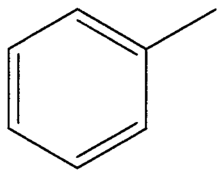
Homework #1: Chemistry 310S 2011; Due February 17, 2011-02-07

Your work is to be yours and your alone! Provide all work to be marked directly on the sheet ~ please assure your work is easy to decipher (be neat). No late work will be accepted.

1. Please calculate the ratio of OH-addition to H-abstraction for the following species present in the atmosphere. Show all calculations and normalize to 1 being the slower reaction (20 marks) → 4 marks each

a)



·OH Addition

$\log k_{add} = -11.71 - (1.34)(-0.31) = -11.3$ (1.5)

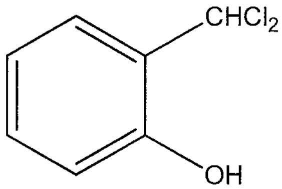
$k_{add} = 5.01 \times 10^{-12}$

H Abstraction

$k_{prim} = (1.36 \times 10^{-13})(1.0) = 1.36 \times 10^{-13}$ (1.5)

Ratio $= \frac{5.01 \times 10^{-12}}{1.36 \times 10^{-13}} = 36.8$ (1)

b)



·OH Addition

$\log k_{add} = -11.71 - (1.34)(-0.58) = -10.93$

$k_{add} = 1.17 \times 10^{-11}$

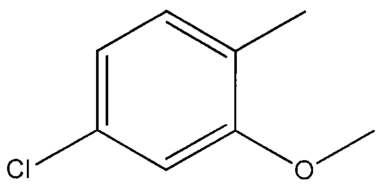
H Abstraction

$k_{ab} = (1.94 \times 10^{-12})(1)(0.38)(0.38) = 2.80 \times 10^{-13}$

Ratio $= \frac{1.17 \times 10^{-11}}{2.80 \times 10^{-13}} = 41.79$

*estimate $CHCl_2$ using values for CH_2Cl and CH_3 (or other)

c)



·OH Addition

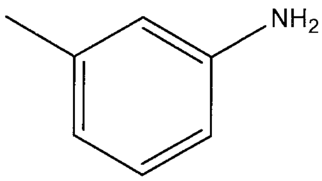
$\log k_{add} = -11.71 - (1.34)(-0.73) = -10.7 \rightarrow k_{add} = 1.85 \times 10^{-11}$

H Abstraction

$k_{ab} = (1.36 \times 10^{-13})(1 + 8.4) = 1.28 \times 10^{-12}$

Ratio $= \frac{1.85 \times 10^{-11}}{1.28 \times 10^{-12}} = 14.49$

d)



·OH Addition

$\log k_{add} = -11.71 - (1.34)(-1.61) = -9.55$

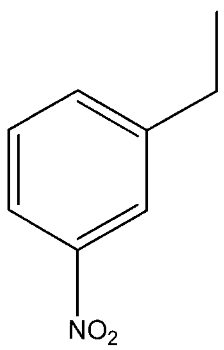
$k_{add} = 2.8 \times 10^{-10}$

H Abstraction

$k_{ab} = (1.36 \times 10^{-13})(1) = 1.36 \times 10^{-13}$

Ratio $= \frac{2.8 \times 10^{-10}}{1.36 \times 10^{-13}} = 2058.8$

e)



·OH Addition

$\log k_{add} = -11.71 - (1.34)(0.51) = -12.39$

$k_{add} = 4.04 \times 10^{-13}$

H Abstraction

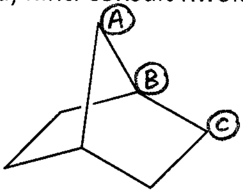
$k_{ab} = (1.36 \times 10^{-13})(1.23) + (9.34 \times 10^{-13})(1)(1) = 1.10 \times 10^{-12}$

Ratio $= \frac{1.07 \times 10^{-12}}{4.04 \times 10^{-13}} = 2.65$

*estimate value using $C(CH_3)_3$ and CH_3

2. Please calculate atmospheric lifetimes of the following, using [•OH]=10^6 molec/cm^3 (15 marks) → 3 marks each

a) hint: consult Kwok and Atkinson for ring strain



$(A) = (1) k_{sec} F(\rightarrow CH) F(\rightarrow CH) F_5 F_5 = (1)(9.34\times10^{-13})(1.23)^2(0.64)^2 = 5.79\times10^{-13}$

$(B) = (2) k_{tert} [F(-CH_2-)]^3 [F_5]^2 F_6 = (2)(1.94\times10^{-12})(1.23)^3(0.64)^2(1) = 2.96\times10^{-12}$

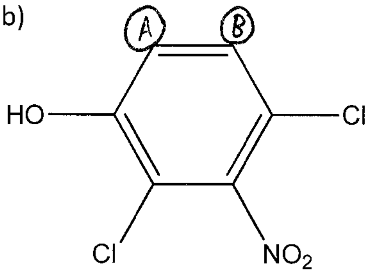
$(C) = (4) k_{sec} F(\rightarrow CH) F(-CH_2-) F_5 F_6 = (4)(9.34\times10^{-13})(1.23)(1.23)(0.64)(1) = 3.62\times10^{-12}$

(2)

$k_{Tot} = \Sigma ABC = 7.16\times10^{-12}$ $cm^3/molec\cdot s$

$\tau = 1/(7.16\times10^{-12}\ cm^3/molec\cdot s)(10^6\ molec/cm^3) = 139665\ s = 1.6\ d.$ (1)

b)



$(A) = (-0.92) + 0.37 + 0.79 + 0.37 = 0.61$

$(B) = (-0.38) + 0.11 + 0.71 + 0.11 = 0.55$

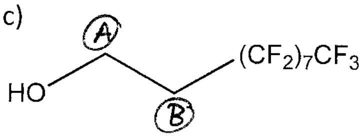
$\log k_{add} = -11.71 - 1.34(0.55)$

$= -12.45$

$k_{add} = 3.57\times10^{-13}$

$\tau = 1/(3.57\times10^{-13})(10^6) = 2801120\ s = 32.4\ d$

c)



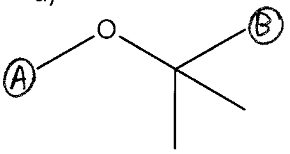
$(A) = (1) k_{sec} F(-OH) F(-CH_2-) = (1)(9.34\times10^{-13})(3.5)(1.23) = 4.02\times10^{-12}$

$(B) = (1) k_{sec} F(-CH_2-) F(-CF_2-) = (1)(9.34\times10^{-13})(1.23)(0.018) = 2.07\times10^{-14}$

$k_{Tot} = \Sigma AB = 4.04\times10^{-12}$

$\tau = 1/(4.04\times10^{-12})(10^6) = 247525\ s = 2.9\ d$

d)



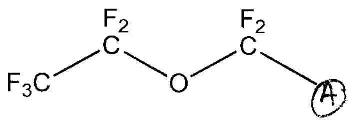
$(A) = (1) k_{prim} F(-O-) = (1)(1.36\times10^{-13})(8.4) = 1.14\times10^{-12}$

$(B) = (3) k_{prim} F(\rightarrow CH) = (3)(1.36\times10^{-13})(1.23) = 5.02\times10^{-13}$

$k_{Tot} = \Sigma AB = 1.64\times10^{-12}$

$\tau = 1/(1.64\times10^{-12})(10^6) = 609756\ s = 7\ d$

e)

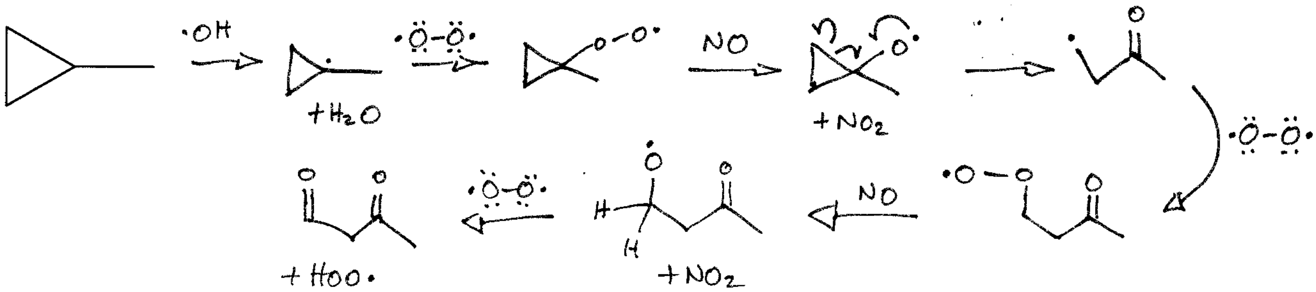


$(A) = (1) k_{prim} F(-CF_2-) = (1)(1.36\times10^{-13})(0.018) = 2.45\times10^{-15}$

$\tau = 1/(2.45\times10^{-15})(10^6) = 4.08\times10^8\ s = 13\ yr.$

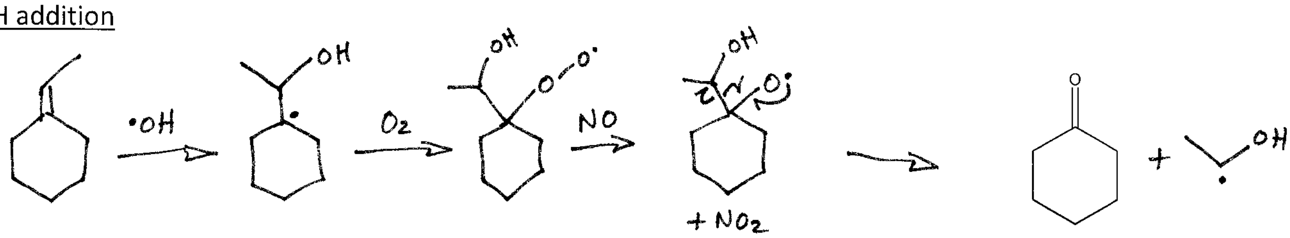
3. Consider the following atmospheric contaminants.

a) Show the most likely route of atmospheric oxidation to the first stable product (3 marks)

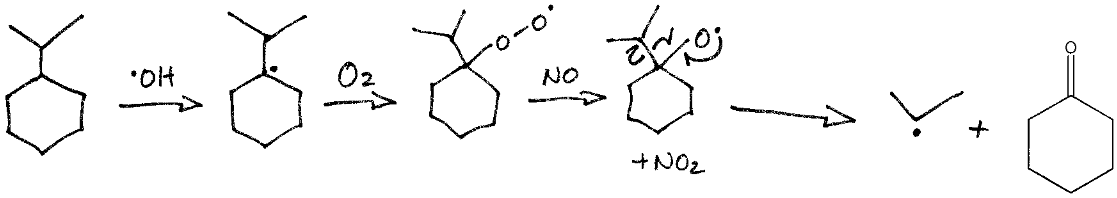


b) Please postulate two atmospheric contaminants that would degrade, via atmospheric oxidation, to cyclohexanone. One contaminant should react via OH addition, the other by H abstraction. Show both mechanisms (6 marks)

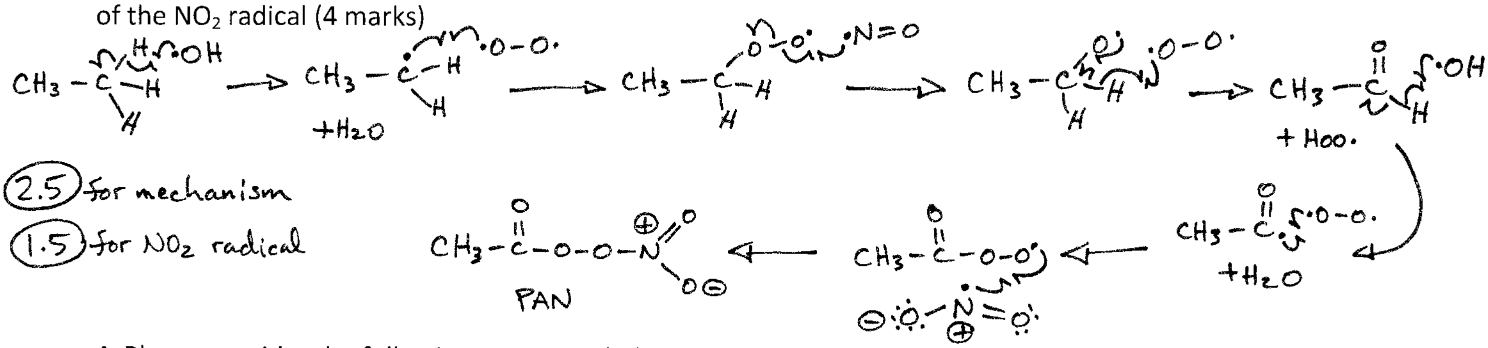
(3) OH addition



(3) H abstraction



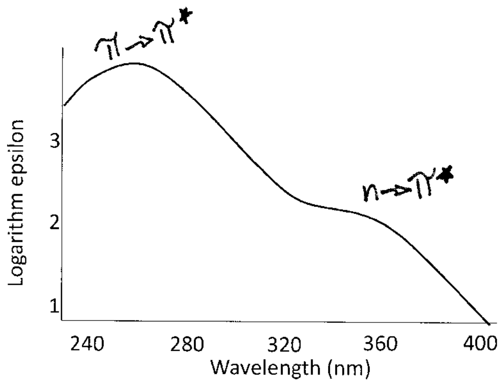
c) Show a detailed curly-arrow mechanism of PAN formation from ethane. Please include the structure of the NO_2 radical (4 marks)

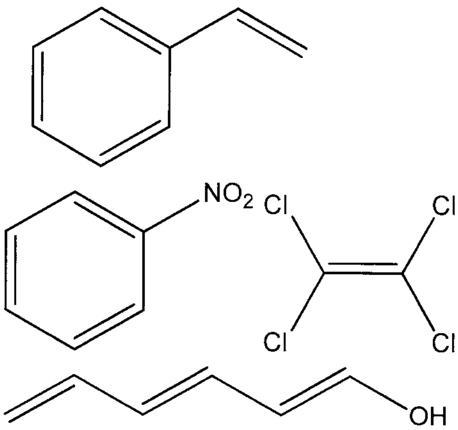


(2.5) for mechanism

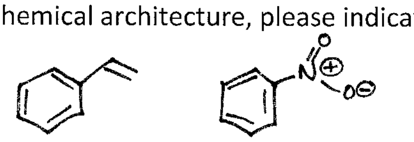
(1.5) for NO2 radical

4. Please consider the following spectrum, belonging to one of the chemicals shown (7 marks)



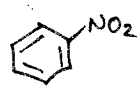


(3) a) Based on their chemical architecture, please indicate which structure(s) you expect to absorb actinic radiation? Why?



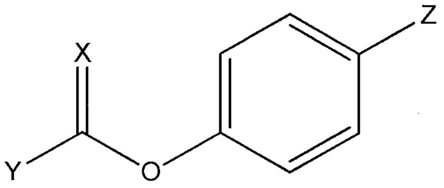
≥4 conjugated double bonds ∴ absorb above 290nm

(2) b) Which one of the four structures best matches the UV-visible spectrum given?



(2) c) Please label the two absorbance bands with the appropriate electronic transitions.

5. Please build a molecule that would undergo the fastest hydrolysis at pH 8.5, explaining your choices of x, y and z (6 marks)



x = CH_2, O, S

y = CH_3 CH_2, $C(CH_3)_3$, CH_2OH

z = NO_2, NH_2, F, H, COOH

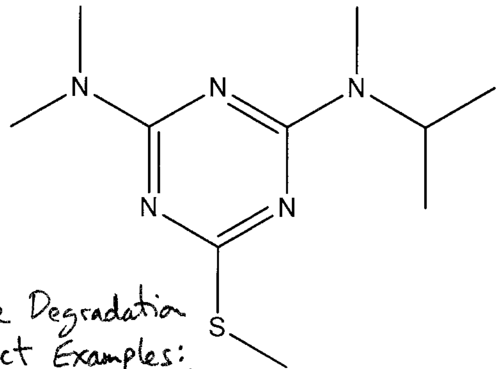
(2) X = O → most electronegative ∴ best polarizes C=X and makes C more electrophilic

(2) Y = CH_2OH → OH electronegative ∴ makes C more electrophilic

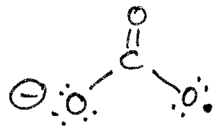
(2) Z = NO_2 → most electron withdrawing ∴ it helps to stabilize negative charge in Leaving group

*part marks for Y = CH_2CH_3 because it is less sterically hindered than $C(CH_3)_3$

6. Please indicate 4 'degradation products' you would expect to observe in sunlit Lake Ontario from the triazine herbicide shown below. Also provide the lewis structure of the carbonate radical (8 marks)

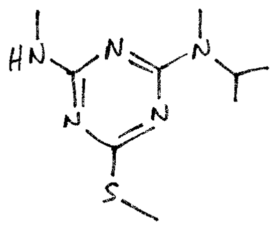


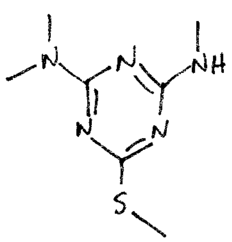
carbonate radical (2)



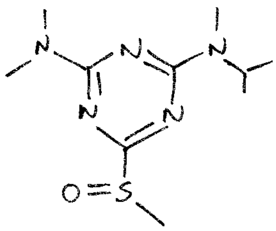
Some Degradation Product Examples: (6) (4 × 1.5 marks)

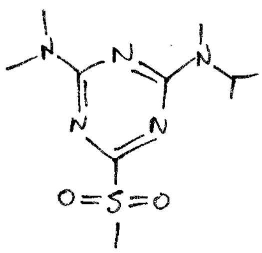
Dealkylation





S-oxidation





Ring oxidation