

70 PTS OVERALL

$\bar{x} \pm s = 51 \pm 7$

All 3 PS's
 $\bar{x} \pm s = 135 \pm 13$

EnvChem
PS 3 Key
p. 1

1. 12 pts total

$$(a) 130 \times 10^{12} \text{ gC} \left(\frac{\text{mole}}{12.01 \text{ gC}} \right) \left(\frac{\text{mole C}_{10}\text{H}_{16}}{10 \text{ mole C}} \right) \left(\frac{6.022 \times 10^{23} \text{ molecule}}{\text{mole}} \right)$$

$$= 6.5_{18} \times 10^{35} \text{ molecule C}_{10}\text{H}_{16} \quad (-2) \text{ Wrong N}$$

$$V = \frac{4}{3} \pi \left[(r_{\text{earth} + \text{boundary layer}})^3 - r_{\text{earth}}^3 \right] \quad (-3) \text{ wrong formula for } V$$

$$= \frac{4}{3} \pi \left[6381^3 - 6380^3 \right] \text{ km}^3 \left(\frac{10^{15} \text{ cm}^3}{\text{km}^3} \right)$$

$$= \frac{4}{3} \pi \left[2.598_{16} \times 10^{11} - 2.596_{94} \times 10^{11} \right] \times 10^{15} \text{ cm}^3$$

$$= \frac{4}{3} \pi \left[0.001_{22} \right] \times 10^{26} \text{ cm}^3 \quad (\text{down to 1 sig fig!})$$

$$V = 5.11 \times 10^{23} \text{ cm}^3 \quad (-2) \text{ unit error}$$

differs from approximate V formula $4\pi r^2 \Delta r$ only in the 3rd figure, which is not significant!

$$\therefore [C_5H_{10}] = \frac{6.5_{18} \times 10^{35} \text{ molecule}}{5.11 \times 10^{23} \text{ cm}^3} = \boxed{1.28 \times 10^{12} \text{ molecule cm}^{-3}}$$

$$(b) \frac{n}{V} = \frac{P}{RT} = \left(\frac{1.000 \text{ atm}}{288 \text{ K}} \right) \left(\frac{\text{mole K}}{0.08206 \text{ L atm}} \right) \left(\frac{6.022 \times 10^{23} \text{ molecule}}{\text{mole}} \right) \left(\frac{\text{L}}{10^3 \text{ cm}^3} \right)$$

$$\frac{n}{V} = [\text{air}] = \boxed{2.54_8 \times 10^{19} \text{ molecule cm}^{-3}} \quad (-2) \text{ wrong order of magnitude}$$

$$(c) \frac{[C_5H_{10}]}{[\text{air}]} \times 10^9 = \frac{1.28 \times 10^{12}}{2.54_8 \times 10^{19}} \times 10^9 = \boxed{50 \text{ ppb}}$$

(-1) sig fig error
(-1) wrong units

(d) (part of your Tropospheric Chem handout)

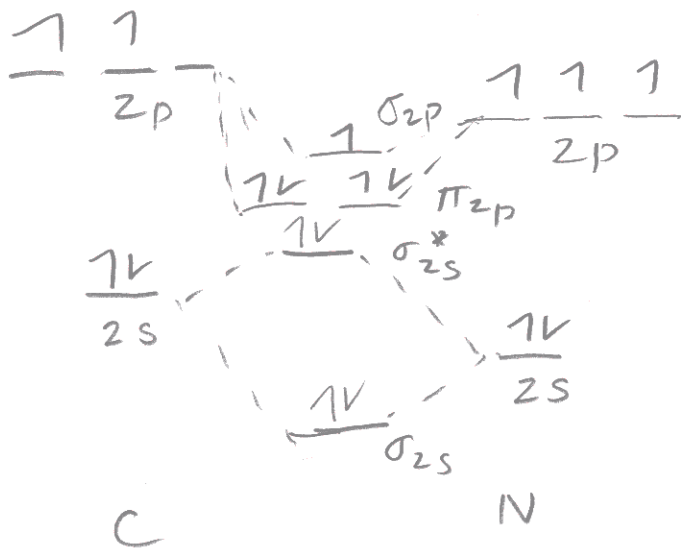
For both α - and β -pinene, the lifetime is shortest with respect to reaction with $\boxed{\text{NO}_3}$. $[\text{NO}_3]$ should therefore have the biggest role in controlling [pinene].

Table 2. Calculated Tropospheric Lifetimes for Selected Biogenic NMOCs with Respect to Gas-Phase Reaction with OH Radicals, NO_3 Radicals, and O_3

biogenic VOC	lifetime ^a for reaction with		
	OH	NO_3	O_3
isoprene	1.4 h	1.6 h	1.3 days
camphene	2.6 h	1.7 h	18 days
3-carene	1.6 h	7 min	11 h
limonene	50 min	5 min	2.0 h
myrcene	40 min	6 min	50 min
β -phellandrene	50 min	8 min	8 h
α -pinene	2.6 h	11 min	4.6 h
β -pinene	1.8 h	25 min	1.1 day
sabinene	1.2 h	7 min	4.6 h
β -caryophyllene	40 min	4 min	2 min
longifolene	3.0 h	1.6 h	> 33 days
methanol	12 days	~1 yr	> 4.5 yr
2-methyl-3-buten-2-ol	2.1 h	8 days	1.7 day
<i>cis</i> -3-hexen-1-ol	1.3 h	4.1 h	6 h
linalool	50 min	6 min	55 min
1,8-cineole	1.0 days	1.5 yr	> 4.5 yr
<i>cis</i> -3-hexenyl acetate	1.8 h	4.5 h	7 h
6-methyl-5-hepten-2-one	55 min	9 min	1.0 h

^a Time for decay of compound to 1/e of its initial concentration, assuming concentrations (molecule cm^{-3}) of OH, 12 h daytime average of 2.0×10^6 , NO_3 , 12 h nighttime average of 5×10^6 , and O_3 , 24 h average of 7×10^{11} .

MO Theory:



The HOMO, which holds the unpaired e^- , is sigma, not pi in character (which is the case for NO and O_2).

Specifically, the HOMO looks something like

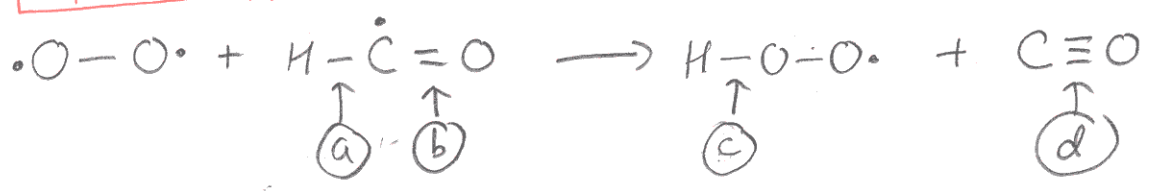


Both models indicate that bonding $H\cdot$ to $\cdot CN$ does not require paying the cost of localizing an e^- .

Also accepted for full credit: Sharing an additional e^- with H atom increases the bond order of CN

- (-3) faulty MO energy-level diagram
- (-2) dubious interpretation of MO diagram.

3. 8 pts total



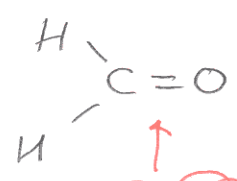
(a) Approximate with H-C bond in

(88.144 kcal mol⁻¹)

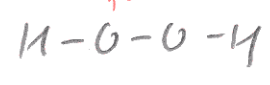
(b) 745 kJ/mol

(c) Approximate with H-O bond in
(87.8 kcal mol⁻¹)

(d) 1046 kJ/mol



~~(3)~~ (3)
neglected mis BDE



-4 no explanation of what BDE's were used

$$\Delta_r H^\circ = \left[88.144 + \frac{745}{4.184} - 87.8 - \frac{1046}{4.184} \right] \text{ kcal mol}^{-1}$$

$$\Delta_r H^\circ = -72 \text{ kcal mol}^{-1}$$

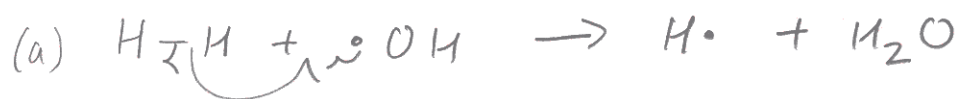
(quite exothermic, so it is at least plausible that the E_a is low)

-2 wrong sign

-2 math error

4. Baird and Conn 5.4

8 pts total



-2 Had O₂ attack
H₂



(b) Catalyst: HO· (-1) if wrong or missing

Intermediates: H·, HO· (-1) if wrong or missing

(c) H₂ oxidation can contribute to O₃ formation because the ·NO₂ product is readily photolyzed in the visible to give atomic O, which is (both in the stratosphere and troposphere) an O₃ precursor.

-2 nothing about NO₂ photolysis
-1 vague about NO₂ photolysis

5. 16 pts total

$$A = e^2 \frac{kT}{h} e^{\Delta S^\ddagger/R}$$

$$e^{\Delta S^\ddagger/R} = \frac{Ah}{e^2 kT} \Rightarrow \Delta S^\ddagger = R \ln \left(\frac{Ah}{e^2 kT} \right)$$

For C=C + $\cdot\text{OH}$, at 250. K

$$\Delta S^\ddagger = \left(\frac{1.987 \text{ cal}}{\text{mol K}} \right) \ln \left[\frac{6.55 \times 10^{-12} \text{ cm}^3}{\text{molecule s}} \left(\frac{1}{e^2} \right) \left(\frac{6.626 \times 10^{-34} \text{ J s particle}^{-1}}{1.381 \times 10^{-23} \text{ J K}^{-1} \text{ particle}^{-1}} \right) \right. \\ \left. \times \left(\frac{1}{250. \text{ K}} \right) \left(\frac{\text{L}}{10^3 \text{ cm}^3} \right) \left(\frac{6.022 \times 10^{23} \text{ molecule}}{\text{mol}} \right) \right]$$

$$\Delta S^\ddagger = -18.3 \text{ cal mol}^{-1} \text{ K}^{-1}$$

$$E_a = RB = \left(\frac{1.987 \times 10^{-3} \text{ kcal}}{\text{mol K}} \right) (-467 \text{ K}) = -0.928 \text{ kcal mol}^{-1}$$

$$k' = k [\text{OH}] = A e^{-B/T} [\text{OH}]$$

$$= (6.55 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}) e^{+467 \text{ K}/250. \text{ K}} \\ \times (2.0 \times 10^6 \text{ molecule cm}^{-3})$$

$$k' = 8.4_8 \times 10^{-5} \text{ s}^{-1}$$

$$\text{so } \tau'_{\text{OH}} = \frac{1}{k'} = \left(\frac{\text{s}}{8.4_8 \times 10^{-5}} \right) \left(\frac{\text{hr}}{3600 \text{ s}} \right) = 3.2_7 \text{ hr}$$

Environmental Chemistry
Problem Set 3
Problem 5

Alkene is 1-butene

R	1.987 cal mol ⁻¹ K ⁻¹
R	1.99E-03 kcal mol ⁻¹ K ⁻¹
h	6.63E-34 J s particle ⁻¹
k	1.38E-23 J K ⁻¹ particle ⁻¹
Na	6.02E+23 molecule mol ⁻¹
T	2.50E+02 K

(-1) per wrong ΔS^\ddagger , E_a , τ (up to -6)
 (-1) unit error
 (-1) multiple sig fig errors
 (-3) wrong T

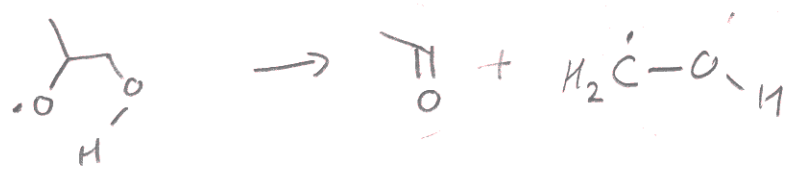
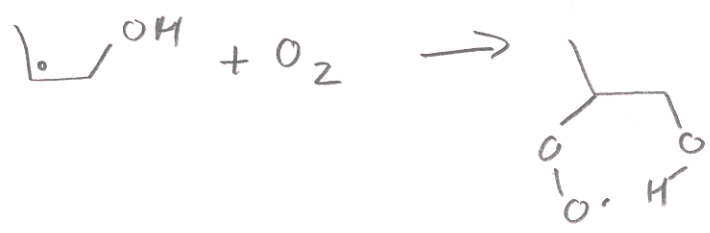
Oxidant	A/cm ³ molecule ⁻¹ s ⁻¹	B/K	Concentration (molecule cm ⁻³)	ΔS (cal mol ⁻¹ K ⁻¹)	E_a (kcal/mol)	Pseudo 1st Order Rate			
						Constant (s ⁻¹)	Lifetime (s)	Lifetime (hr)	Lifetime (days)
OH	6.55E-12	-467	2.0E+06	-18.3	-0.928	8.48E-05	1.18E+04	3.27	0.136
NO ₃	3.14E-13	938	5E+08	-24.3	1.86	3.68E-06	2.71E+05	75.4	3.14
O ₃	3.36E-15	1744	7E+11	-33.3	3.47	2.20E-06	4.55E+05	126	5.27

(b) For OH, the B parameter is negative. This means that the OH reaction constant actually gets smaller with increased temperature! (This is because increased temperature favors the dissociation of the pre-reactive complex, pushing the OH reaction back to the original reactants.) Thus, the lifetime with respect to OH will increase. For NO₃ and O₃, the B parameter is positive. This means that the rate constants get larger with increased temperature, leading to decreased lifetimes with respect to NO₃ and O₃.

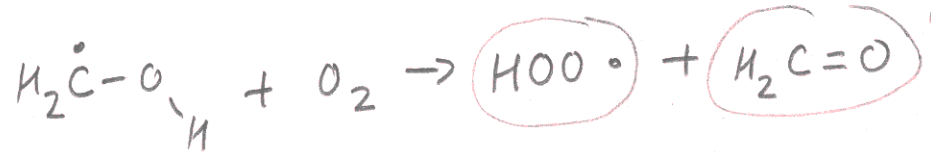
(-2) no recognition that OH has the opposite T dependence
 (-4) no answer to part (b)

6. Baird and Cann Problem 5.9 (16 pts total)

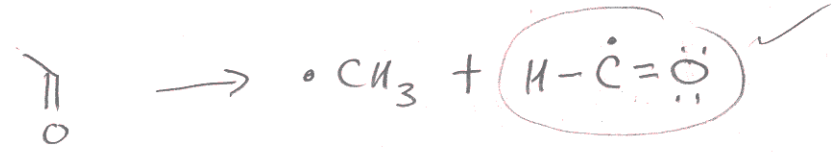
PS3
p.9



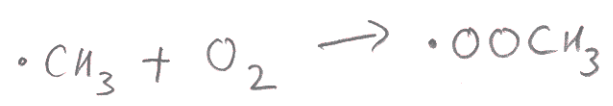
-2 error in one species



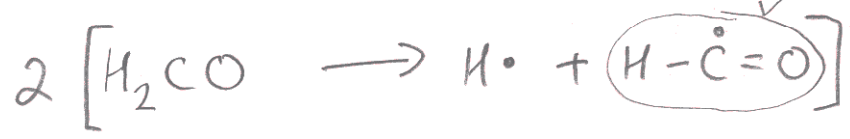
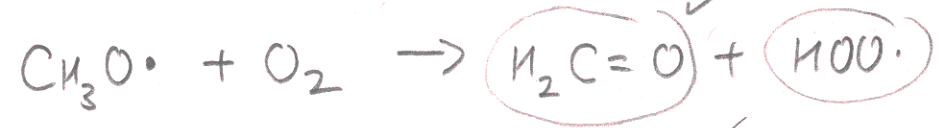
-4 errors in representing formyl



(H-C=O)



-6 no overall rxn



PS 3
p.10

