*Supplement #6: Free Radical Mechanisms and the Ozone Layer*

*Chemistry 3514 Organic Chemistry I*

Most of you have heard popular news accounts concerning the near disappearance of the Earth’s ozone layer, a key stratospheric component that prevents terrestrially damaging uv light in the 250-300 nm range from reaching (and frying) the planet’s surface.

Because we have monitored ozone concentrations for only a short period (< 50 years), the layer’s disappearance may reflect a natural cycle of concentration variation. However, most atmosphere scientists think that the ozone layer’s loss (which accelerated sharply in the mid 20th century) was caused by our inadvertent introduction of refrigerant Freons (halogenated alkanes) into the atmosphere. As described below, the mechanism by which Freons evidently kill ozone is similar to the free radical pathway you’ve already encountered in turning alkanes into halogenated alkanes. (See Supplement 5)

MECHANISM OF NATURAL OZONE GENERATION AND CFC-INDUCED DEATH

Rowland and Molina (University of California, Irvine 1970)

***The natural ozone life cycle***

<250 nm uv light

**1) O2 2O *chain initiation***

O2 captures most, but not all, the of `bad’ uv

**2) O + O2 + M (can be N2 ) --🡪 O3 + M\* *chain propagation*** (2,3,2…)

M=a third body that bleeds

energy & prevents O3 split

250-300 nm light

**3) O3 O2 + O** part of cycle that absorbs

remaining `bad 250-300 nm light

**4) O + O 🡪O2  *chain termination***

**O + O3 🡪2O2** slow and `in balance’ with O3

creation

***The ozone killer reaction***

any uv light <350 nm

**a) F3C-Cl F3C + Cl *chain* *initiation***

(..= CFC=chlorinated fluorocarbon)

**b) Cl + O3 ClO + O2 *chain* *propagation***

Ozone directly and indirectly killed.

**c) ClO + O Cl +O2** Note that ClO intercepts and `kills’

**(b +c) O3 + O 🡪 2O­2** the critical O radical from O3

cleavage in **3** and O2 +O -->O3 in **2**

**The bad chemical news..**

**Reactions b,c are way more efficient than 2,3 =>100,000 O3 dead/1 CFC**

**PS: T**he peak of the CFC concentration has already reached the critical stratospheric height and

is evidently going down, thanks to the legislation first pushed by Molina and Rowland in the 1970’s, Back then, Congress still listened to sense and science rather than to Rush Limbaugh.