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Chemistry schemes: An introduction to modelling chemistry in UKCA.

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Centre *for* **Atmospheric Science**

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Outline of this talk

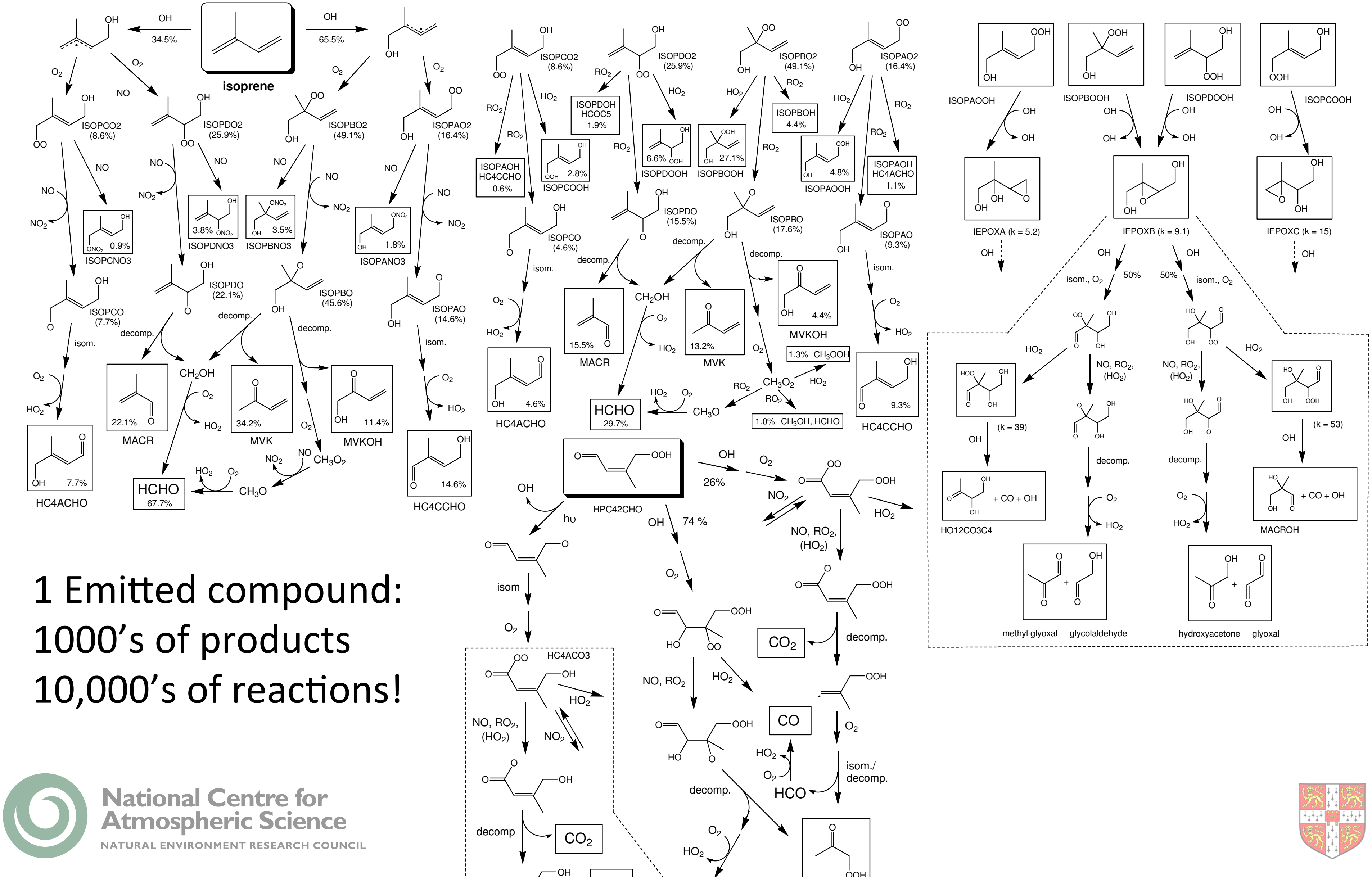
- Why do we need to model atmospheric chemistry?

- What is a chemistry scheme?
- Chemistry in the atmosphere
- Types of reactions
    - Photolysis
    - Gas phase reactions

- Key chemical processes:
    - The formation of O_3 in the stratosphere
    - The formation of O_3 in the troposphere

- Steps towards building a new scheme.

Chemistry is complex!!!



1 Emitted compound:

1000's of products

10,000's of reactions!

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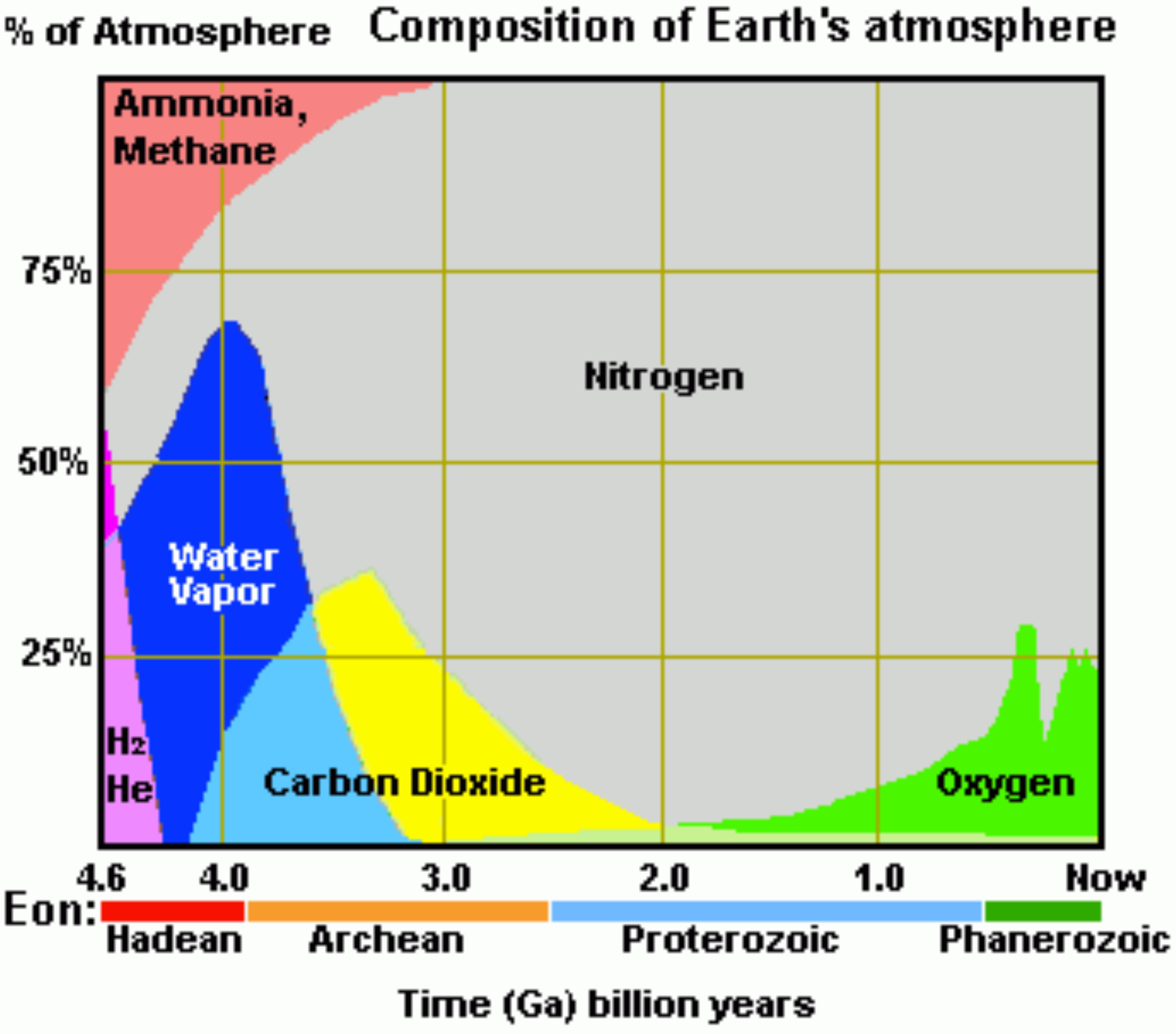
Composition of the atmosphere.

Most of these data are based on model calculations. For example, [CO_2] can be calculated based on the [CO_2] needed to maintain liquid water during periods when the sun was much fainter.



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Composition of the lower atmosphere.

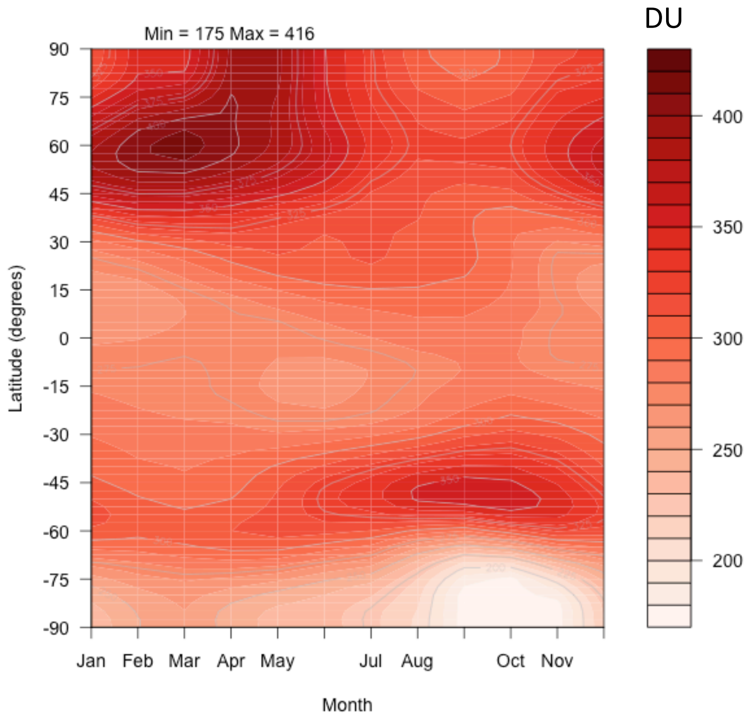
Major constituents	Mole fraction	Lifetime / yr
N_2	0.781	1.6 x 10^7
O_2	0.209	9000
Ar	0.0093	4.5 x 10^9
CO_2	0.00039	5
H_2O	0 - 0.04	5 days
CH_4	1700 ppb	10
H_2	550 ppb	4
N_2O	320ppb	150
CO	40 - 200 ppb	0.2
O_3	20 - 80 ppb	0.05
C_2H_6	1 ppb	0.2
SO_2	0.1 ppb	5 days
NO_2	0.1 ppb	2 days
OH	0.1 ppq	<0.1 s

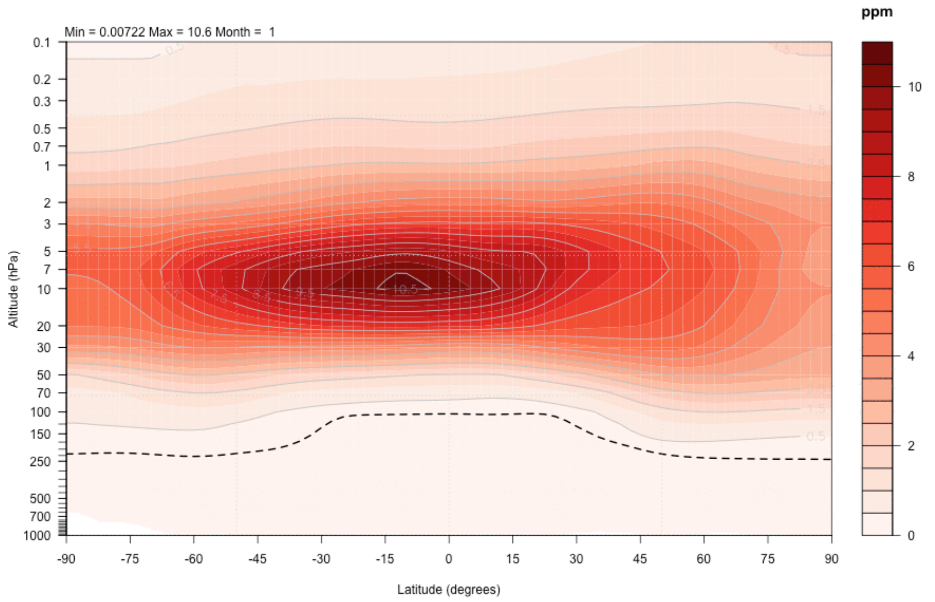
(ppb = 10^{-9}, ppt = 10^{-12}, ppq = 10^{-15})

Ozone in the atmosphere

Distribution of O_3:

- Non-uniform – maximum mixing ratios seen in the mid stratosphere (the ozone layer).





Total column = $\int [O_3] dz$

What is a chemistry scheme?

- You can think of a chemistry scheme as being a massive paramaterisation for the very complex chemistry that goes on in the atmosphere.

- The chemistry scheme contains information about the reactions which are being modelled; the stoichiometry of the reactions, the kinetics, the yields, all these data are used in the model to calculate the continuity equation:

$$\frac{\partial[x]}{\partial t} = -\mathbf{U} \bullet \nabla[x] + P_x - L_x$$

U = wind vector

P_x = chemical (local) source of chemical *x*

L_x = chemical or physical (local) sink

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What is a chemistry scheme cont.

- Most of the work you will probably do will be adding to existing chemistry schemes.

- In UKCA we have developed a number of chemistry schemes. These different schemes are defined by the number of **tracers** (or chemical species), the number of **reactions** (for which there are several types – see later) and the use of certain boundary conditions (now becoming a bit defunct).

- For most applications of UKCA you will probably use a combined tropospheric and stratospheric chemistry scheme: We call this **CheST**, in the code it is referred to as **strattrop**.

What is a chemistry scheme cont.

- **CheST** contains all the tracers and reactions for simulating the chemistry of ozone from the boundary layer to the stratopause (0 – 84km).

- *What does that mean?*

- It means that **CheST** has a “comprehensive” non-methane hydrocarbon (NMHC) chemistry and the chemistry of the Ox, NOx, HOx and halogen(chlorine and bromine) *families* appropriate for the stratosphere.

- There are ~ 80 **tracers** which compete in ~ 300 **reactions**.

Reactions in the atmosphere.

Photolysis reactions:

When a photon (energy = $h\nu$) is absorbed by a molecule it can promote the molecule to an excited state

$A + h\nu \rightarrow A^*$ (excited ‘A’ molecule)

The excited molecule has extra energy (= $h\nu$), it can release this energy back out as radiation:

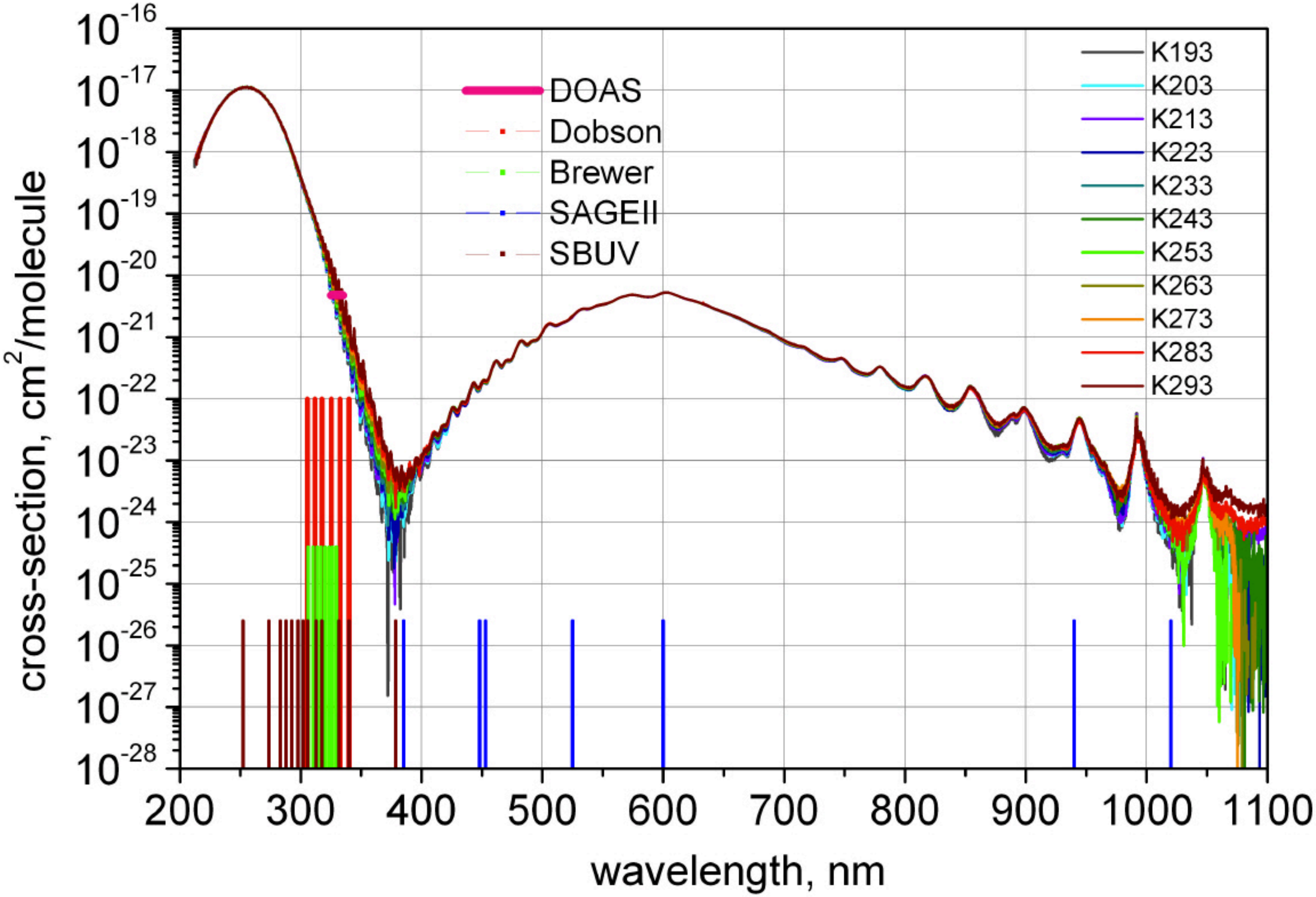
$A^* \rightarrow A + h\nu$ (**photo fluorescence**)

Or, the excited molecule may poses a bond which can break and so turn into other products:

$A^* \rightarrow$ products (**photo dissociation**)

Whether or not a molecule will absorb a photon depends on the molecules absorption cross section:

The O_3 absorption cross section.



(Image from www.iup.uni-bremen.de)

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Reactions in the atmosphere.

Photolysis reactions:

Whether or not a molecule will absorb a photon depends on the molecules absorption cross section:

But whether or not a molecule will "react" also depends on the quantum yield for the photo dissociation (θ), and the amount of photons over the wavelengths that the molecule absorbs at (I).

We can say that the photolysis rate constant (s^{-1}) can be calculated from:

$$J_i = \int_{v=0}^{v=\infty} \theta_{i,v} \sigma_{i,v} I_v$$

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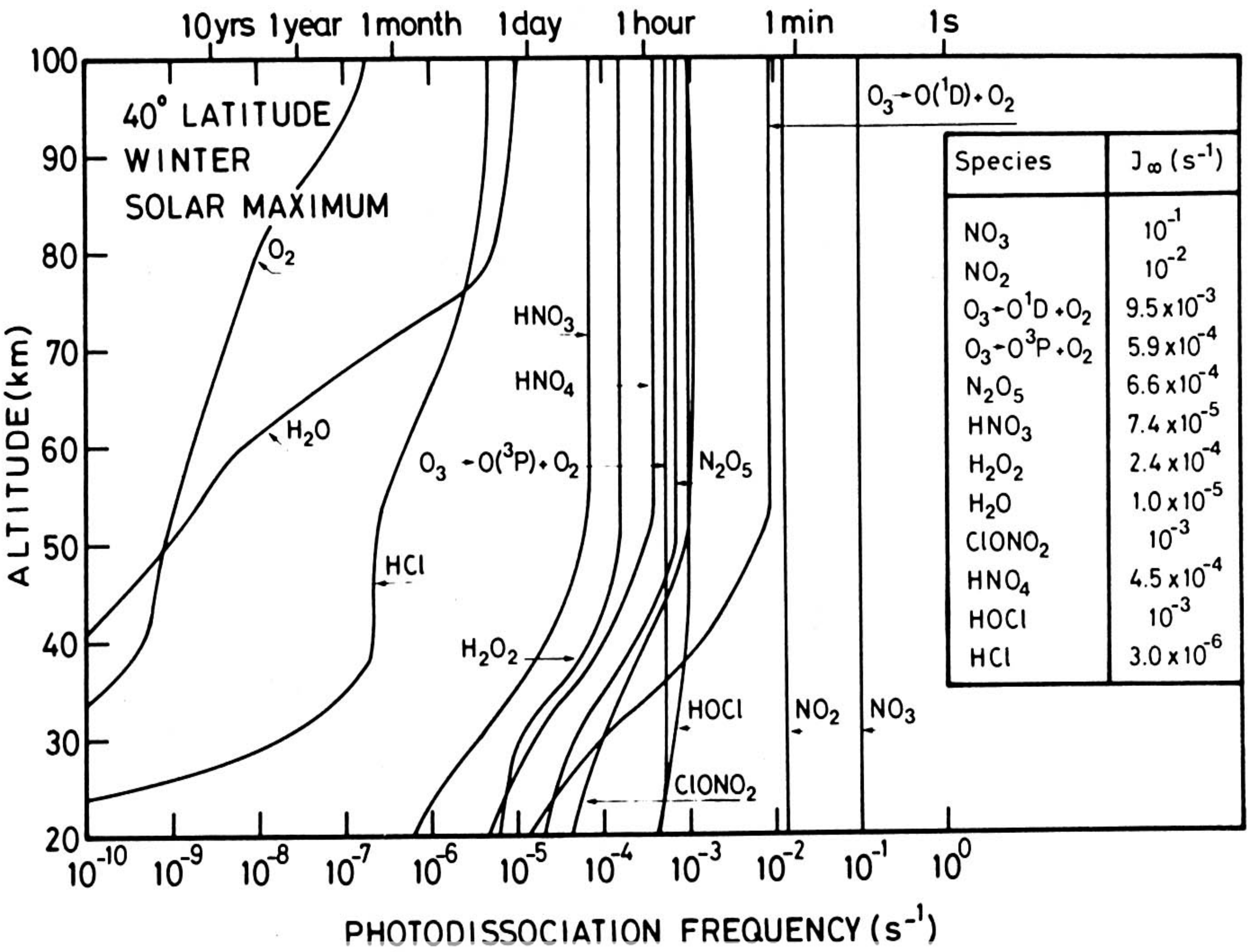
Reactions in the atmosphere.



Species	J_∞ (s^{-1})
NO_3	10^{-1}
NO_2	10^{-2}
$O_3 \rightarrow O^1D + O_2$	9.5×10^{-3}
$O_3 \rightarrow O^3P + O_2$	5.9×10^{-4}
N_2O_5	6.6×10^{-4}
HNO_3	7.4×10^{-5}
H_2O_2	2.4×10^{-4}
H_2O	1.0×10^{-5}
$ClONO_2$	10^{-3}
HNO_4	4.5×10^{-4}
HOCl	10^{-3}
HCl	3.0×10^{-6}

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Reactions in the atmosphere.

Gas phase collision reactions:

Collisions between phase molecules can lead to a number of outcomes:

A + B -> A + B (elastic scattering)
A + B -> A* + B^{-}* (inelastic scattering)
A + B -> products (reactive collisions)

It is only the last type of collision that we are interested in. There are many text books which discuss the theoretical (quantum mechanical) nature of why these sorts of reactions happen. We don't need to go into that level of detail here.

Instead we need to note that there are two general type of gas phase reactions.

Reactions in the atmosphere.

Gas phase collision reactions:

Bimolecular reactions:
A + B -> products

The rate constant for this reaction can be written as:
$k_{A+B(T)} = A \times (T/300)^n \times \exp(-Ea/RT)$ $\quad$ $cm^3\ s^{-1}\ molecule^{-1}$

Where ***A*** is a constant, determined experimentally, ***Ea*** represents the activation energy for the reaction (the energy barrier to overcome if A and B collide to produce *products*, ***R*** is the gas constant, ***T*** is absolute temperature (K) and the coefficient **n** is found from a fit of the observed rate constant over a range of temperatures (this is often blank/missing).

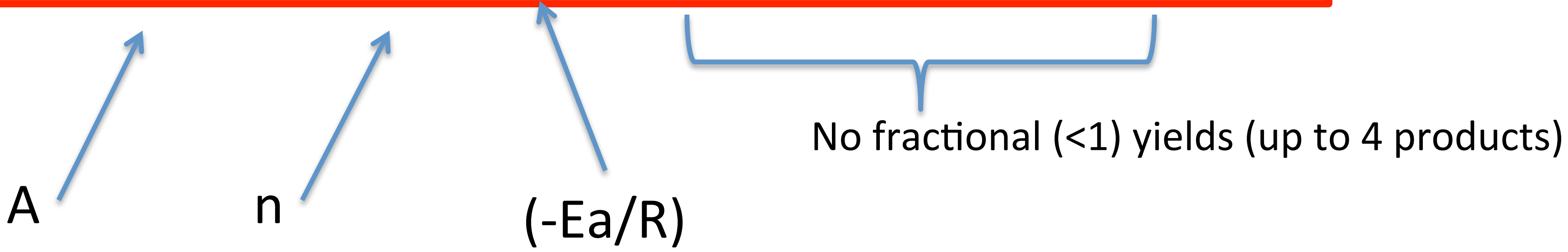
Reactions in the atmosphere.

Gas phase collision reactions:

Bimolecular reactions:
$Br + Cl_2O_2 \rightarrow BrCl + Cl + O_2$

The block of code below comes from `ukca_chem_strattrop.F90`
It includes a comment line telling us where the kinetic data came from to calculate $k_{(T)}$.

```
! B001 JPL2011
ratb_t('Br        ','Cl2O2     ','BrCl      ','Cl        ','O2        ',&
'          ',  5.90E-12,  0.00,    170.00, 0.000, 0.000, 0.000, 0.000), &
```



No fractional (<1) yields (up to 4 products)

A

n

(-Ea/R)

Reactions in the atmosphere.

Gas phase collision reactions:

Special bimolecular reactions:

$HO_2 + NO \rightarrow OH + NO_2$ (a)

$ \rightarrow HONO_2$ (b)

The second channel in this reaction is "special". It depends on temp. and pressure but does not follow the normal form of a bimolecular reaction.

```
! B060a added Alex
ratb_t('HO2      ','NO       ','HONO2    ','         ','         ',&
'         ',  3.60E-12,  0.00,   -270.00, 0.000, 0.000, 0.000, 0.000) ,&
```

```
! HO2 + NO -> HONO2 (with extra temp and pressure dependence)
! Added by Alex 2012
rk(1:n_points,iho2no)=rk(1:n_points,iho2no)*                 &
      ((530.0/t(1:n_points)) + 8.53E-4*(1E-2*p(1:n_points))-1.73)/100.0
```

The block above is from asad_bimol.F90, the routine used to calculate $k_{(T)}$.

Reactions in the atmosphere.

Gas phase collision reactions:

Termolecular reactions:
A + B + M -> products

The rate constant for this reaction can be written as:

$$k_{obs(M,T)} = \left(\frac{k_{0,T}[M]}{1 + \frac{k_{0,T}[M]}{k_{\infty,T}}} \right) F \left\{ 1 + \left[\log_{10} \left(\frac{k_{0,T}[M]}{k_{\infty,T}} \right) \right]^2 \right\}^{-1} \text{ molecules}^{-2} \text{ cm}^6 \text{ s-1}$$

Which is a complex function of k(T) expressions analogous to those for bimolecular reactions (i.e. functions of Ea, T etc).

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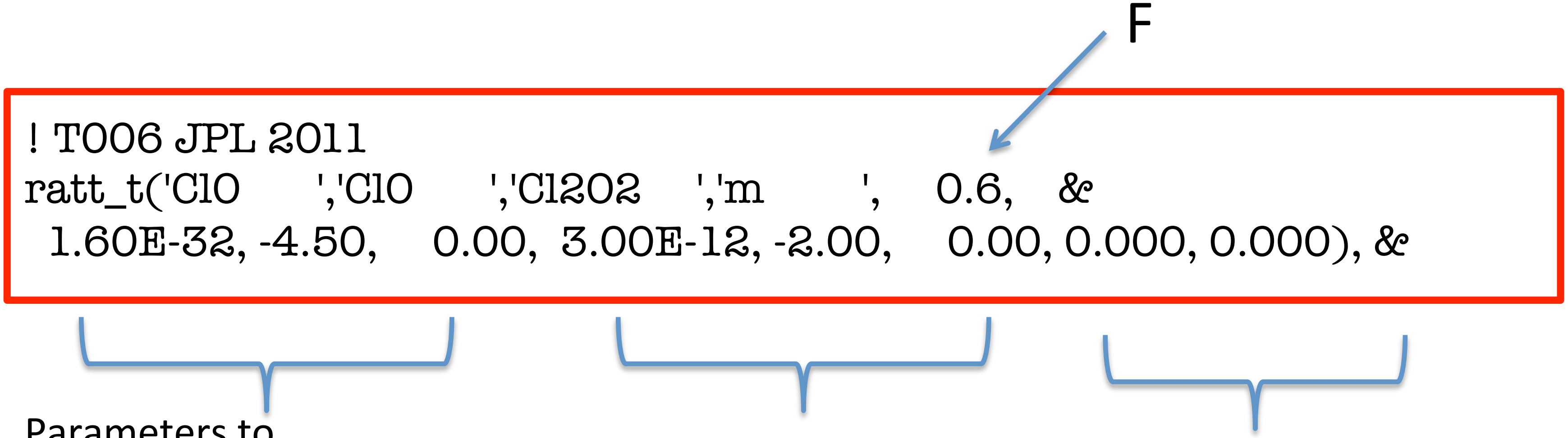
Reactions in the atmosphere.

Gas phase collision reactions:

Termolecular reactions:

$ClO + ClO + M \rightarrow Cl_2O_2 + M$ (N.B. M is not a tracer! So it does not need to be conserved in the chemistry reactions)



F

```
! T006 JPL 2011
ratt_t('ClO      ','ClO      ','Cl2O2    ','m        ',    0.6,   &
  1.60E-32, -4.50,    0.00,  3.00E-12, -2.00,    0.00, 0.000, 0.000), &
```

Parameters to calculate $k_{0(T)}$, the low pressure limit (A, n factor and -Ea/R).

Parameters to calculate $k_{inf(T)}$, the high pressure limit (A, n factor and -Ea/R).

No fractional (<1) yields (only two products)

Reactions in the atmosphere.

Gas phase collision reactions:

Special termolecular reactions:

$HO_2 + HO_2 + M \rightarrow H_2O_2 + O_2 + M$

F

```
! T010 JPL 2011 see also asad_trimol.F90
ratt_t('HO2      ','HO2      ','H2O2     ','O2       ',    0.0,   &
  2.10E-33,  0.00,  -920.00,  0.00E+00,  0.00,     0.00, 0.000, 0.000), &
```

```
! HO2 + HO2 [+ M]
!        h2o is an advected tracer
         DO jl = 1, n_points
          rk(jl,iho2) = rk(jl,iho2)  *                      &
          ( 1.0 + 1.4E-21 * f(jl,ih2o) * EXP(2200./t(jl)) )
         END DO
```

Extra code on the left is from asad_termol.F90 which is used to calculate k(T). In this case $k_{HO2+HO2(T)}$ has an extra term for $[H_2O]$ dependence.

Formation of an O_3 layer.

Stratospheric Ozone:

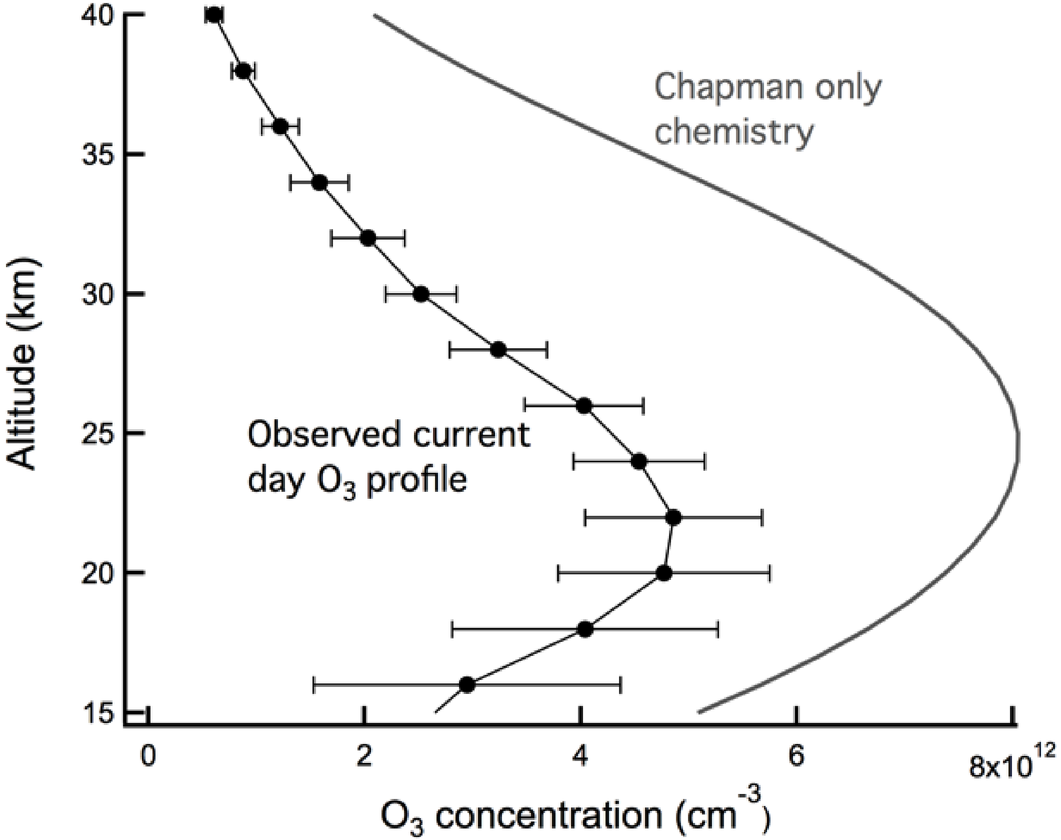
- The Chapman mechanism:

1.	$O_2 + hv \rightarrow O + O$	(J1)	Slow
2.	$O + O_2 + M \rightarrow O_3 + M$	(k2)	Fast
3.	$O_3 + hv \rightarrow O + O_2$	(J3)	Fast
4.	$O + O_3 \rightarrow O_2 + O_2$	(k4)	Slow

- The layered like structure of O_3 (maximum mixing ratio ~ 10 hPa) occurs due to the competition of these reactions.

Simple mechanism overestimates [O_3]

Vertical profile of [O_x]:



- Clearly need other loss processes for Ox to explain observed profile.

Catalytic O_3 loss reactions needed.

e.g. NOx mediated Ox destruction:

- Effectively we need to speed up reaction 4 in the Chapman mechanism:

$$\begin{aligned} X + O_3 &\rightarrow XO + O_2 \\ XO + O &\rightarrow X + O_2 \\ \text{net} \quad O + O_3 &\rightarrow O_2 + O_2 \end{aligned}$$

- For NOx, X = NO

$NO + O_3 \text{ -> } NO_2 + O_2$ k5~ 1.8E-14 $cm^3\ s^{-1}$

$NO_2 + O \text{ -> } NO + O_2$ k6~ 1E-11 $cm^3\ s^{-1}$

NET: $O_3 + O \text{ -> } O_2 + O_2$

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How well does this compare with obs?

Observed vs (early) modelled Ox loss:

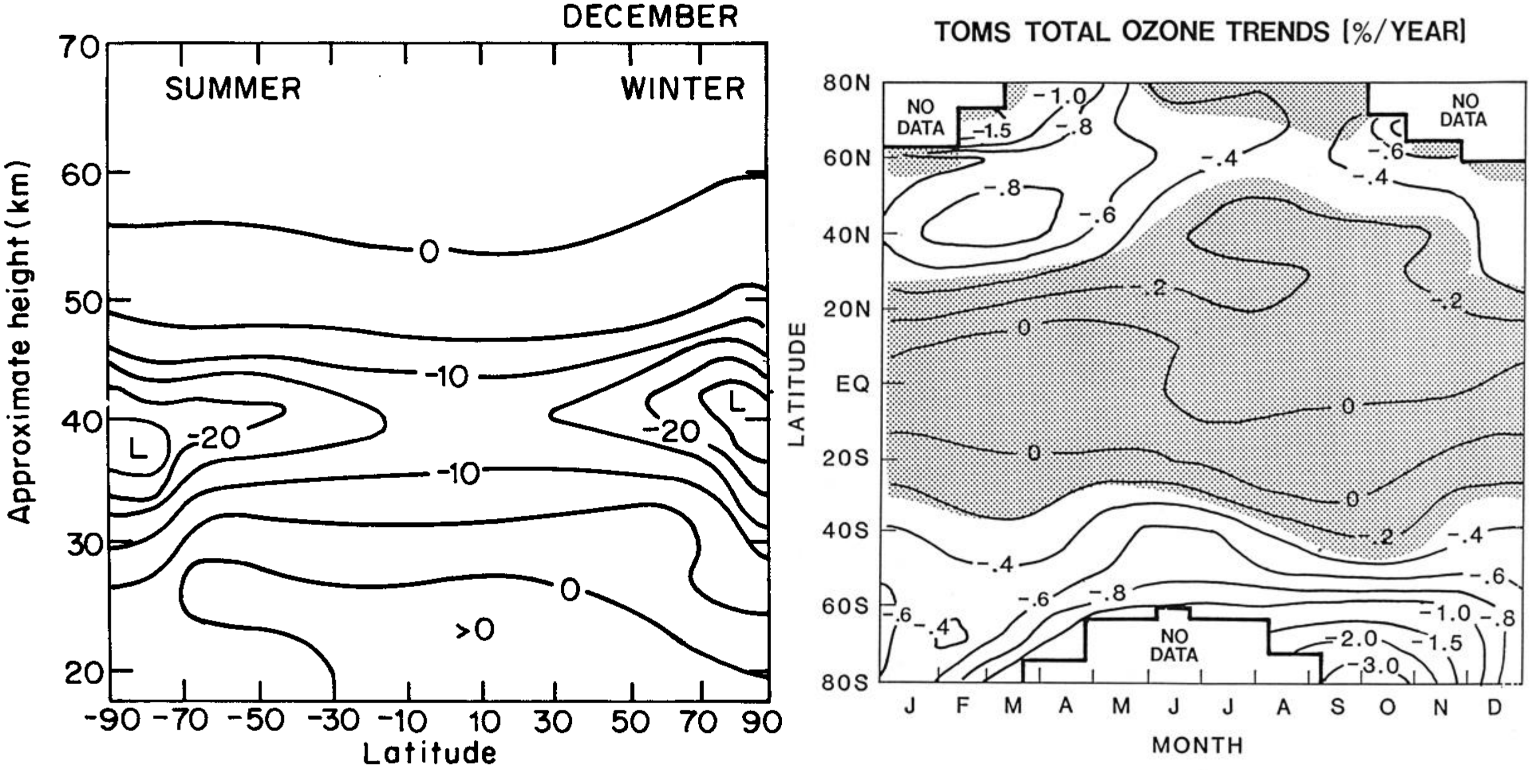


Figure 4.3 Modelled % change in O_3 for a change in ClOx from around 1ppbv to 3ppbv (left panel). Observed rate of change of ozone %/yr (right panel).

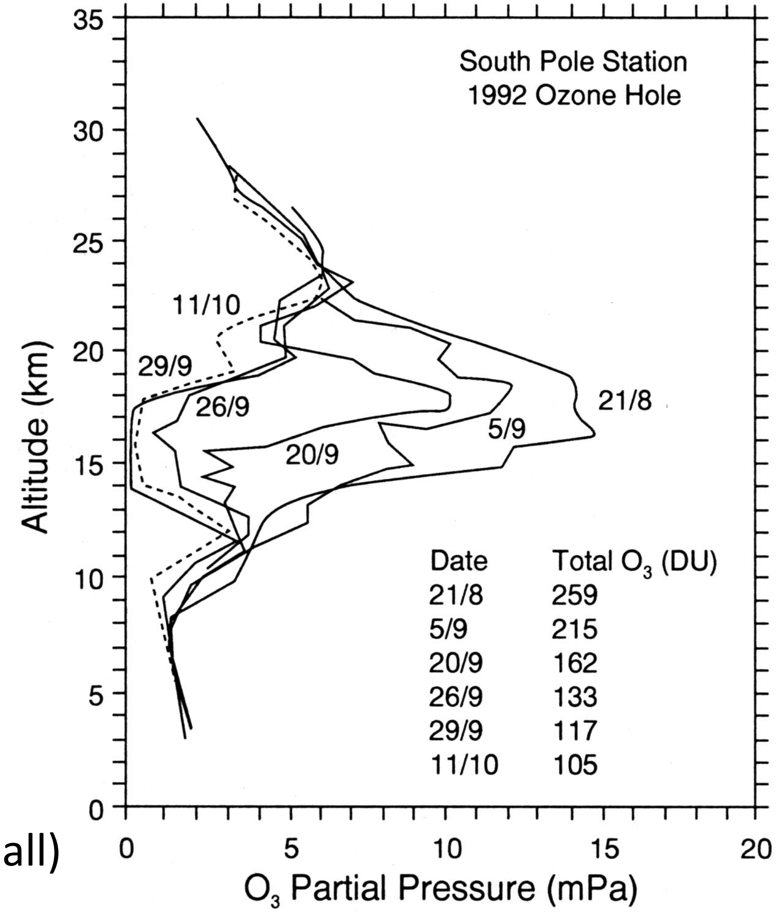
Antarctic O_3 depletion.

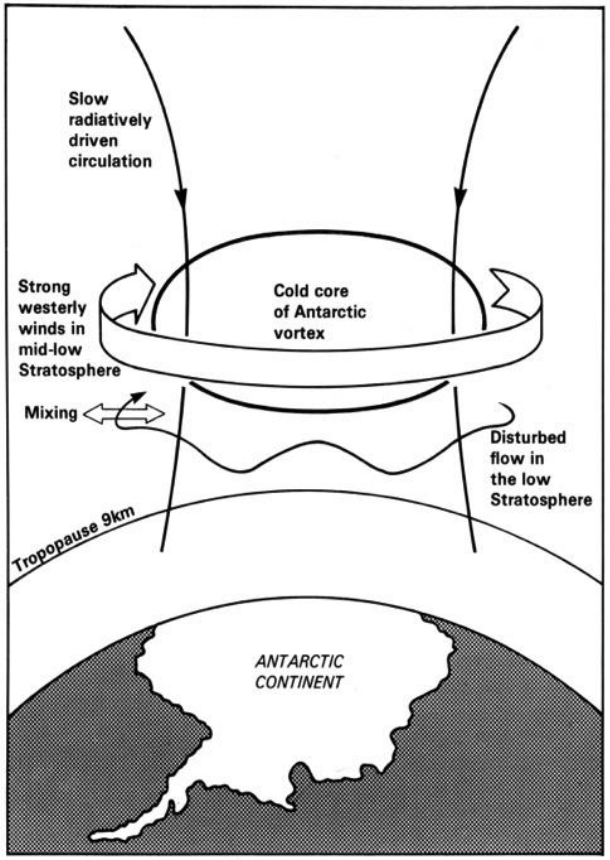
Significant O_3 depletion over Antarctica only.

Why?

Ox loss happens in spring when [ClOx] should be low

(J_{HCl} and J_{ClONO2} small)

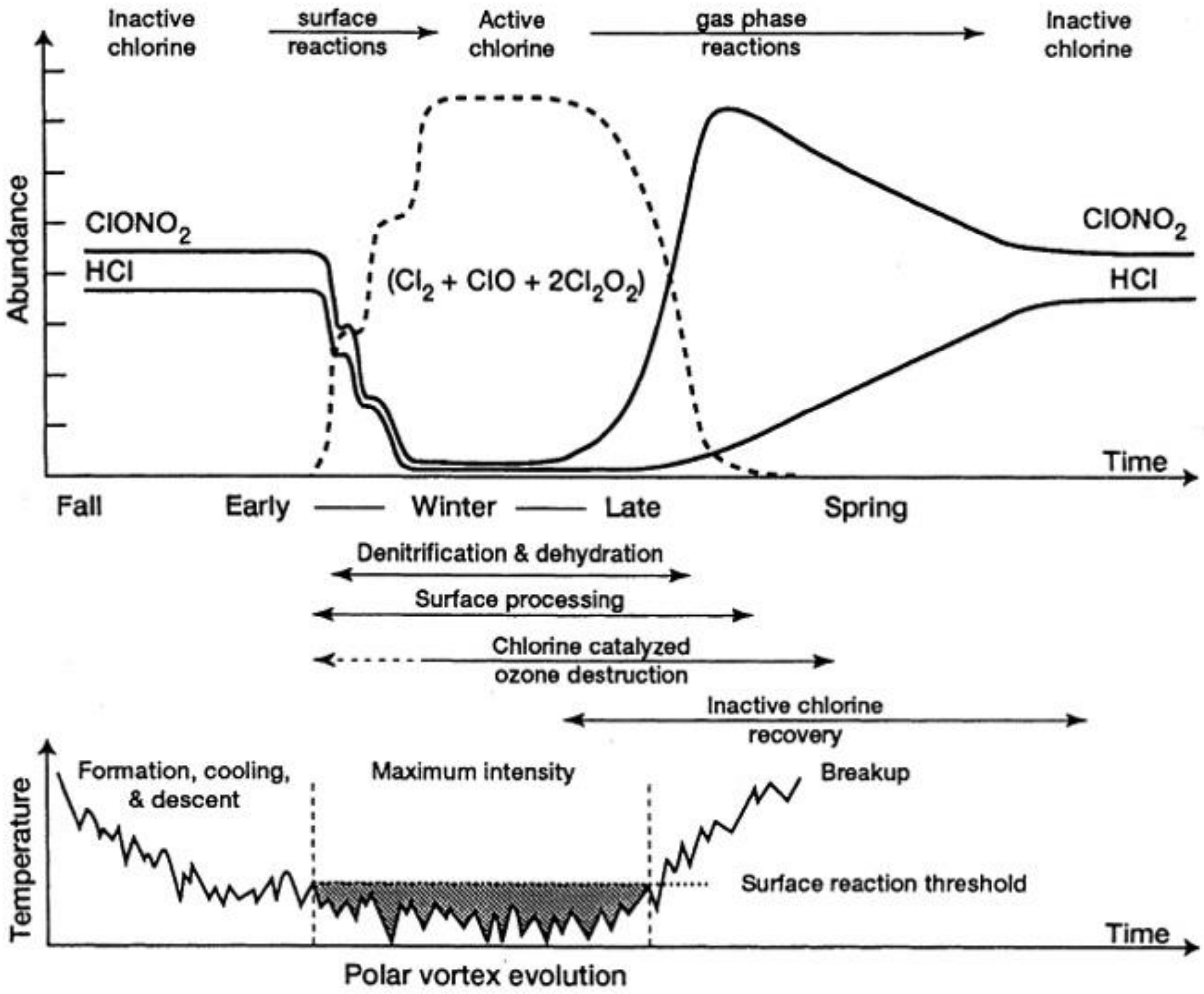




Chemistry in the dark.

Cold temperatures found in the vortex allow Polar Stratospheric Clouds to form

All the NOx is locked up in HNO_3 – this solidifies under the cold T.



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Heterogeneous chemistry wins!

PSC mediated Ox destruction:

$HCl + ClONO_2 \xrightarrow{PSC} Cl_2 + HONO_2 \quad \gamma = 0.6$

~~$ClO + NO_2 \rightarrow Cl + NO$~~

$ClO + ClO + M \rightarrow Cl_2O_2 + M$ k1~ 9E-12 $cm^6\ s^{-1}$

$Cl_2O_2 + hv \rightarrow Cl + ClO_2$ J2~ 1E-2 s^{-1}

$ClO_2 + M \rightarrow Cl + O_2$ k3~ 9E-34 $cm^3\ s^{-1}$

$d[O_3]/dt = -2k1[ClO]^2[M]$

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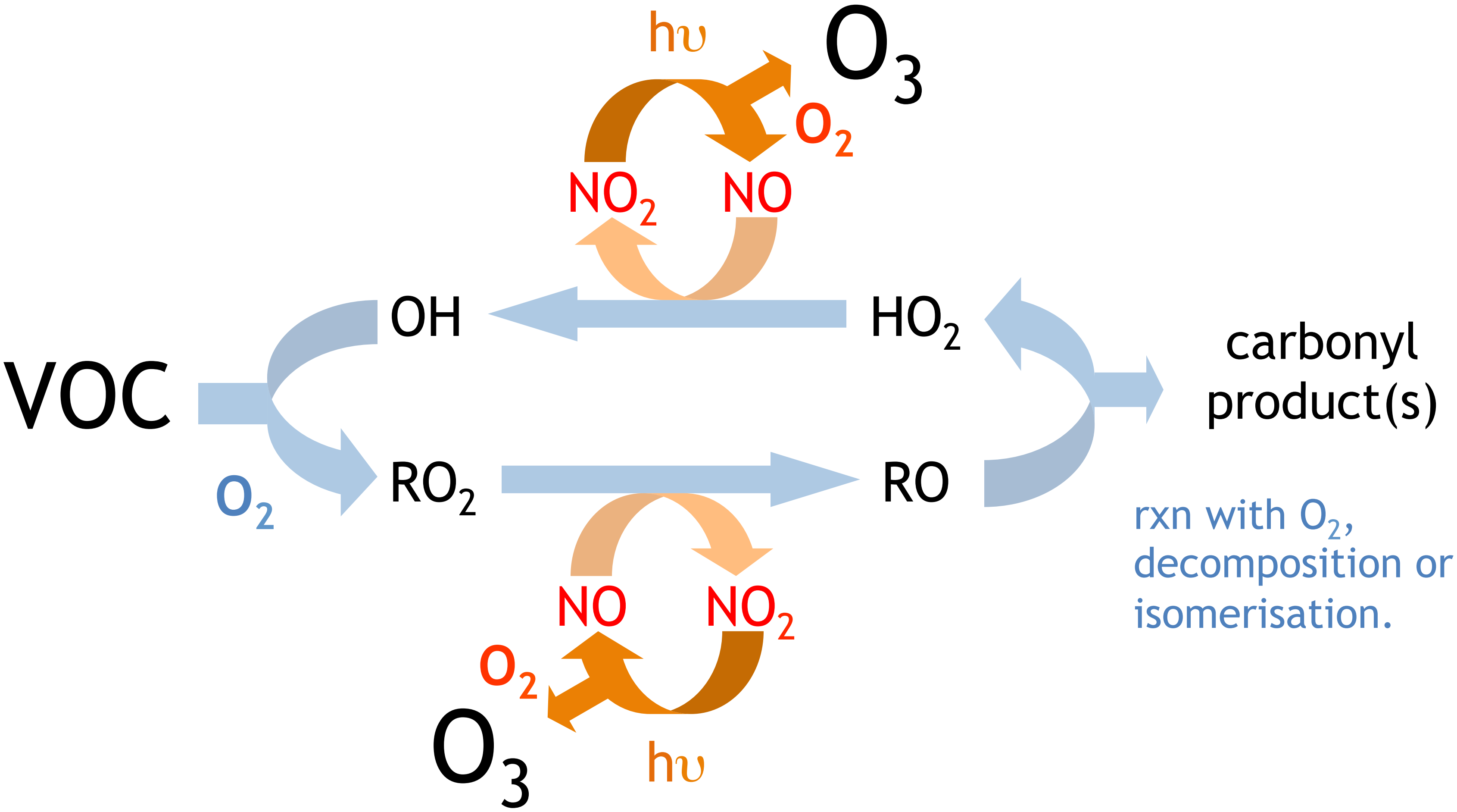
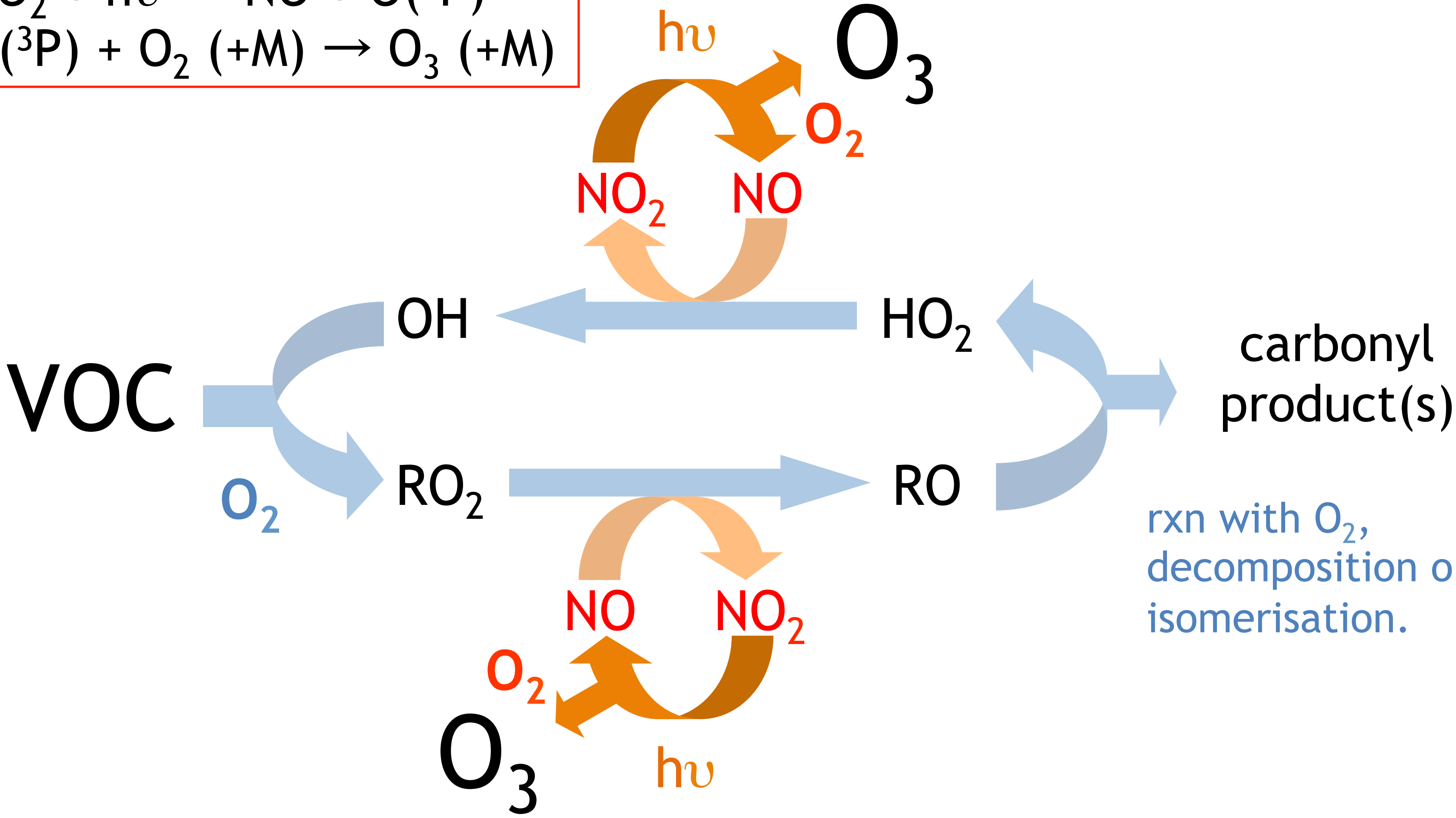
VOC propagated O_3 production



rxn with O_2, decomposition or isomerisation.

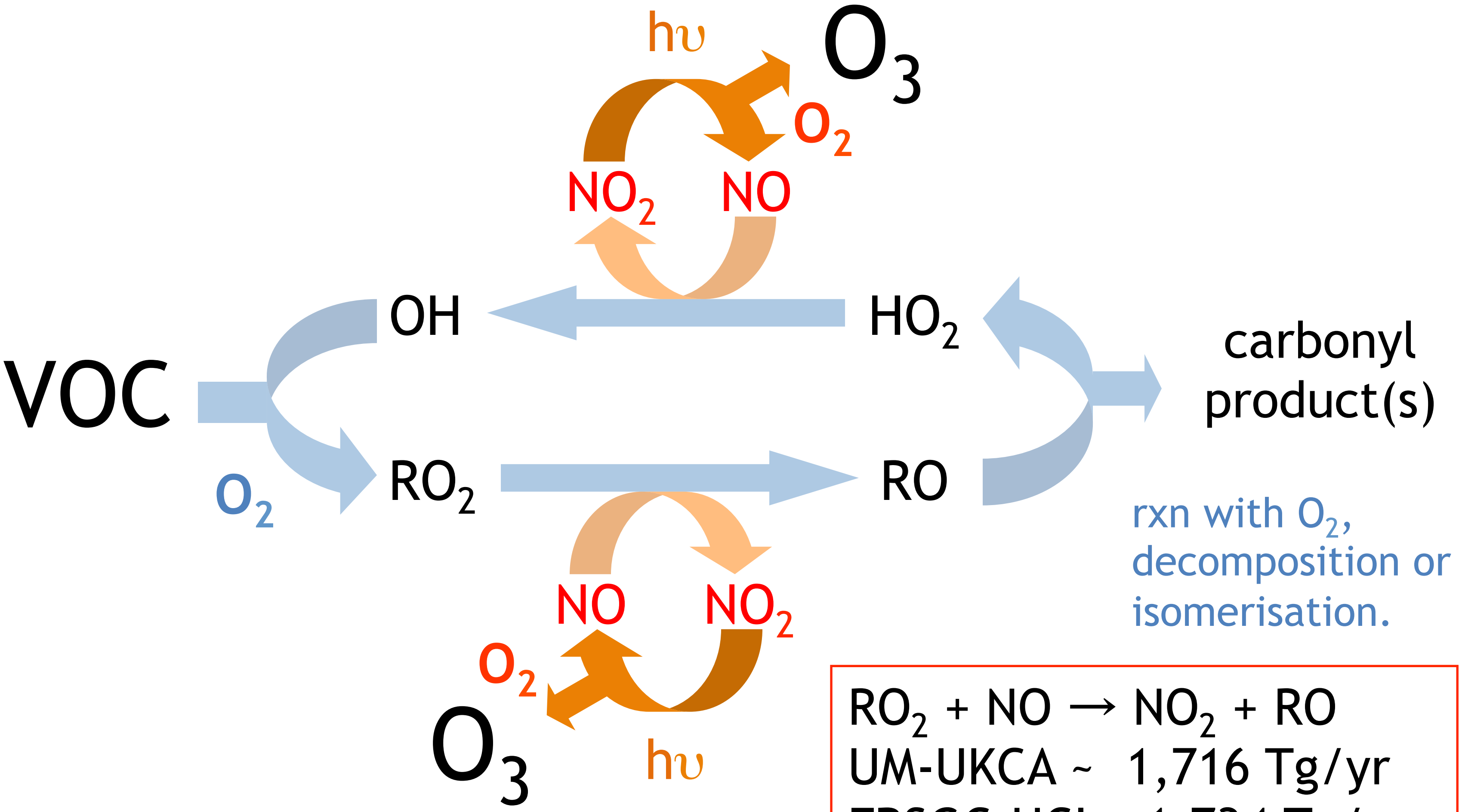
VOC propagated O_3 production

$NO_2 + h\upsilon \rightarrow NO + O(^3P)$
$O(^3P) + O_2\ (+M) \rightarrow O_3\ (+M)$



rxn with O_2, decomposition or isomerisation.

VOC propagated O_3 production



rxn with O_2, decomposition or isomerisation.

$RO_2 + NO \rightarrow NO_2 + RO$
UM-UKCA ~ 1,716 Tg/yr
FRSGC-UCI ~ 1,734 Tg/yr

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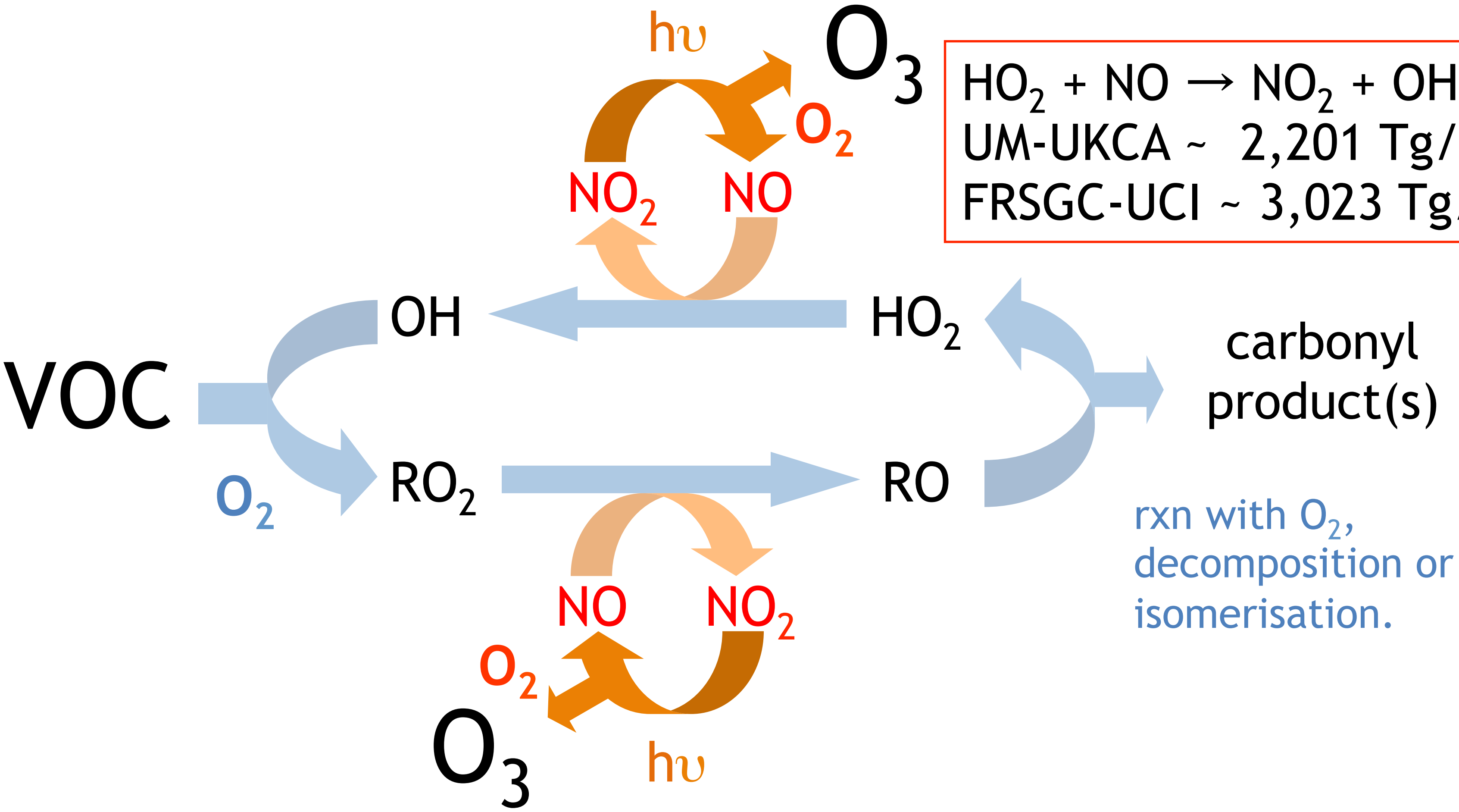
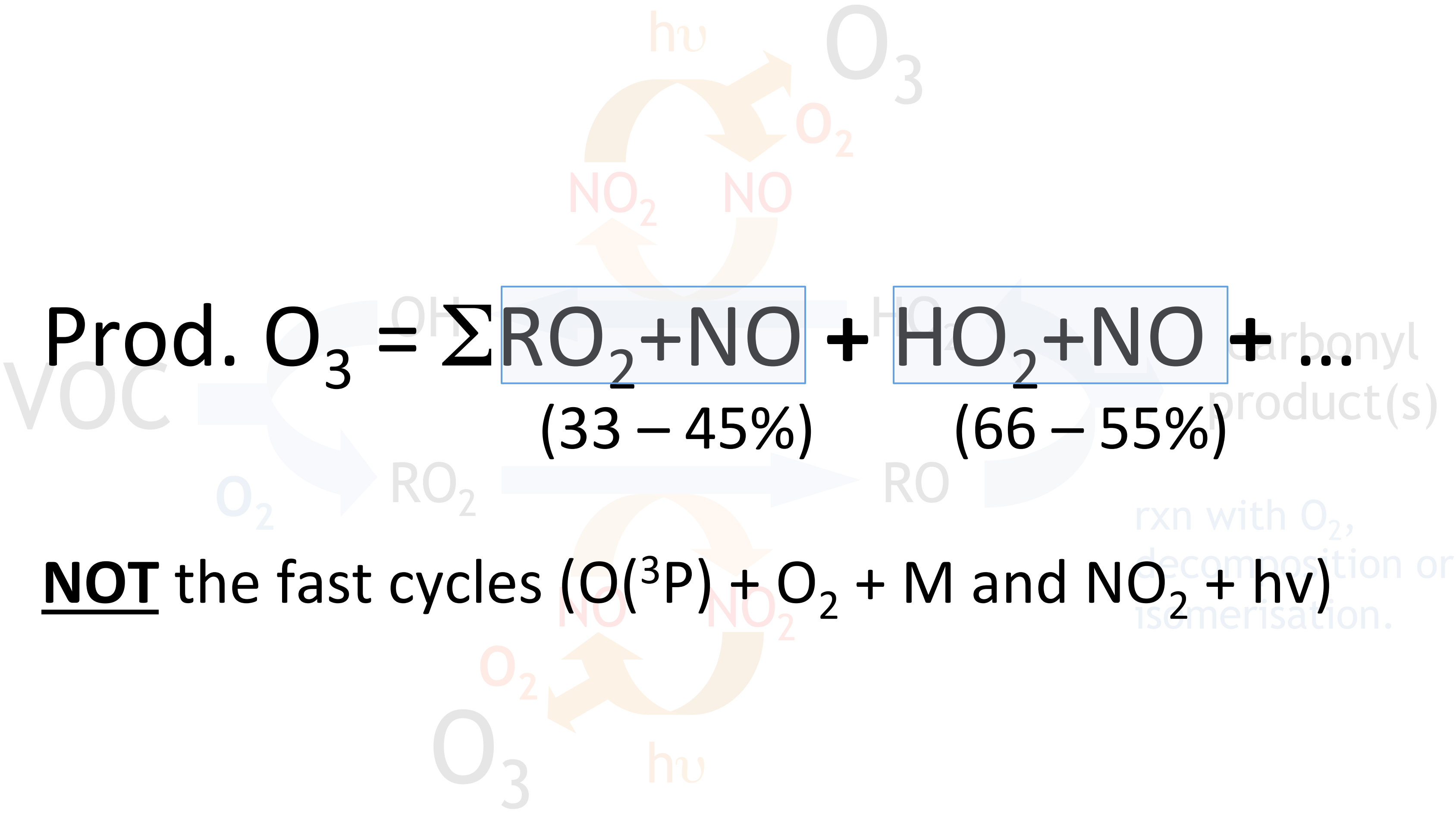
VOC propagated O_3 production



$HO_2 + NO \rightarrow NO_2 + OH$
UM-UKCA ~ 2,201 Tg/yr
FRSGC-UCI ~ 3,023 Tg/yr

VOC propagated O_3 production

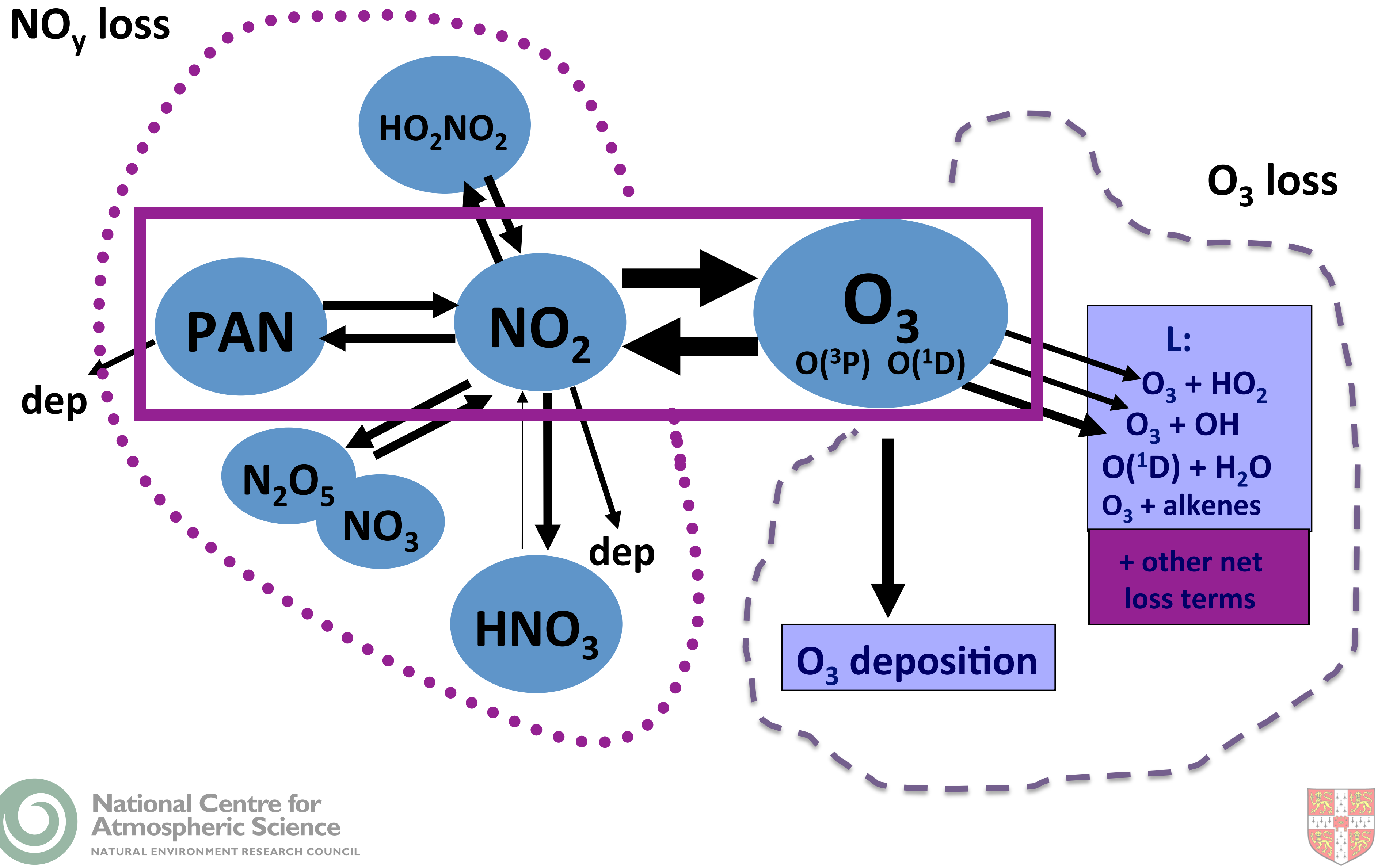


$$\text{Prod. } O_3 = \Sigma \boxed{RO_2 + NO} + \boxed{HO_2 + NO} + \ldots$$

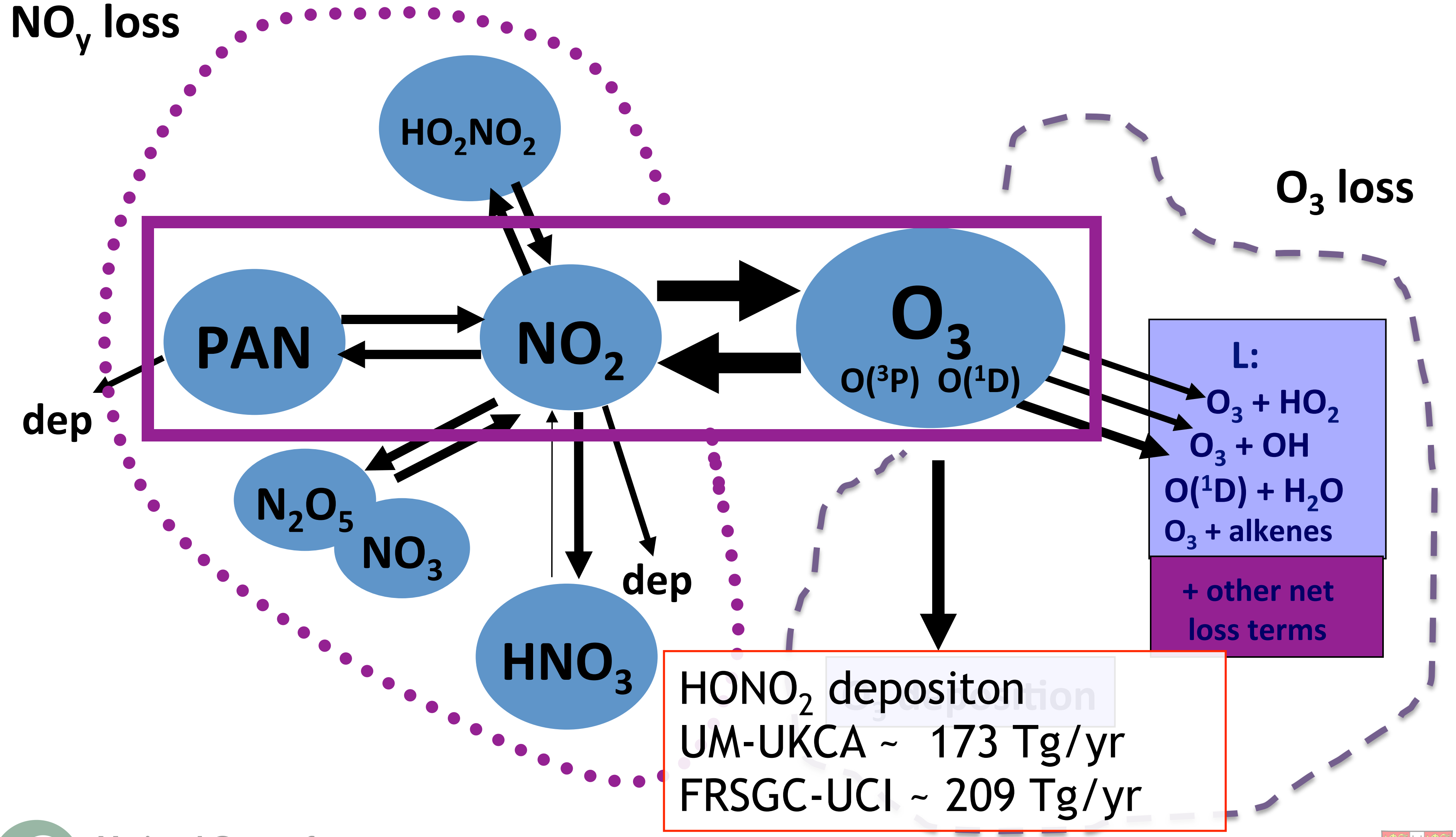
(33 – 45%) (66 – 55%)

NOT the fast cycles ($O(^3P) + O_2 + M$ and $NO_2 + hv$)

Defining O_3 loss



Defining O_3 loss



NO_y loss

HO_2NO_2

PAN

NO_2

O_3

$O(^3P)$ $O(^1D)$

dep

N_2O_5

NO_3

HNO_3

dep

O_3 loss

L:

$O_3 + HO_2$

$O_3 + OH$

$O(^1D) + H_2O$

O_3 + alkenes

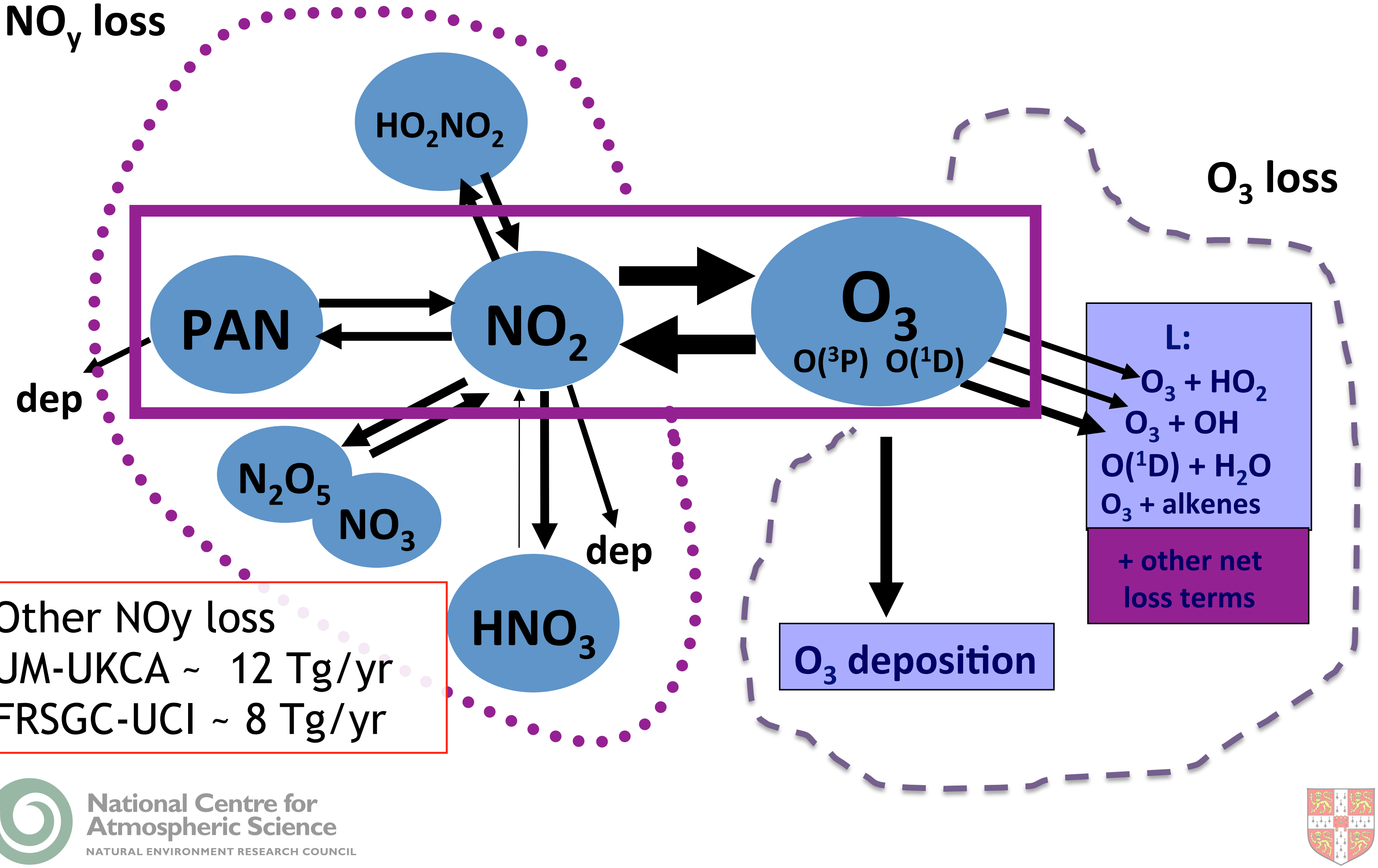
+ other net loss terms

$HONO_2$ depositon

UM-UKCA ~ 173 Tg/yr

FRSGC-UCI ~ 209 Tg/yr

Defining O_3 loss



NO_y loss

HO_2NO_2

PAN

NO_2

O_3

$O(^3P)$ $O(^1D)$

dep

N_2O_5

NO_3

HNO_3

dep

O_3 loss

L:

$O_3 + HO_2$

$O_3 + OH$

$O(^1D) + H_2O$

O_3 + alkenes

+ other net loss terms

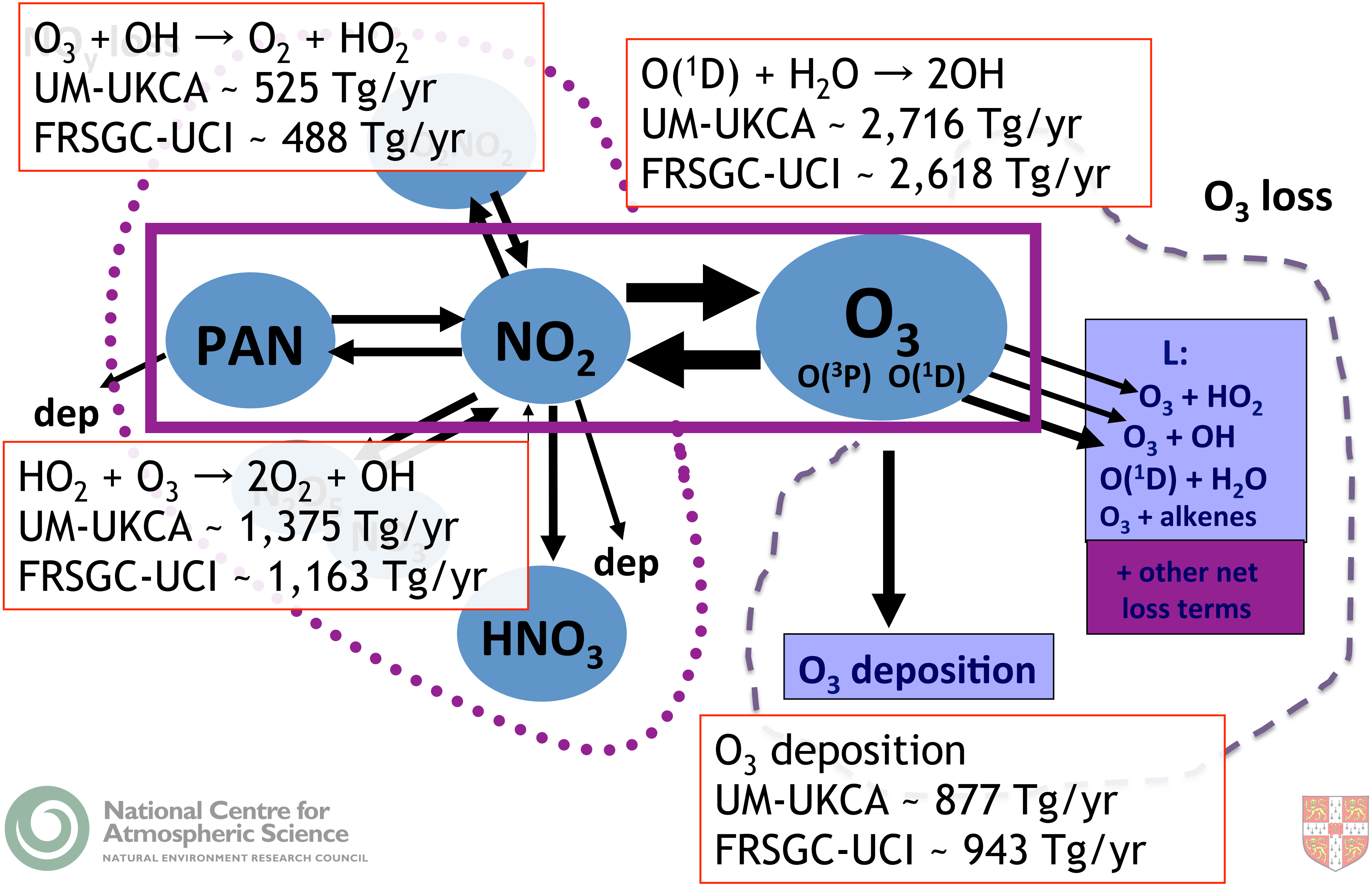
O_3 deposition

Other NOy loss

UM-UKCA ~ 12 Tg/yr

FRSGC-UCI ~ 8 Tg/yr

Defining O_3 loss



$O_3 + OH \rightarrow O_2 + HO_2$
UM-UKCA ~ 525 Tg/yr
FRSGC-UCI ~ 488 Tg/yr

$O(^1D) + H_2O \rightarrow 2OH$
UM-UKCA ~ 2,716 Tg/yr
FRSGC-UCI ~ 2,618 Tg/yr

$HO_2 + O_3 \rightarrow 2O_2 + OH$
UM-UKCA ~ 1,375 Tg/yr
FRSGC-UCI ~ 1,163 Tg/yr

O_3 deposition
UM-UKCA ~ 877 Tg/yr
FRSGC-UCI ~ 943 Tg/yr

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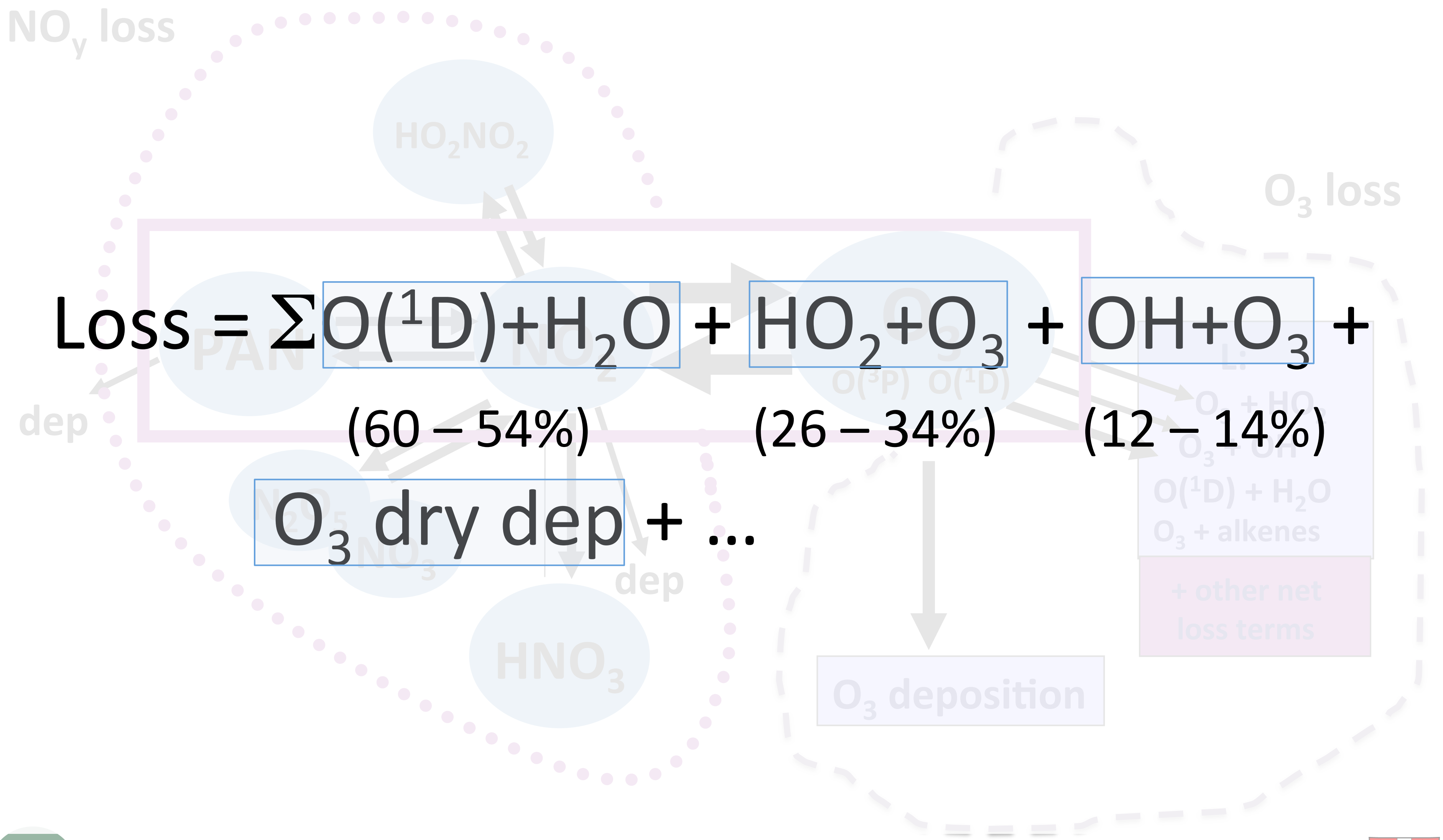
Defining O_3 loss

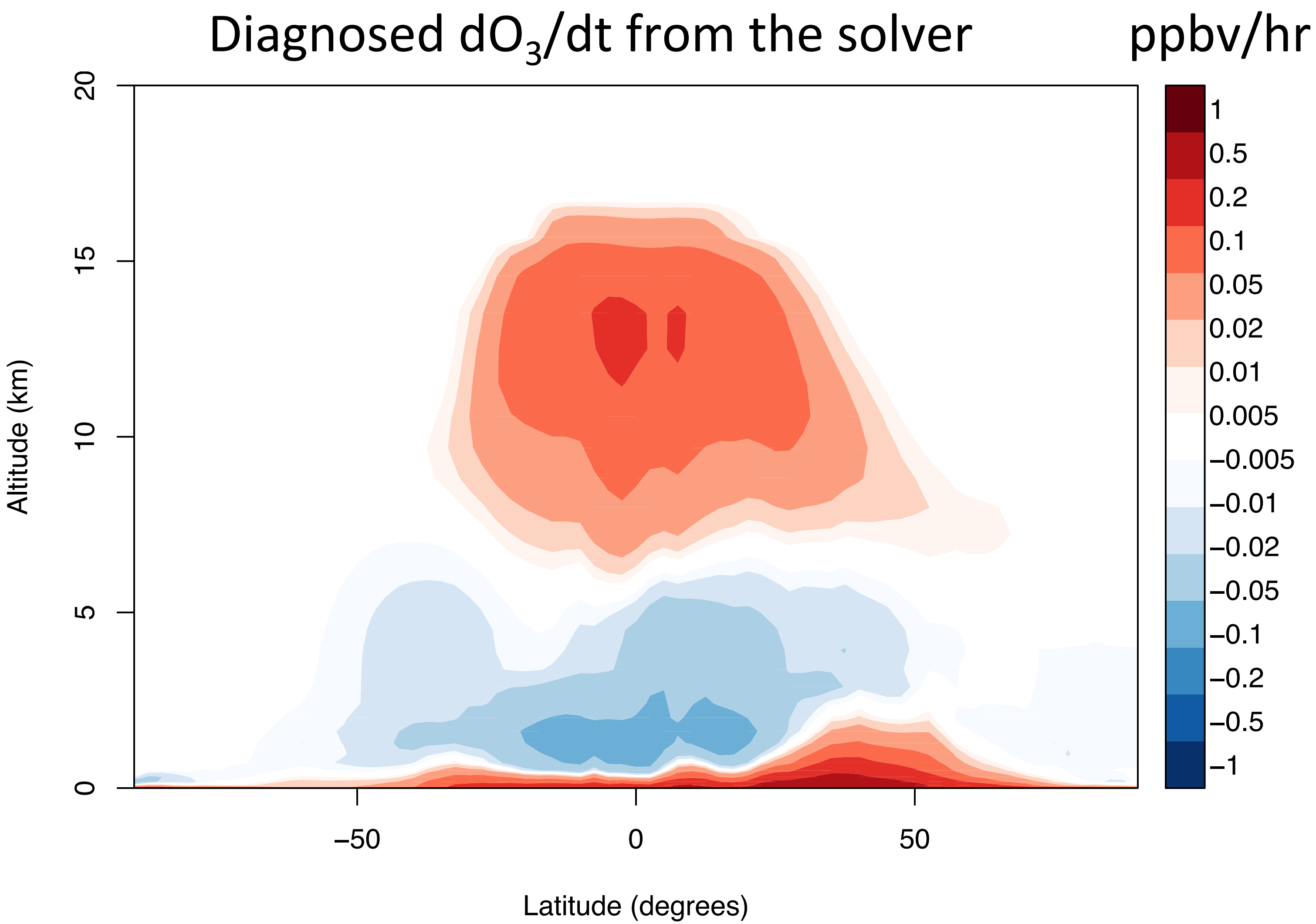


$$\text{Loss} = \Sigma\,\boxed{O(^1D)+H_2O} + \boxed{HO_2+O_3} + \boxed{OH+O_3} + \boxed{O_3\ \text{dry dep}} + \ldots$$

(60 – 54%) (26 – 34%) (12 – 14%)

Distribution of NCP

Diagnosed dO_3/dt from the solver



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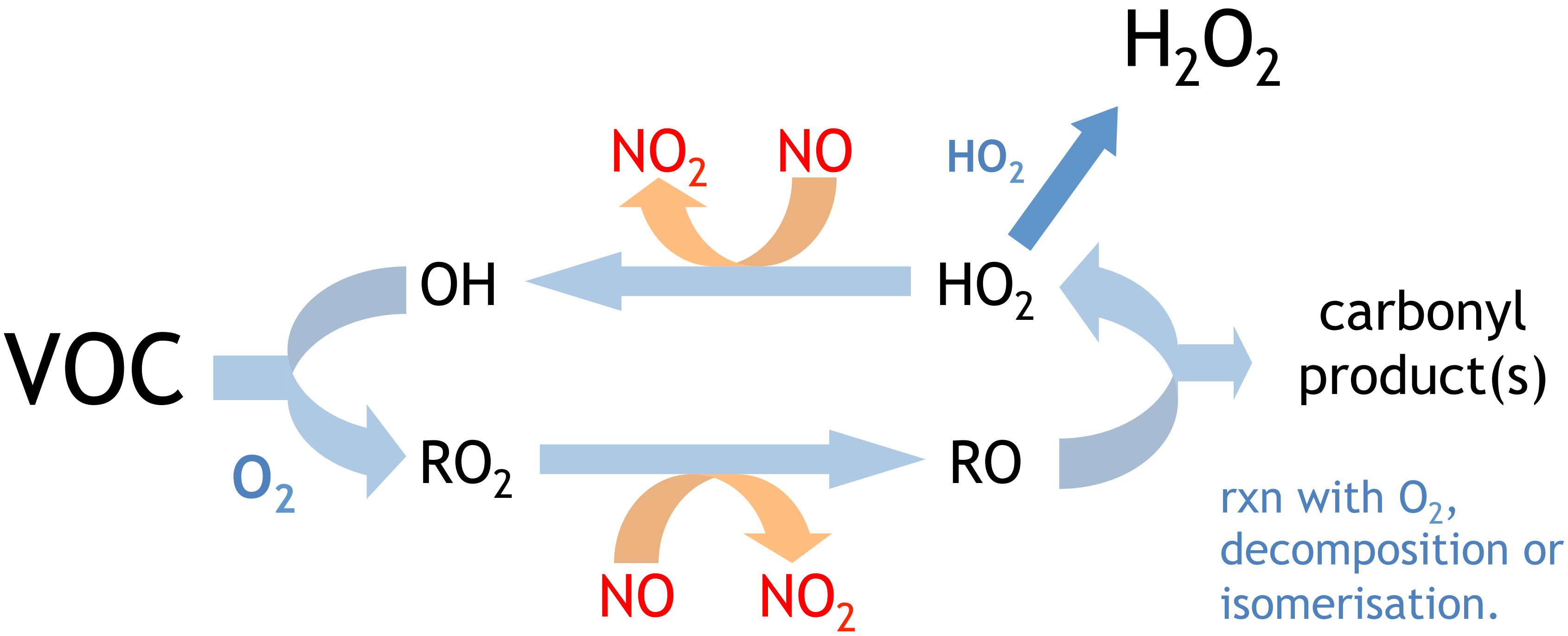
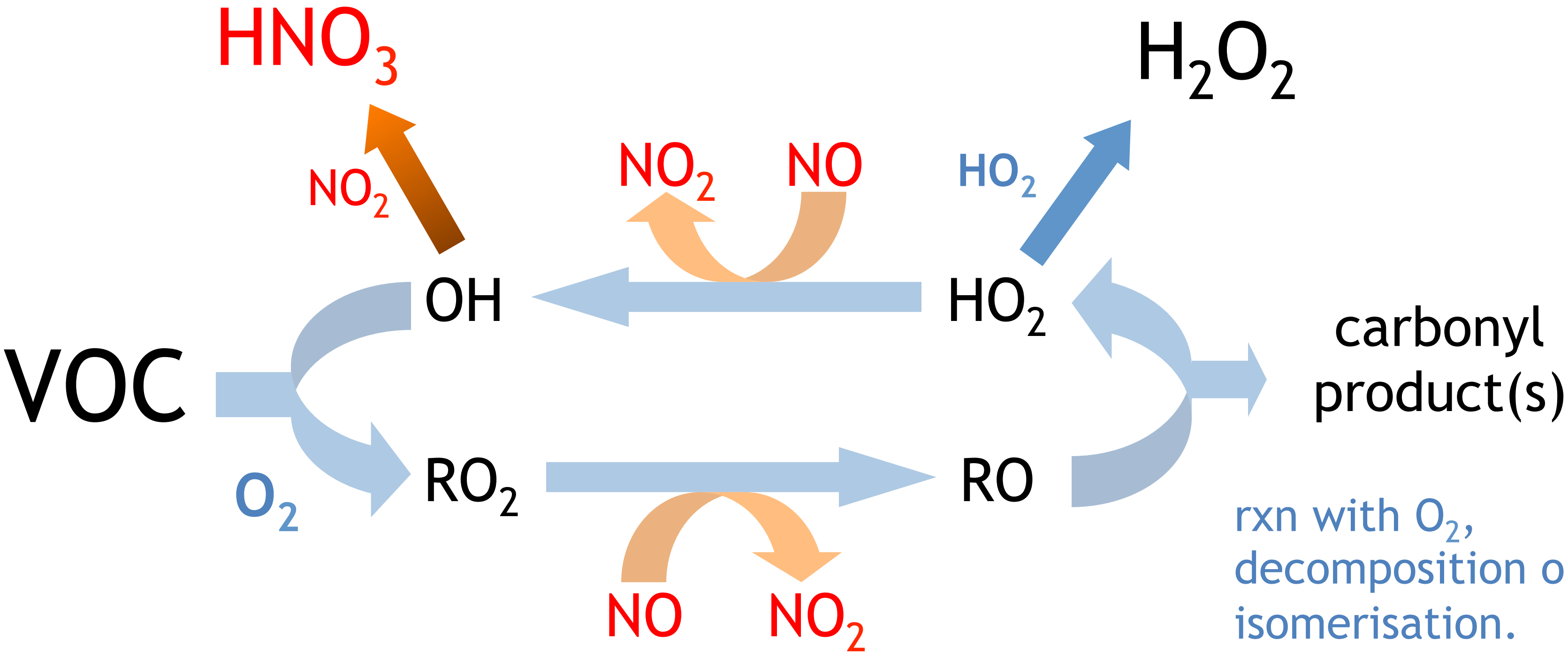
Other radical termination reactions



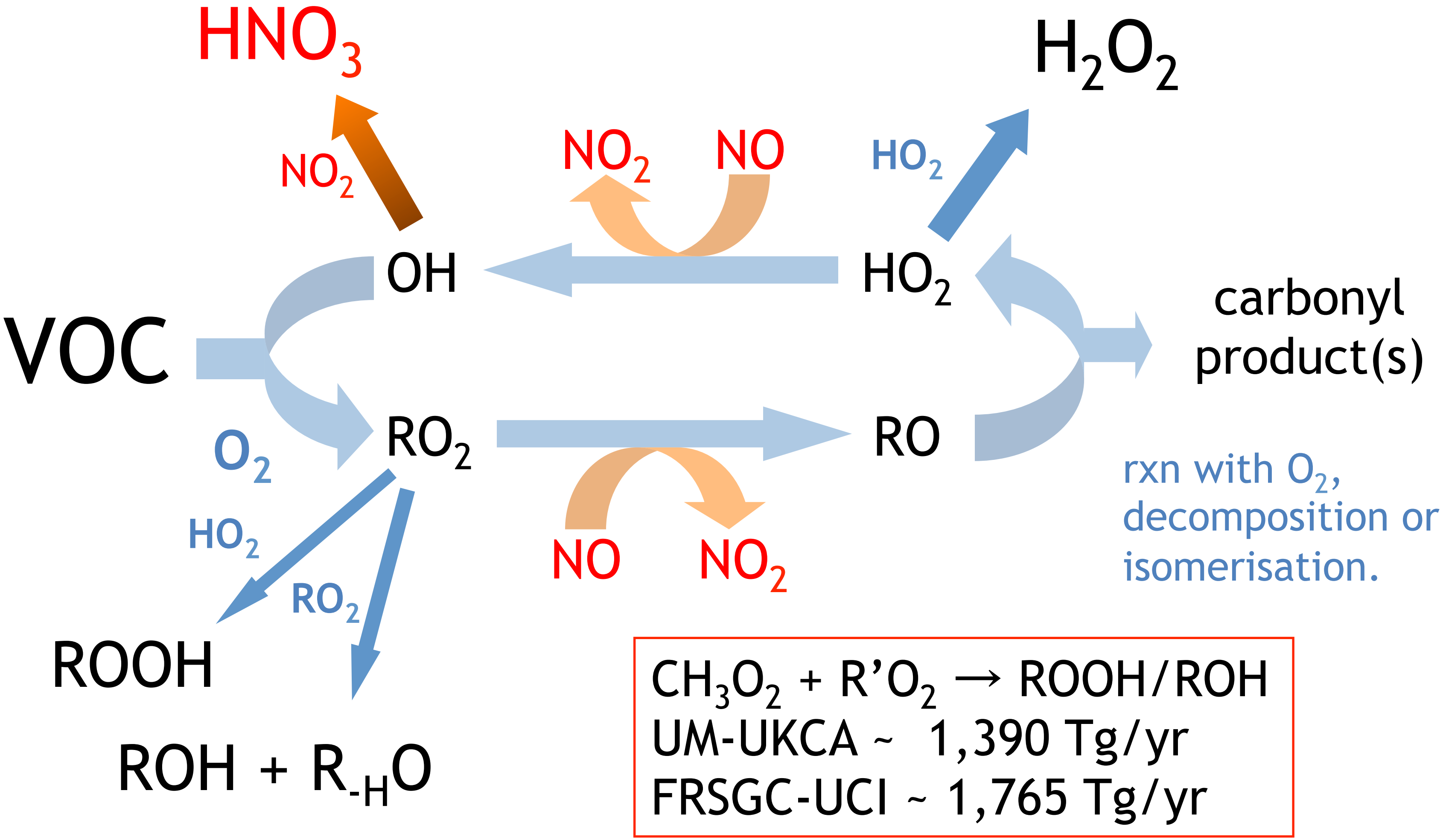
$HO_2 + HO_2 \rightarrow H_2O_2$
UM-UKCA ~ 2,212 Tg/yr
FRSGC-UCI ~ 2,280 Tg/yr

Other radical termination reactions



$NO_2 + OH \rightarrow HONO_2$
UM-UKCA ~ 111 Tg/yr
FRSGC-UCI ~ 178 Tg/yr

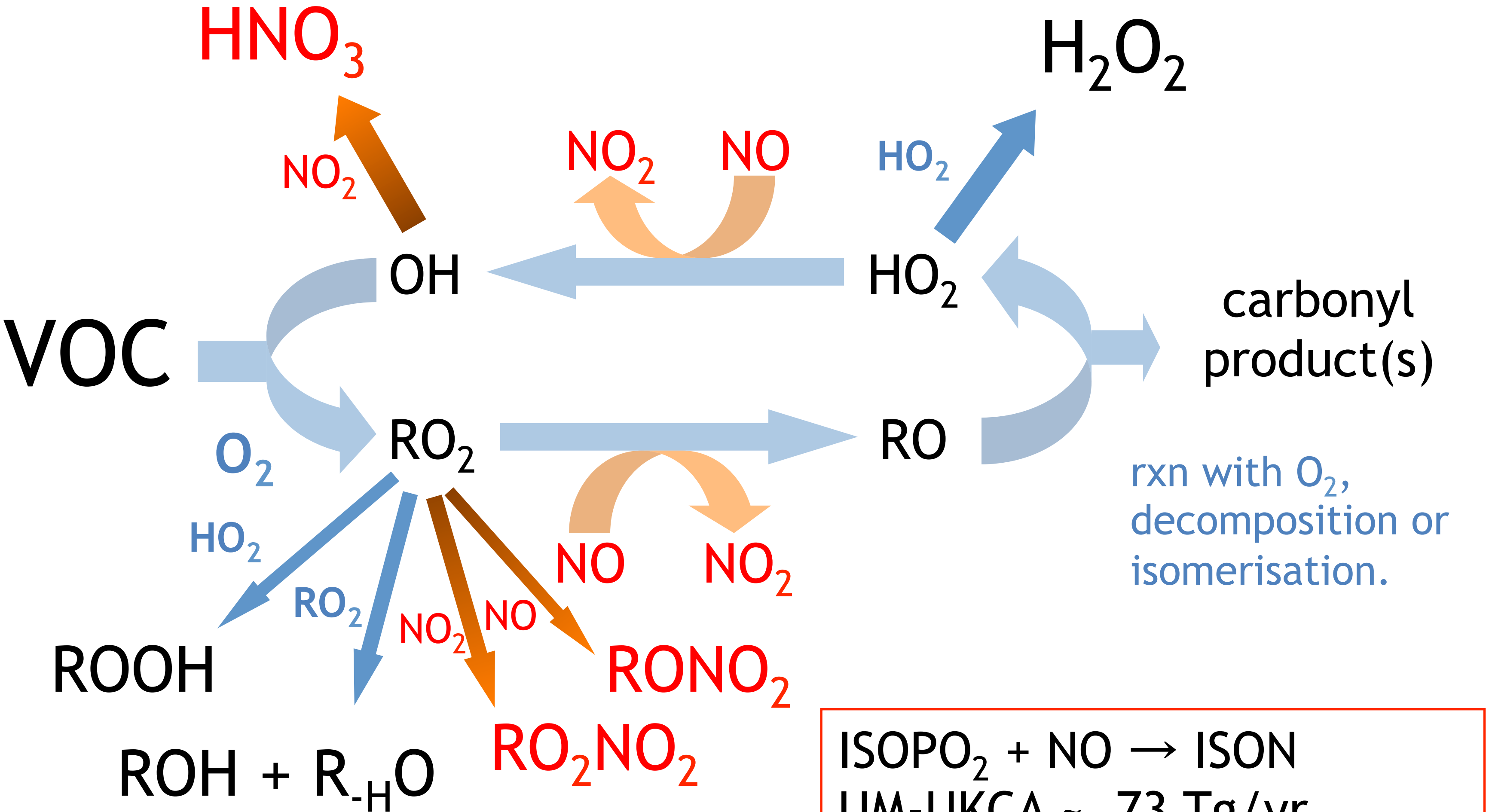
Other radical termination reactions



CH_3O_2 + $R'O_2$ → ROOH/ROH
UM-UKCA ~ 1,390 Tg/yr
FRSGC-UCI ~ 1,765 Tg/yr

($R'O_2 = \Sigma RO_2 + HO_2$)

Other radical termination reactions



HNO_3

NO_2

NO_2 NO

HO_2

H_2O_2

OH

HO_2

VOC

carbonyl product(s)

O_2

RO_2

RO

HO_2

RO_2

NO_2

NO

NO

NO_2

rxn with O_2, decomposition or isomerisation.

ROOH

$RONO_2$

ROH + $R_{-H}O$

RO_2NO_2

$ISOPO_2$ + NO → ISON
UM-UKCA ~ 73 Tg/yr
FRSGC-UCI ~ NA

What is missing from CheST?

- *So what doesn't* ***CheST*** *do?*

- The comprehensive NMHC chemistry is similar in detail to that used in most other CCMs (e.g. CESM, GEOS-CCM, CHASER) and CTMS (e.g. TOMCAT, GEOS-chem) but is still far from complete. We have a very limited coverage of reactive hydrocarbons (e.g. butane, alkenes) and no aromatic compounds (e.g benzene).

- The coverage of stratospheric chemistry is good, but we lump many of the CFCs and their replacements into a small number of emitted compounds.

What is missing from CheST cont.

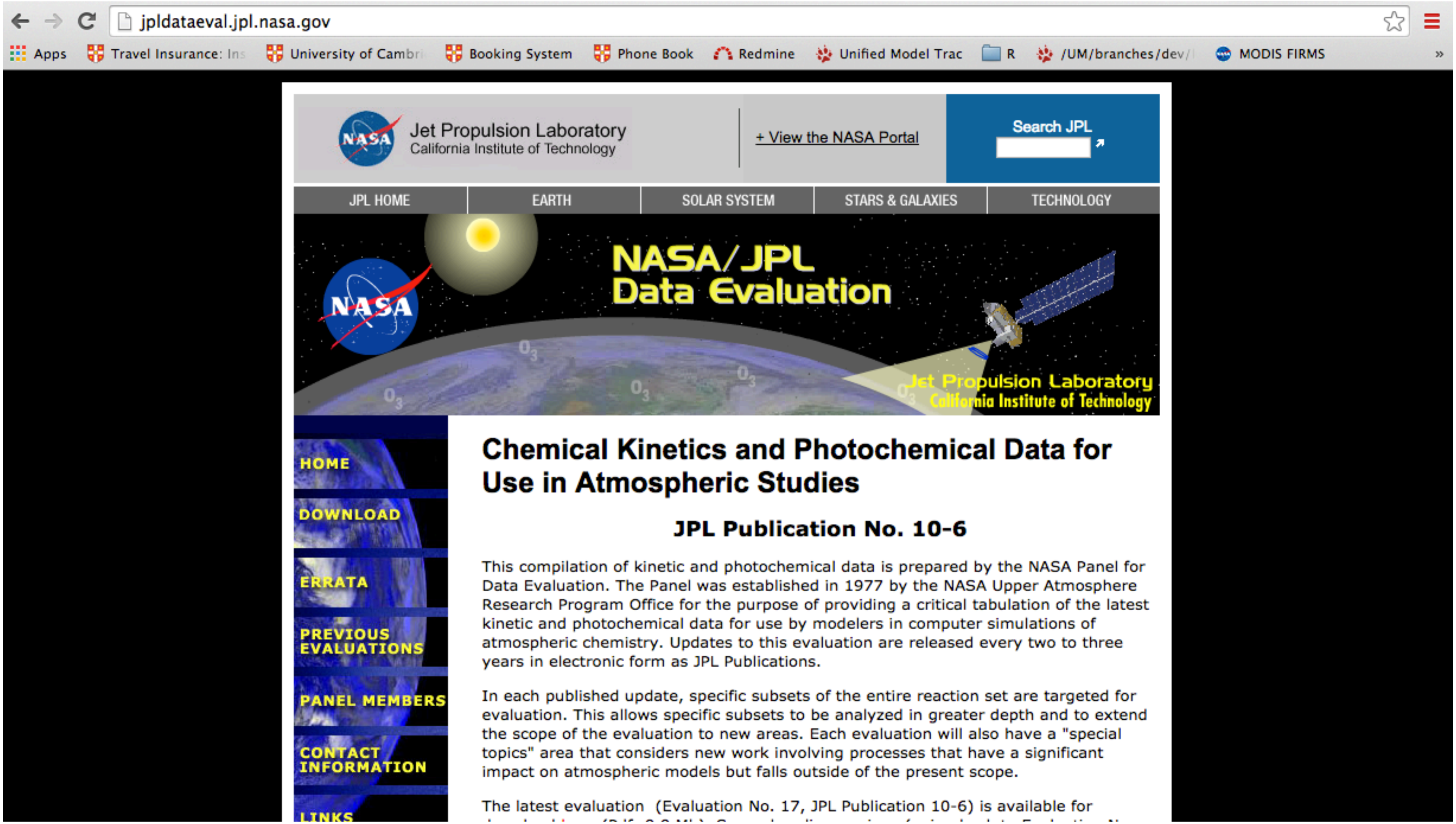
- *So what doesn't **CheST** do?*
- There is no, zero, relevant mesospheric chemistry. There is only one model that is really any good in the mesosphere (WACCM).
- Whilst bromine and chlorine are well represented in the stratosphere, there is scope for more inclusion of tropospheric compounds (e.g. $CHBr_2Cl$ and other VSLS).
- There is no Iodine chemistry.

Building a chemistry scheme.

1. Define the problem you want to look at:
    - Am I interested in fast photo chemistry (radicals) or are the lifetimes of the things I'm interested in intermediate?
    - Am I going to compare the results to observations, if so what type (satellite, ground based, aircraft etc)?
    - Do I need to run a complex model – can I "get away with" a back of the envelope or box model?

2. Develop a comprehensive scheme:
    - Include as many reactions as you can. If the scheme is based on a published scheme use that. If it's speculative do your home work! There are many reaction data bases out there (e.g. http://kinetics.nist.gov/kinetics/index.jsp)

Building a chemistry scheme.



Chemical Kinetics and Photochemical Data for Use in Atmospheric Studies

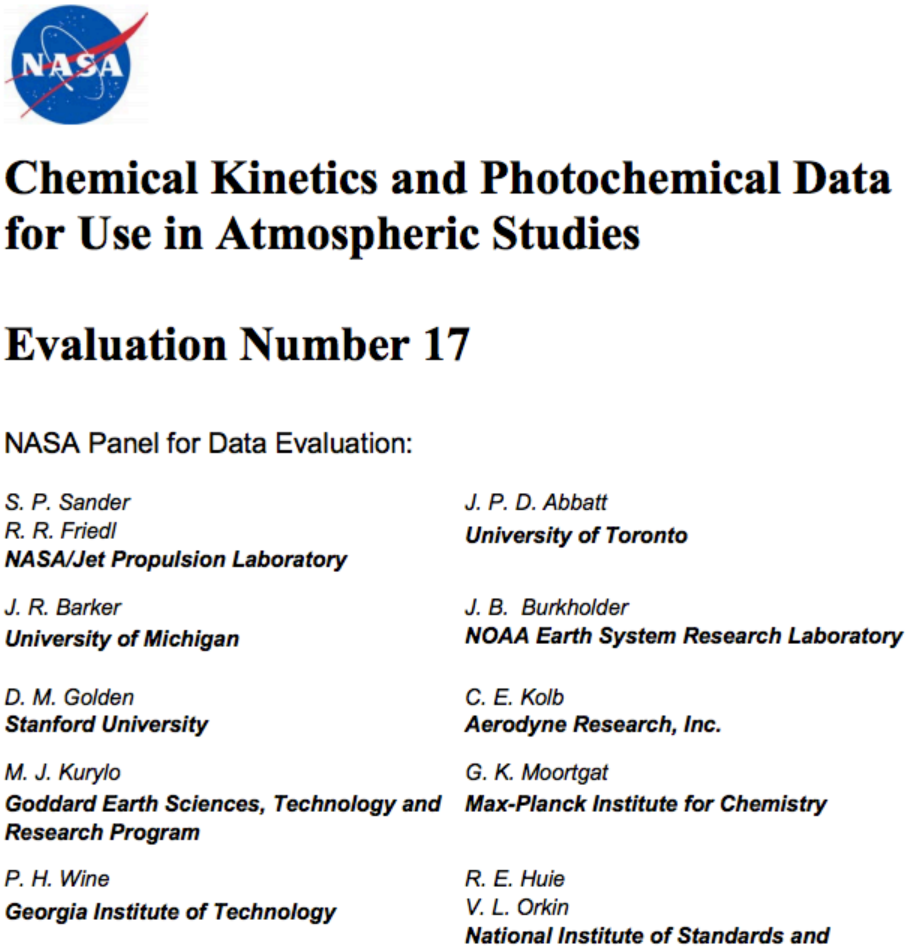
JPL Publication No. 10-6

This compilation of kinetic and photochemical data is prepared by the NASA Panel for Data Evaluation. The Panel was established in 1977 by the NASA Upper Atmosphere Research Program Office for the purpose of providing a critical tabulation of the latest kinetic and photochemical data for use by modelers in computer simulations of atmospheric chemistry. Updates to this evaluation are released every two to three years in electronic form as JPL Publications.

In each published update, specific subsets of the entire reaction set are targeted for evaluation. This allows specific subsets to be analyzed in greater depth and to extend the scope of the evaluation to new areas. Each evaluation will also have a "special topics" area that considers new work involving processes that have a significant impact on atmospheric models but falls outside of the present scope.

The latest evaluation (Evaluation No. 17, JPL Publication 10-6) is available for

Building a chemistry scheme.



Chemical Kinetics and Photochemical Data for Use in Atmospheric Studies

Evaluation Number 17

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The NASA JPL data evaluation team.

Each member has relevant experience (senior position) and is an accredited expert in their field.

Predominantly stratospheric focus.

Uncertainty in JPL recommendations

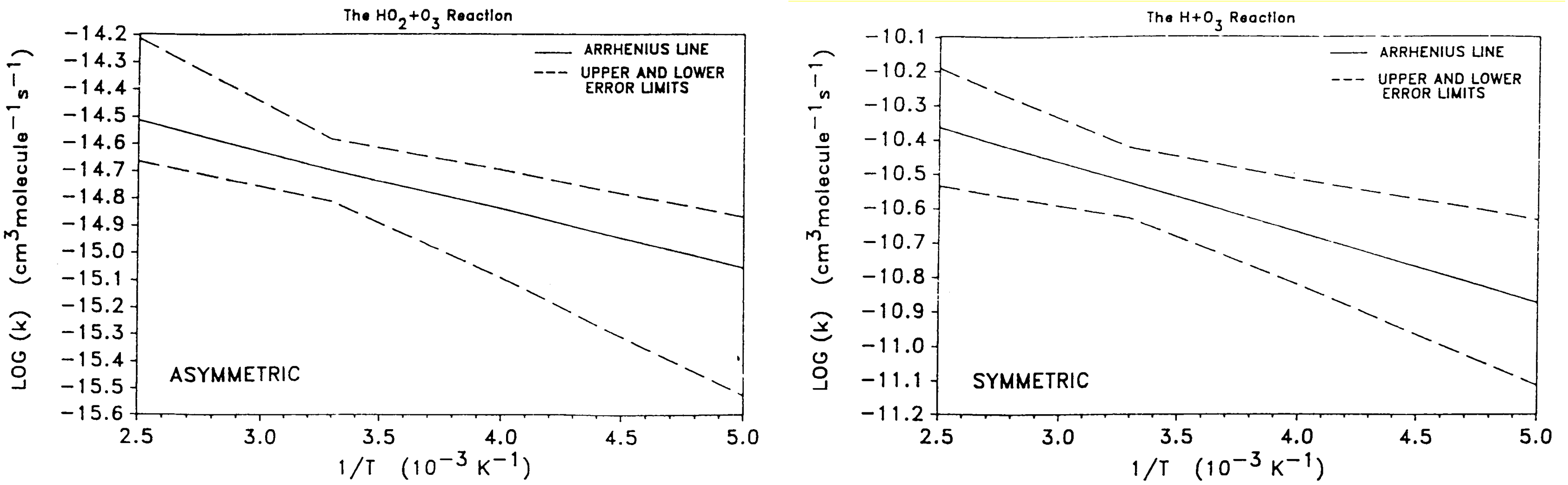


Figure 1. Symmetric and Asymmetric Error Limits

$$f(T)=f(298\ K)\exp\left|g\left(\frac{1}{T}-\frac{1}{298}\right)\right|$$

Table 1-1. Rate Constants for Second-Order Reactions

Reaction	A-Factor[a]	E/R	k(298 K)[a]	f(298 K)[b]	g	Notes
O_x Reactions						
$O + O_2 \xrightarrow{M} O_3$	(See Table 2)					
$O + O_3 \rightarrow O_2 + O_2$	8.0×10^{-12}	2060	8.0×10^{-15}	1.10	200	A1

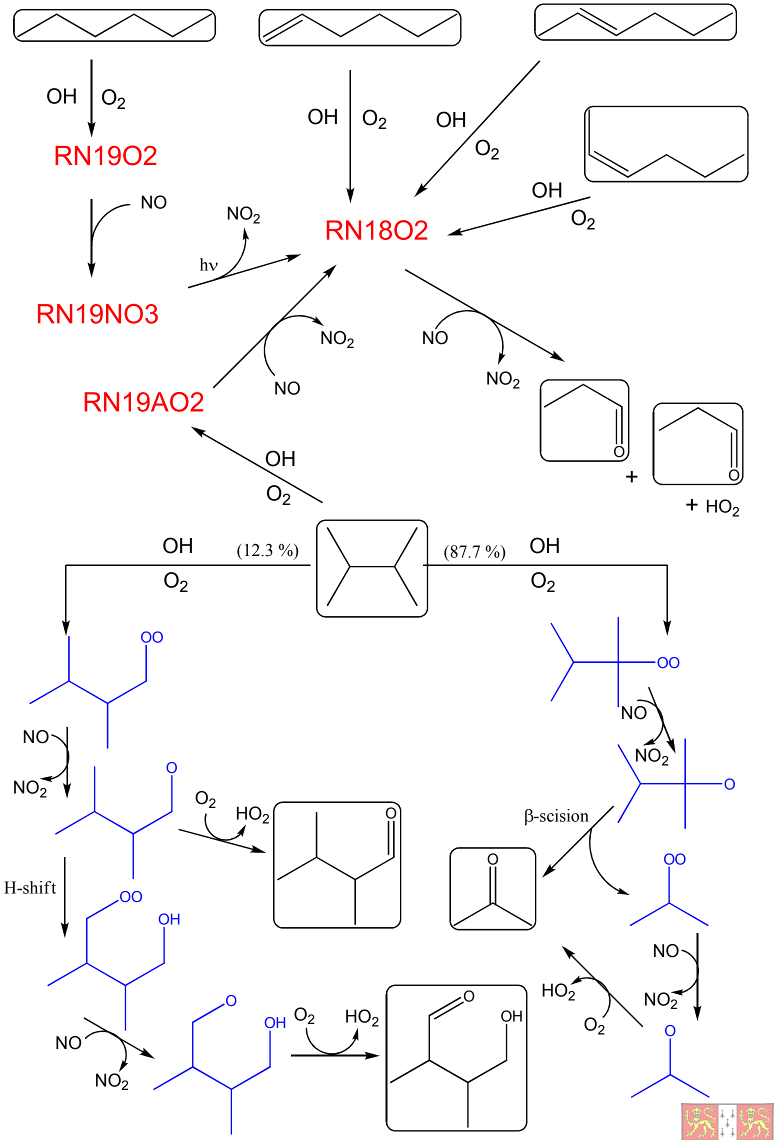
Building a chemistry scheme, cont.

3. Simplify things
   - Probably the hardest job!
   - Break the problem down, are there several different approaches you can make to simplifying things?
   - Can you split up the problem into different time scales, remove the fast steps (steady state approximation)
   - Are there reaction channels that only a small fraction of the reactants go through:

$A + C \rightarrow L$ (0.01 % loss of A) vs $A + B \rightarrow K$ (99.99% loss of A)

Building a chemistry scheme, cont.

3. Simplify things
    - Lumping (structural vs reactivity)
    - E.g. The Common Representative Intermediates approach (Jenkin et al.) looks at the number of reactive bonds a molecule has (C-H, C=C, C=O) and assigns an index to these. The maximum number of RO_2/HO_2 + NO interconversions a molecule can promote is related to this index.



Building a chemistry scheme, cont.

Have fun using UKCA!!