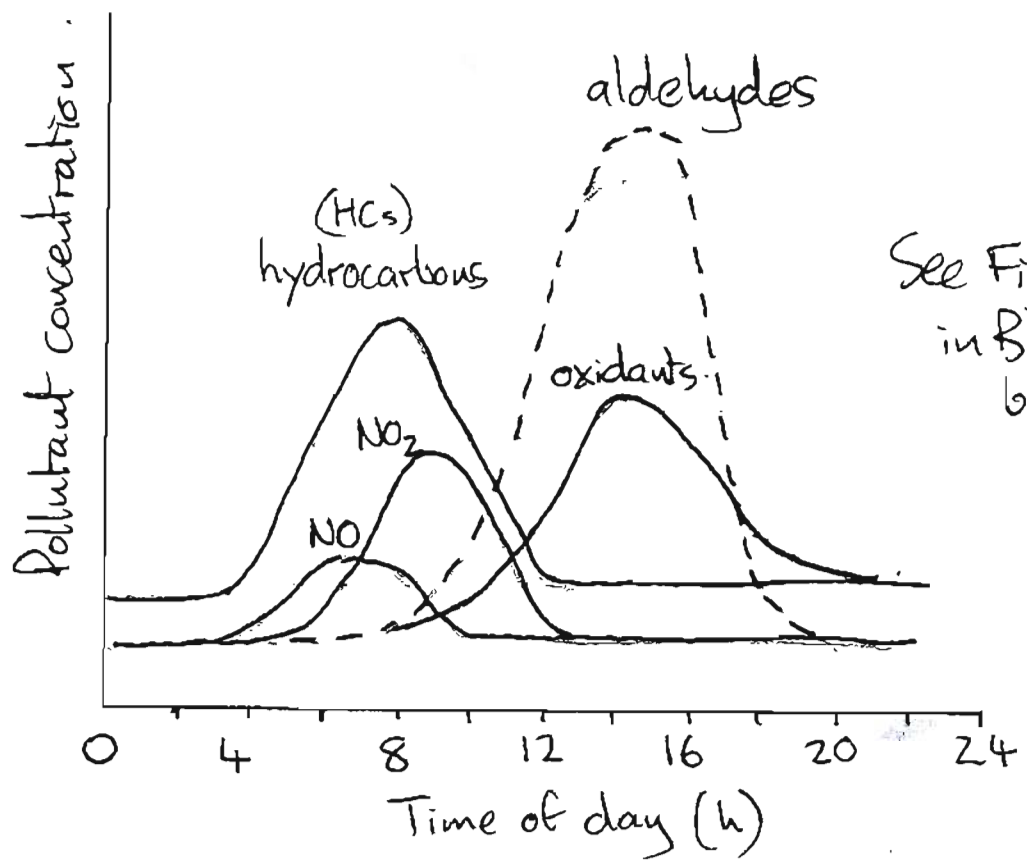


# Sequence of chemical species appearing during a photochemical smog event



See Fig 3.1 in Bunce book.

early a.m. • traffic hits the streets ... increase in NO and HCs

- [NO]  $\nearrow$  max  $\searrow$  then down.
- simultaneously NO<sub>2</sub> rises

later in morning

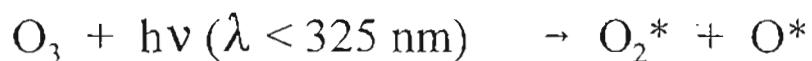
- HCs and NO<sub>2</sub> concns. fall  
 $\nwarrow$  sink rx,  $\text{NO}_2 + \text{OH} \xrightarrow{M} \text{HNO}_3$
- elevated levels of oxidising agents (inc. O<sub>3</sub>) and aldehydes are detected (latter via formation of OH and HC radicals)

at night

- lowering of all concns to background levels - - - remain constant.

Photochemical rate constants:  $J(X)$ 

Only two important tropospheric examples:



rx 1

rx 2

$\text{O}^*$  = an excited state oxygen atom

To estimate photochemical rate constants we have to know:

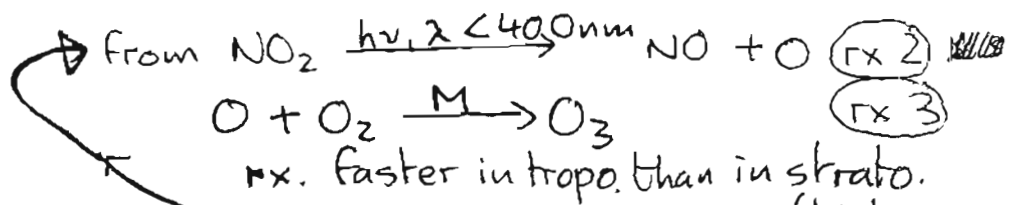
- the strength (intensity) of the photon flux,  $I_0$ : photons per second per  $\text{cm}^2$  of the Earth's surface.  $I_0$  is a function of  $\lambda$  and zenith angle,  $Z$
- the efficiency with which the photons are absorbed to give excited molecules, e.g.,  $\sigma \times [\text{NO}_2]$ .  $\sigma$  is the absorption cross section ( $\text{cm}^2$  per molecule: compare Beer's law), and is a function of wavelength  $\lambda$
- the efficiency with which the excited  $\text{NO}_2$  molecules dissociate,  $\phi$ , the quantum yield of dissociation.  $\phi$  is also a function of wavelength  $\lambda$ , and is dimensionless.

$$\phi = \frac{\text{number of molecules dissociated}}{\text{number of photons absorbed}}$$

- $(I_0 \times \sigma \times \phi)_{\lambda, Z} = J$ , units,  $\text{s}^{-1}$ . Must be summed over all  $\lambda$  relevant to the particular zenith angle
- rate of photolysis (of  $\text{NO}_2$ ) =  $(I_0 \times \sigma \times \phi) \cdot [\text{NO}_2]$

photolysis part      concn. part  
product gives

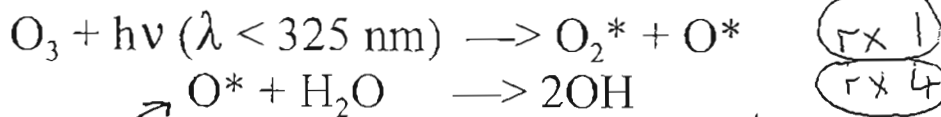
NO<sub>2</sub> from  
oxidation of NO  
N<sub>2</sub> + O<sub>2</sub> ↑



**Tropospheric formation and reactions of OH radical** (higher concns)

- Formation by photolysis of ozone in the UV-B region (295-325 nm)

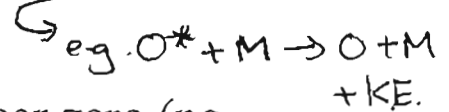
O<sub>2</sub> + M  
(63)



note: only a small fraction of O\* reacts with H<sub>2</sub>O.

Because O\* reacts with other mols. also

The reaction O<sub>3</sub> + hv → O<sub>2</sub> + O also occurs but does not lead anywhere because ground state O cannot react with H<sub>2</sub>O - why??



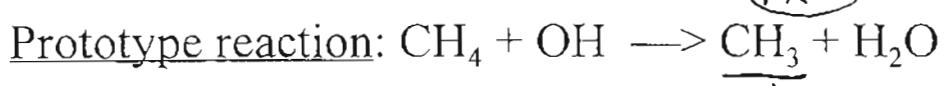
- in darkness, concentration of OH falls to near zero (no photolysis of ozone) because OH is so reactive that it disappears in seconds

**Tropospheric concentration of OH**

- global average = 9.7 × 10<sup>5</sup> molec cm<sup>-3</sup> (day/night; winter/summer; poles/tropics)
- experimental measurements very difficult, but day-time **maxima** in southern Canada ~ 10<sup>5</sup> molec cm<sup>-3</sup> in winter and ~ 10<sup>7</sup> molec cm<sup>-3</sup> in summer with high ozone

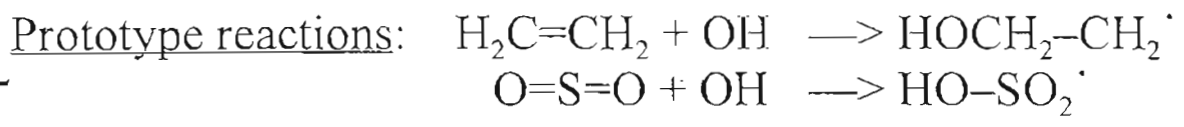
### Characteristic reactions of OH radicals

1. Abstract hydrogen atoms



OH bond in water is stronger than CH bond

2. Add to double bonds



3. Terminate with another odd-electron species



- Before considering oxidation of VOCs further we must consider NO<sub>x</sub> chemistry
- Be careful to distinguish the OH radical from the hydroxide ion OH<sup>-</sup>. Their chemistries are quite different!

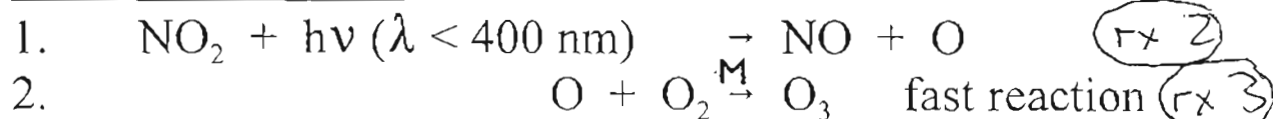
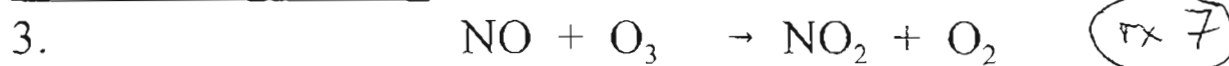
→ CH<sub>3</sub> radicals are very reactive toward O<sub>2</sub>



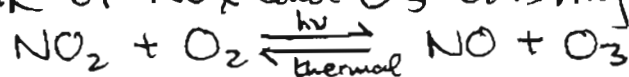
peroxy radical

(can oxidise the NO radical → NO<sub>2</sub>)

Peroxy radicals show up in the oxidation of VOCs (see below).

The formation of ozone: the NO/NO<sub>2</sub> cycleClean troposphere: no significant parallel VOC oxidationFormation of ozone:Destruction of ozone:

Net reaction = "null cycle", in which sunlight is degraded to heat. Can think of NO<sub>x</sub> and O<sub>3</sub> existing in a pseudo-equilib.



Steady state: NO<sub>2</sub> formed and destroyed at equal rates — so equate rates of 1. and 3.

$$k_3 \cdot [\text{NO}] \cdot [\text{O}_3] = J(\text{NO}_2) \cdot [\text{NO}_2]$$

(note reaction (2) is fast).

$$\text{or } [\text{O}_3] = \frac{J(\text{NO}_2) \cdot [\text{NO}_2]}{k_3 \cdot [\text{NO}]} \quad [\text{A}]$$

- Steady state – not equilibrium! – achieved in minutes in strong sunlight. [O<sub>3</sub>]<sub>ss</sub> depends on solar intensity of solar radiation, ∴ on latitude, season, and time of day. Because they are rapidly interconverted, the sum {[NO] + [NO<sub>2</sub>]} is known as NO<sub>x</sub>.

*Question: What happens at night? More NO<sub>2</sub>, less NO<sub>2</sub>?*

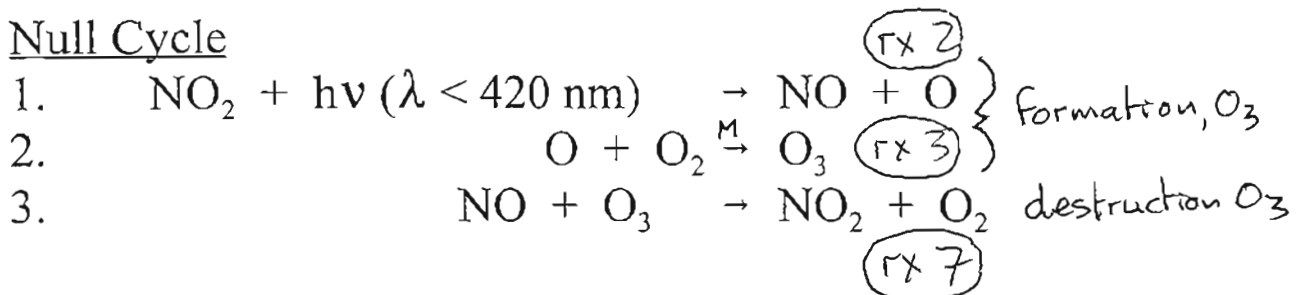
Let us reconsider Equation [A]

$$[O_3] = \frac{J(NO_2) \cdot [NO_2]}{k_3 \cdot [NO]} \quad [A]$$

↙ "Ground level" ozone

- Actual concentrations of  $O_3$  in urban air are larger than Eq. [A] predicts,  $\therefore$  there must be other sources
- Photodissociation of  $NO_2$  is the **only** important reaction by which  $O_3$  is formed in the troposphere.
- In the polluted troposphere, ozone is formed as a **byproduct** of VOC oxidation. *Specifically NO is converted to  $NO_2$  by reactions that do not consume  $O_3$*

Null Cycle

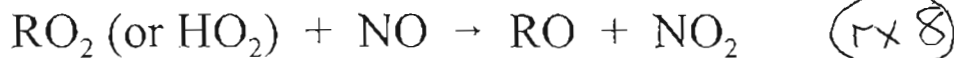


$\therefore$  In order to build up  $O_3$ , we need different oxidants for NO besides  $O_3$ : these are **peroxy radicals  $R-O-O^\cdot$**

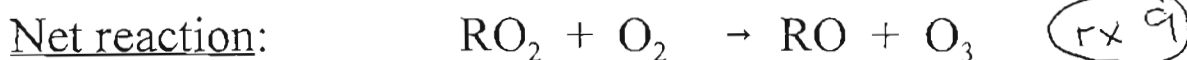
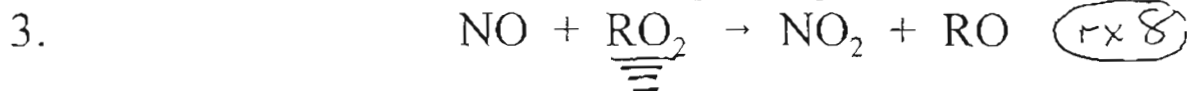
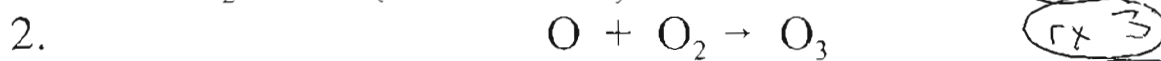
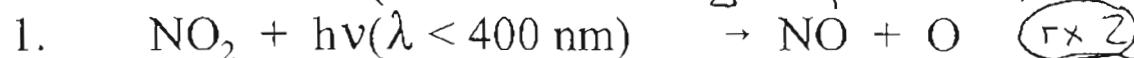
Every NO molecule that is oxidized to  $NO_2$  while bypassing Reaction [3] yields one additional ozone molecule, because the "extra"  $NO_2$  is photolyzed to restore the steady state

↙  
NO/ $NO_2$

Peroxy radical R-O-O' chemistry in the context of NO ⇒ NO<sub>2</sub>



Modified scheme (compare "null" cycle, previous page)

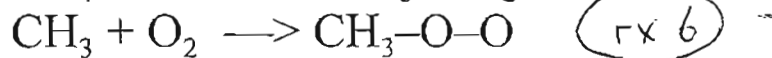


*Conclusion:* If NO is oxidized by O<sub>3</sub>, then the steady state predicted by Equation [A] is valid. If NO is oxidized by peroxy radicals, there will be an excess of O<sub>3</sub> compared with Equation [A]. (page 65)

**Source of peroxy radicals**

- addition of O<sub>2</sub> to a carbon-based radical

Example:



and, since a single organic radical can give many peroxy radicals (ROO') by successive rounds of O<sub>2</sub> combination and fragmentation, the ozone concn can build to levels exceeding the NO<sub>x</sub> concn.

## Summary comments so far:

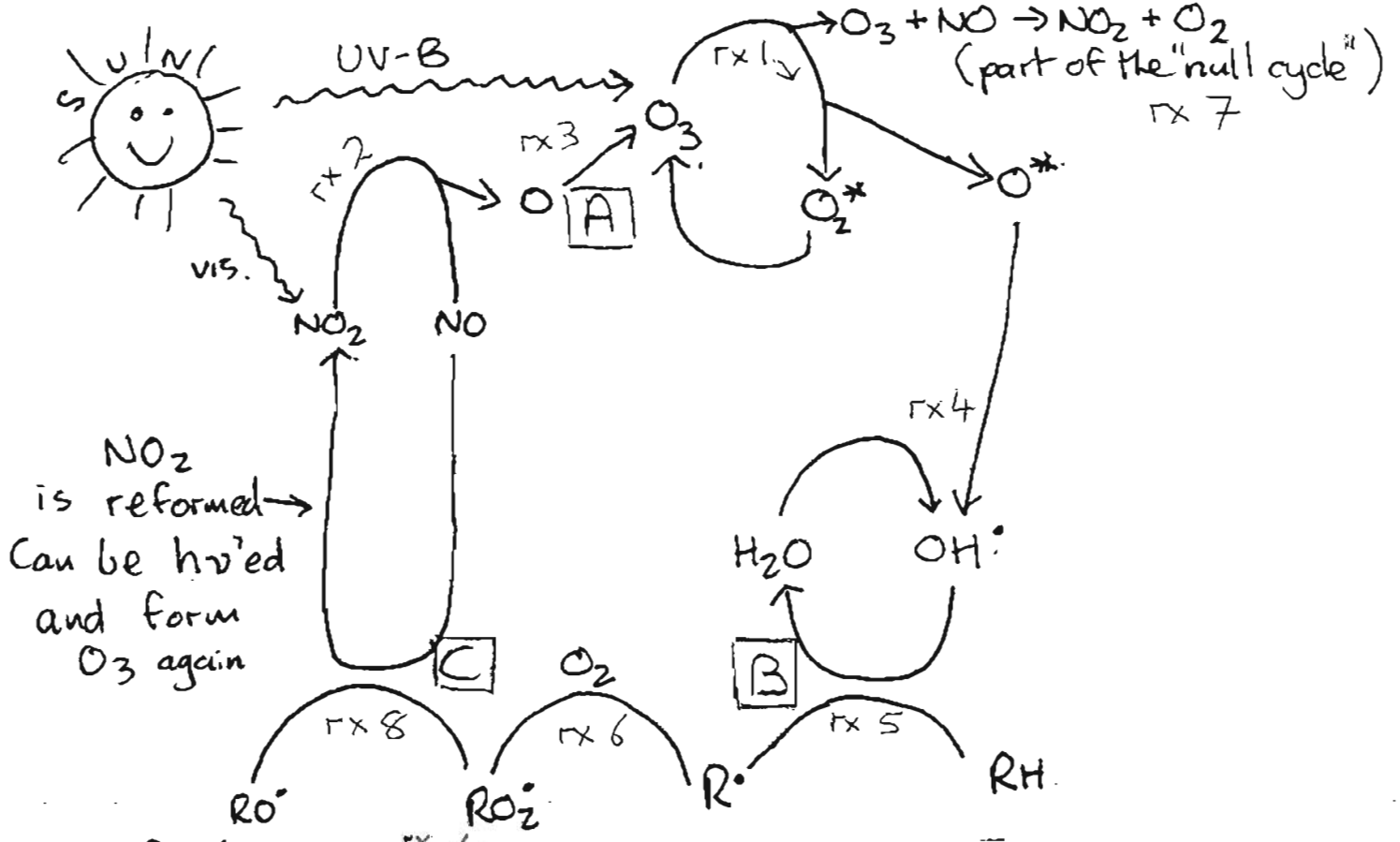
- $\text{NO}_x$  is indispensable to the *formation* of  $\text{O}_3$  in the troposphere (the only other tropospheric source of ozone is downwards transport from the stratosphere)

IF

- $\wedge$  Background levels of  $\text{NO}_x$  are very low  $\rightarrow$  low background levels of  $\text{O}_3$ ;  $\text{NO}_x$  polluted urban air has higher levels of  $\text{NO}_x \rightarrow$  enhanced levels of  $\text{O}_3$
- Peroxy radicals (ROO) are formed as intermediates in the oxidation of VOCs
- In polluted air ( $\text{NO}_x$  present), ROO radicals oxidize NO;  $\text{O}_3$  is formed when the NO: $\text{NO}_2$  steady state is restored
- $\text{O}_3$  is a byproduct of VOC oxidation in polluted air

# Summary illustrating the interweaved $\text{NO}_x, \text{O}_3$ and hydrocarbon (HC) radical cycles.

Remember: smog formation requires  $\text{O}_3, \text{NO}$ , hydrocarbons and sunlight.



$\text{NO}_2$  is reformed  
Can be hv'd  
and form  
 $\text{O}_3$  again

loss process for  $\text{O}_3$   
 $\text{O}_3 + \text{NO} \rightarrow \text{NO}_2 + \text{O}_2$   
(part of the "null cycle")  
rx 7

- A**  $\text{O}_3$  formed by O atoms from  $\text{NO}_2$  photol.
- B** HC radicals made by  $\text{OH}^*$  from  $\text{O}_3$  UV photolysis
- C**  $\text{NO}$  oxidation to  $\text{NO}_2$  catalysed by HC radicals. This process gives an excess of  $\text{O}_3$  (bypasses rx 7), i.e. reacts with  $\text{NO}$  before  $\text{O}_3$  does (rx 7)

(with  $\text{R} = \text{C}_2\text{H}_5$ )  
get  $\text{CH}_3\text{CHO}$   
 $\Downarrow$  can go on to  
PAN: Bunce  
P82  
 $\text{CH}_3\text{C}(=\text{O})\text{OOONO}_2$   
peroxyacetyl nitrate