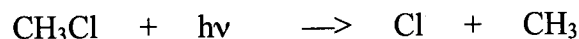


KEY

1. Use the mean *bond dissociation enthalpy* (a.k.a. bond energy – from the handout in class) for the bond broken in the reaction below to calculate the longest wavelength that has sufficient energy to “drive” it (i.e. the *threshold wavelength*, λ_{THRESH}).



2. More on the Chapman Cycle – photochemical considerations

a) Using the O_2 bond dissociation energy from the handout in class, calculate λ_{THRESH} for O_2 . Do most or all of the wavelengths absorbed by O_2 (in the UV) cause photo-dissociation?

b) O_2 absorbs strongly below 200nm, and somewhat weakly between 200-240nm (see handout from class). How would you expect J_1 , and in turn τ , to vary with altitude through the stratosphere? How would J_1 & τ in the troposphere compare to that in the stratosphere? This process is the primary source of O atoms (the sole Ox source in the stratosphere). So, among the three following regions (i) high in the stratosphere, ii) low in the stratosphere, iii) or in the troposphere, in which would you expect the mixing ratio of O to be the highest? In which would it be the lowest?

c) Some authors will add an additional step in the cycle: $\text{O} + \text{O} + \text{M} \rightarrow \text{O}_2 + \text{M}$, but this reaction is not significant for two reasons, one being that reactions that need an M are often slow because they require three things to collide (simultaneously) instead of just two. Why else might this reaction be slow – except for at very high altitudes?

d) How does the Chapman cycle allow us to rationalize an ozone layer (or “region”)? (see i and ii)

- i) Provide a conceptual rationale, on the basis of factors that affect the rates of the reactions that result in the net production of Ox and/or O_3 .
- ii) Provide a quantitative rationale, based on the equation below (which is derived in eth textbook and should be 100% consistent with your rationale in “i”). (Note Ox production rate constants are on top of the big fraction – and loss rate constants are on the bottom!)

$$X_{\text{O}_3}^{\text{alt}} \sim \frac{[\text{O}_3]}{[\text{O}_2]} = \left(\frac{J_1 k_2 [\text{M}]}{J_3 k_4} \right)^{1/2}$$

e) How does the amount of stratospheric ozone predicted by the Chapman mechanism compare to what’s observed? What are the specific differences?

3. “Differential” light penetration: Because of absorption of UV light by ozone (O_3) and oxygen (O_2), we separated UV light into three different wavelength regions (or “bins”) that penetrate to different altitudes in the atmosphere.

- i) Which wavelengths are available for photochemistry at only very high altitudes (above the stratosphere)?
- ii) Which wavelengths are absorbed by O_3 (and O_2 to some extent) and are filtered in the stratosphere – rendering them available high in the stratosphere, and only slightly in the lower stratosphere – but are absent in the troposphere?
- iii) Radiation beyond what wavelength penetrates to the troposphere/surface?

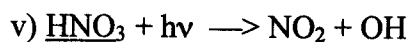
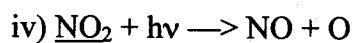
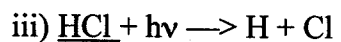
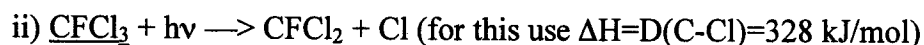
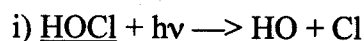
4. In this problem, we (a.k.a. *you*) will assess the photo-reactivity of each molecule listed as a reactant in the “photolysis” reactions below. (i-v). For each substance, examine the absorption spectra (displayed on the next page), use the ΔH_f values listed below to calculate ΔH_{rxn} , and in turn, λ_{THRESH} , and consider what altitudes the key wavelengths would penetrate to. Then, provide a brief assessment of each molecule’s overall photo-reactivity, either:

A) Unreactive except at very high altitudes,

B) Moderately photo-reactive in the stratosphere – not in the troposphere, or

C) Photo-reactive at all altitudes, even in the troposphere

(There may be a couple of borderline cases... I will elaborate in the key)



You'll need the following data - ΔH_f values (in kJ/mole) – for all reactions except “ii”.

H: 218.0; Cl: 121.3; HO: 39.0; NO: 90.3; NO₂: 33.1;
HOCl: -74.5; HCl: -92.3; O: 249.2; HNO₃: -134.3;

1. BOND BROKEN IS \rightarrow C-Cl $D = 328 \text{ kJ/mol}$

$$E_{\text{BOND}} = \frac{328 \text{ kJ}}{\text{mol}} \cdot \frac{1000 \text{ J}}{\text{kJ}} \cdot \frac{1 \text{ mol}}{6.02 \times 10^{23} \text{ molec}} = 5.5 \times 10^{-19} \text{ J/molec}$$

$$\lambda_{\text{THRESH}} = \frac{hc}{E_{\text{BOND}}} = \frac{6.63 \times 10^{-34} \text{ J}\cdot\text{sec} \cdot 3.0 \times 10^8 \text{ m/s}}{5.5 \times 10^{-19} \text{ J}} = 3.62 \times 10^{-7} \text{ m} = \underline{\underline{362 \text{ nm}}}$$

2^o) $D(\text{O}_2) = 495 \text{ kJ/mol} \rightarrow E_{\text{BOND}} = 8.22 \times 10^{-19} \text{ J}$

$$\lambda_{\text{THRESH}} = \frac{hc}{E_{\text{BOND}}} = 2.42 \times 10^{-7} \text{ m} = \underline{\underline{242 \text{ nm}}}$$

5) THE 200-240 PART IS IN THE "MIDDLE BIN" WHICH IS FILTERED (TOP-TO-BOTTOM) IN THE STRATOSPHERE.

\rightarrow THIS I_0 WILL BE HIGHEST IN UPPER STRATOSPHERE, LOW IN LOW STRATOSPHERE, AND ≈ 0 IN TROPOSPHERE. $\rightarrow I_{\text{O}_2}$ WILL BE THE INVERSE (QUITE LITERALLY...) $\rightarrow I$ ^(RELATIVELY) LARGE IN UPPER STRAT, LOW IN LOW STRAT, $\sim \infty$ IN TROP (RESPIRATION NOT WITH STANDING)

\rightarrow THE ONLY PLACE WHERE THERE IS A LARGE X_0 IS ABOVE THE STRATOSPHERE $\rightarrow > 90\%$ OF OX IS O_3 AT 50 KM $\rightarrow 75\%$ OF OX IS O AT 70 KM (SEE LAST HW KEY...)

c) THIS REACTION IS SLOW BECAUSE CO_3 IS SO SMALL \uparrow

d) i) THE ONLY OX PRODUCTION REACTION IS $\rightarrow \text{O}_2 + h\nu \rightarrow 2\text{O}$ AND THERE IS ONLY $\lambda < 242 \text{ nm}$ AVAILABLE ABOVE A CERTAIN ALTITUDE (STRATOSPHERE) \rightarrow SO NO OX PRODUCTION IN TROP. VERT HIGH (ABOVE STRAT) THERE IS NOT ENOUGH "M" TO MAKE CHAPMAN #2 GO ($\text{O}_2 + \text{M} \rightarrow \text{O}_3 + \text{M}$), THUS, O_3 PEAKS IN THE MIDDLE \rightarrow WHERE THERE'S A BALANCE BETWEEN

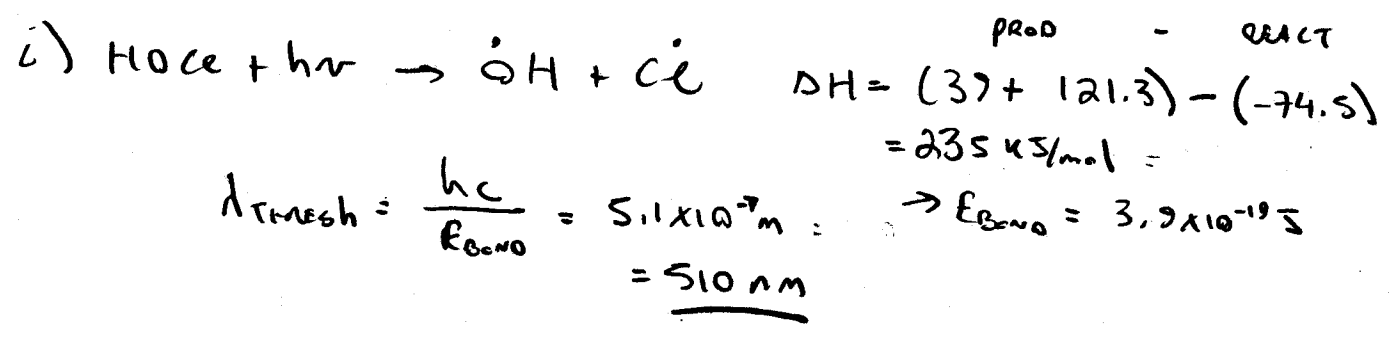
2. a) ii) NOTE HOW IN THE NUMERATOR - BOTH FACTORS THAT LEAD TO O₃ (IN "i") ARE PRESENT. $\text{S}_1 \rightarrow \text{O}_3$ PRODUCTION

$\text{K}_2(\text{M}) \rightarrow \text{O}_3$ PRODUCTION } O₃ WILL PEAK WHEN BOTH ARE SIGNIFICANT.

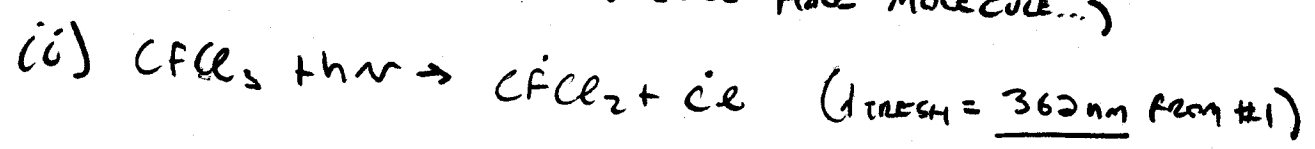
e) IT PREDICTS 2X TOO MUCH - AND A PEAK THAT IS TOO HIGH!

3. i) $\lambda < 200 \text{ nm}$ ii) $200 \text{ nm} < \lambda < 300 \text{ nm}$ iii) $\lambda > 300 \text{ nm}$

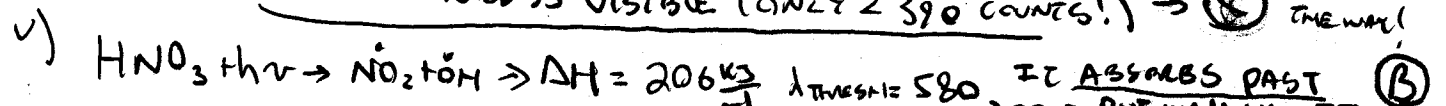
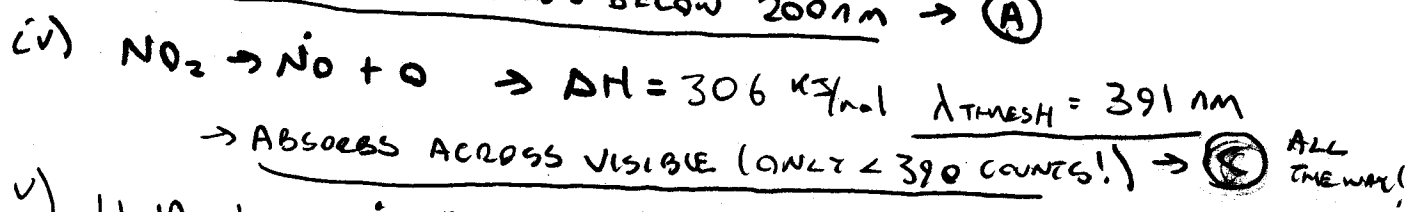
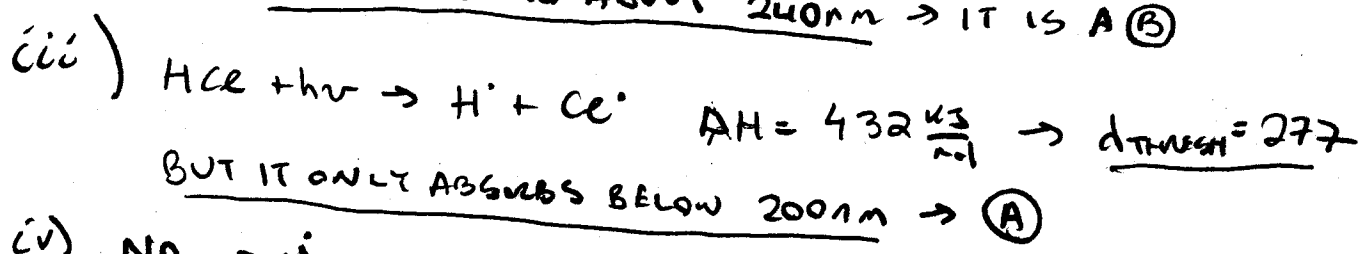
4.) (REALLY #4 - NOT #3)



IT ABSORBS PRETTY STRANGELY OUT PAST 300 nm \rightarrow IT IS ALMOST A C - IT IS VERY PHOTO-REACTIVE IN STRATOSPHERE (STAT TUNED - THIS IS A KEY OZONE-HAVE MOLECULE...)



IT ABSORBS OUT TO ABOUT 240 nm \rightarrow IT IS A B



THE BORDERLINE CASES...

HOCl - IT IS NOT CLEAR (PERHAPS)

AS TO HOW EXTENDED THAT ABSORPTION PAST 300 IS -

AND HOW STRONG IT IS. THE ABSORPTION PAST 300 IS

SIGNIFICANT - BUT THERE IS SOME PRESENT IN THE

STRATOSPHERE, BUT THERE IS SOME PRESENT IN THE STRATOSPHERE -

SO → SPECTRUM SAYS "C" (THERE PROBABLY IS SOME TROPOSPHERIC
PHOTOCHEM...)

→ DATA ON ACTUAL ABUNDANCE SAYS "B"

(IT IS ~~NOT~~ MORE PHOTO-REACTIVE THAN HNO_3)

HNO_3 < THE ABSORPTION SPECTRUM SEEMS TO EXTEND WELL

BEYOND 300NM → BUT THOSE ABSORPTION CROSS-

SECTIONS ARE VERY SMALL. THERE IS NO TROPOSPHERIC

PHOTOCHEM TO ANY GREAT EXTENT → THIS

IS MOST DEFINITELY A B