Chemistry mechanisms

结果的第一节先讲一下对流层臭氧的基本化学反应模式，用图的形式来呈现。

臭氧的生成有NO2光解，这一步非常迅速，所以臭氧生成率近似为NO2生成率。

点一下几种自由基的重要性。

最后讲明，在CMIP6系统中，哪些是已知的，哪些是未知的。

O3 + hv → O(1D) + O2(a1△g) λ<310 nm

Where the photolysis rate of O3 to give O(1D) is dependent on the photon flux in the troposphere, the absorption cross section, and the quantum yield for O(1D) production.

With the abundant water vapour in the troposphere, around 5% of the O(1D) atoms will react with H2O to give the hydroxyl radical.

O(1D) + H2O → 2OH, k = 2.2×10-10 molecule-1 cm3 s-1

In the unpolluted atmosphere, since O2 and M are so sufficient in the troposphere, the rate of H+O2+M will be very fast, with OH+CO therefore effectively converting OH to HO2.

OH + CO → CO2 + H

H + O2 + M → HO2 + M

HO2 + O3 → 2 O2 + OH

The above reactions rapidly establish a steady state between HO2 and OH, which is the reason to define odd hydrogen family: HOX = OH + HO2.

Loss of HOX:

HO2 + HO2 → H2O2 +O2

OH + NO2 + M → HNO3 + M

Methane oxidation

CH4 + OH → ·CH3 + H2O

·CH3 + O2 + M → CH3O2 + M

The loss of radicals in a low NO2 (unpolluted environment) is:

HO2 + CH3O2 → CH3OOH(aq) + O2

By steady-state assumption, [HO2] depends on the square root of the O3 photolysis frequency.

Saturated VOCs react by abstraction of a hydrogen atom to form an alkyl radical plus water, while reaction with unsaturated molecules is initiated by electrophilic addition of OH at the multiple bond. In unsaturated VOCs, multiple bonds imply higher electron densities, making those points more susceptible to attack by electrophiles.

Nitric oxide (NO) and nitrogen dioxide (NO2) inter-convert rapidly and are often considered collectively as NOX (NOX ≡ NO + NO2).

HO2 contributes to the loss of O3, however HO2 also oxidise NO to give O3.

HO2 + O3 → 2O2 + OH

HO2 + NO → OH + NO2, k = 8.1×10-12 molecule-1 cm3 s-1

Above is the critical reaction in forming tropospheric O3. 应该是对流层化学占比最大的反应

OH-initiated oxidation of CO leads to the net production of O3. In an analogue way, NO reacts with peroxy radicals.

CH4 + OH → ·CH3 + H2O

·CH3 + O2 + M → CH3O2 + M

CH3O2 + NO → CH3O + NO2

CH3O + O2 → HCHO + HO2

HO2 + NO → OH + NO2

Therefore, this series of reactions leads to the production of two molecules of NO2, and the subsequent photolysis of NO2 and recombination of O atom with O2 then leads to the production of 2 molecules of O3.

上述过程产生了formaldehyde，甲醛，甲醛acts as a positive feedback to accelerate the rate of hydrocarbon oxidation (and the concomitant production of tropospheric O3)。

HCHO + hv (λ<330 nm) → HCO + H

HCO + O2 → CO + HO2

H + O2 + M → HO2 + M

Net: HCHO + 2O2 + hv → CO + 2HO2

O3 production or destruction?

CO, CH4, and VOCs themselves will lead to O3 loss in low NOX environments, while in high NOX environments, they cause O3 production. 关键的平衡点是HO2的作用，因为HO2源自CO和VOCs，可以氧化NO，也可以破坏O3.

The balance point occurs when the rates of these two reactions become equal. Approximately, for a typical ozone concentration of ~40 ppb, and balance point occurs at [NO] ~ 10 ppt.

剑桥化学系的教材P53给出了一个表，讲述了对流层各种反应的占比。我们同时可以参考Daniel Jacob的哈佛教材P216。O3生成上，NO+HO2占据65%，NO+CH3O2占据22.5%。O3 loss上，O(1D) + H2O占据了56%，O3+HO2占据了31%。 Daniel的教材里估算，NO+HO2占据70% ，NO+CH3O2占据20%，O(1D) + H2O占据了40%, O3+HO2占据了40%. 这都是针对整个对流层来估算的。