KEY

CHEM 304
SPRING ~~2006~~ 2010
HW/Learning Goals #6: Tropospheric Chemistry: Photochemical Smog, Acid Rain, and Aerosol Formation

1. Oxidation of atmospheric CH_4:
   a) Write a series of 5 reactions showing how CH_4 oxidation leads to tropospheric O_3 production.
   b) Add two reactions to those in "a", thereby completing a series of reactions that depicts the oxidation of CH_4 to CH_2O (in which O_3 is also produced, and NO, OH can be regarded as catalysts). Also write the net reaction.
   c) Write three more reactions that show how the CH_2O is ultimately converted to CO_2.

2. a) Following the "Generalized Hydrocarbon Oxidation Mechanism", write a series of reactions that shows how CH_3CH_3 (*ethane*, which is RCH_3 w/ R=CH_3) is oxidized to CH_3CHO (*acetaldehyde*), and also write the net reaction.
   b) Write the additional reactions that show how "PAN" (*peroxyacetyl nitrate*, or $CH_3CO\text{-}OO\text{-}NO_2$) is formed from CH_3CHO under "Hi NO_x" conditions.
   c) In context of this reaction scheme, what are the primary pollutants, what are the secondary pollutants?

3. "Thermal inversions" enhance the formation of O_3 and other component of photochemical smog. What is a thermal inversion, and what effect does it have on smog chemistry?

4. NOx contribution to acid rain and aerosol formation:
   a) What is the acidic species in (enhanced) acid precipitation that originates from NOx?
   b) Write a two-step reaction sequence that shows how NO is oxidized to this acid.
   c) What subsequent reaction results in the formation of solid *ammonium nitrate*?

5. SOx contribution to acid rain and aerosol formation:
   a) What is the acidic species in (enhanced) acid rain that originates from emission of SO_2?
   b) Write a series of 3 gas-phase reactions that shows how SO_2 is oxidized to this acid.
   c) What subsequent reaction results in the formation of solid *ammonium sulphate*?
   d) Write a reaction by which SO_2 is oxidized in the aqueous-phase.

6. What are the main (natural and human) sources of NO_x and SO_2 that "feed" the cycles in 4 & 5.

7. The natural acidity of rainwater comes primary from CO_2. Calculate the pH of rainwater that results from the current mixing ratio of CO_2 (370 ppm). Is this significantly more acidic than what results from "pre-industrial levels of CO_2 (280ppm) as we calculated in class?

1. a) 1) $CH_4 + \dot{O}H \rightarrow \dot{C}H_3 + H_2O$

2) $\dot{C}H_3 + O_2 \xrightarrow{M} CH_3OO^{\cdot}$

3) $CH_3OO^{\cdot} + \dot{N}O \rightarrow \dot{N}O_2 + CH_3O^{\cdot}$

(4) $NO_2 + h\nu \rightarrow NO + O$) x2

(5) $O_2 + O \xrightarrow{M} O_3$) x2

b) 6) $CH_3O^{\cdot} + O_2 \rightarrow HO_2^{\cdot} + CH_2O$

7) $HO_2^{\cdot} + \dot{N}O \rightarrow \dot{N}O_2 + \dot{O}H$

NET $CH_4 + 4O_2 \rightarrow CH_2O + 2O_3 + H_2O$

c) $CH_2O + h\nu \rightarrow H\dot{C}O + H^{\cdot}$ ($\xrightarrow{O_2}$ MORE HO_2)

$H\dot{C}O + O_2 \rightarrow HO_2^{\cdot} + CO$

$CO + \dot{O}H \rightarrow CO_2 + H$ ($\xrightarrow{O_2}$ MORE HO_2)

2) a) (JUST LIKE 1a w/ CH_3CH_3)

$CH_3CH_3 + \dot{O}H \rightarrow CH_3\dot{C}H_2 + H_2O$

$CH_3\dot{C}H_2 + O_2 \xrightarrow{M} CH_3CH_2OO^{\cdot}$

$CH_3CH_2O\dot{O} + \dot{N}O \rightarrow \dot{N}O_2 + CH_3CH_2O^{\cdot}$

($NO_2 + h\nu \rightarrow NO + O$) x2

($O + O_2 \xrightarrow{M} O_3$) x2 ↓ AS ABOVE

$CH_3CH_2O + O_2 \rightarrow HO_2 + CH_3CHO$

$HO_2 + NO \rightarrow NO_2 + HO$

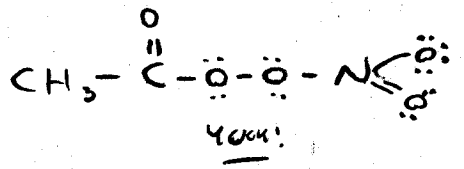
NET $CH_3CH_3 + 4O_2 \rightarrow CH_3CH_2O + 2O_3 + H_2O$

304 HW#6 KEY

2 b) $CH_3CHO + h\nu \rightarrow CH_3CO$ (i.e. $CH_3-\overset{O}{\overset{\|}{C}}\cdot$) (2)

$CH_3CO + O_2 \xrightarrow{M} CH_3CO\text{-}OO$ (i.e. $CH_3-\overset{O}{\overset{\|}{C}}-\ddot{O}-\ddot{O}\cdot$)

$CH_3CO\text{-}OO\cdot + NO_2 \rightarrow CH_3CO\text{-}OO\text{-}NO_2$ = PAN

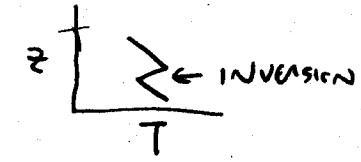


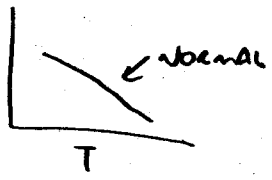
YUCK!

c) PRIMARY POLLUTANTS → NO, CH_3CH_3

SECONDARY → CH_3CHO, O_3, PAN (NO_2 MAYBE?)

3) THERMAL INVERSION IS WHEN WARM AIR OCCURS ABOVE COLD AIR IN THE TROPOSPHERE





THIS IMPEDES VERTICAL MIXING AND ALLOWS AIR TO "STEW" - THUS ALLOWING TIME FOR SECONDARY POLUTANTS TO FORM.

4) a) HNO_3 b) $\dot{N}O + HO_2\cdot$ (OR $RO_2\cdot$) → $\dot{N}O_2 + HO\cdot$ (OR RO)

$\dot{N}O_2 + \dot{O}H \xrightarrow{M} HNO_3$

PROCESS ENHANCED BY HYDROCARBONS

c) $HNO_3 + NH_3 \xrightarrow{M} NH_4NO_3(s)$ → THESE OCCUR AS SOLID PARTICULATES...

5) a) H_2SO_4 b) $SO_2 + \dot{O}H \xrightarrow{M} HO\dot{S}O_2$

$HO\dot{S}O_2 + O_2 \rightarrow HO_2\cdot + SO_3$

$SO_3 + H_2O \xrightarrow{M} H_2SO_4$

c) $H_2SO_4 + 2NH_3 \rightarrow (NH_4)_2SO_4(s)$

d) $SO_2(aq) + H_2O_2(aq) \rightarrow H_2SO_4(aq)$

6. NO_x IS PRODUCED BY ALL COMBUSTION PROCESSES: K_{eq} FOR $N_2 + O_2 \rightarrow 2NO$ INCREASES DRAMATICALLY W
   - ↳ CARS + INDUSTRY ARE MAJOR SOURCES (ANTHRO)
   - → LIGHTING + SOME OXIDATION IN SOILS MAIN NATURAL SOURCES

SO_x → COAL IS MAJOR ANTHRO SOURCE – THIS DOMINATES
→ VOLCANOES, SOME OXIDATION OF H_2S + OTHER "REDUCED" SULFUR COMPOUNDS ARE MAIN NATURAL SOURCES

7. $CO_2 + H_2O \rightarrow H_2CO_3(aq)$ $\quad K_H = \frac{[H_2CO_3]}{P_{CO_2}} = 3\times10^{-2}\left(\frac{M}{atm}\right)$

$H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$ $\quad K_{a1} = 4.3\times10^{-7}$

$X_{CO_2} = 370$ ppm → $P_{CO_2} = 370\times10^{-6}$ atm

$[H_2CO_3] = P_{CO_2} \times K_H = 1.1\times10^{-5}$

	H_2CO_3	$\rightleftharpoons H^+$	+ HCO_3^-
I	1.11×10^{-5}	0	0
C	$-x$	$+x$	$+x$
E	$\approx 1.11\times10^{-5}$ (BAD!)	x	x

$\frac{x^2}{1.15\times10^{-5}-x} = 4.3\times10^{-7}$

NOTE HOW ASSUMING $1.11\times10^{-5} - x \approx 1.11\times10^{-5}$ ANSWER IS THE SAME!

$K_{a1} = \frac{x^2}{1.11\times10^{-5}} = 4.3\times10^{-7}$ → $x = \sqrt{1.1\times10^{-5} \cdot 4.3\times10^{-7}}$

$= 2.2\times10^{-6}$

$pH = -\log[H^+] = -\log x = 5.66 = 5.7$

(ESSENTIALLY THE SAME RESULT WE GOT IN

K_{eq} for $N_2 + O_2 \rightarrow 2NO$ increases dramatically with

↳ cars + industry are major sources (anthro)

→ lightning + some oxidation in soils main natural sources

SO_x → coal is major anthro source – this dominates

→ volcanoes, some oxidation of H_2S + other "reduced" sulfur compounds are main natural sources

7. $CO_2 + H_2O \rightarrow H_2CO_3(aq)$ $K_H = \frac{[H_2CO_3]}{P_{CO_2}} = 3 \times 10^{-2} \left(\frac{M}{atm}\right)$

$H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$ $K_{a1} = 4.3 \times 10^{-7}$

$X_{CO_2} = 370$ ppm → $P_{CO_2} = 370 \times 10^{-6}$ atm

$[H_2CO_3] = P_{CO_2} \times K_H = 1.1 \times 10^{-5}$

	$H_2CO_3 \rightleftharpoons$	H^+	+ HCO_3^-
I	1.11×10^{-5}	0	0
C	$-x$	$+x$	$+x$
E	$\approx 1.11 \times 10^{-5}$ (BAD!)	x	x

$\frac{x^2}{1.15 \times 10^{-5} - x} = 4.3 \times 10^{-7}$

NOTE HOW ASSUMING $1.11 \times 10^{-5} - x \approx 1.11 \times 10^{-5}$ ANSWER IS = THE SAME!

$K_{a1} = \frac{x^2}{1.11 \times 10^{-5}} = 4.3 \times 10^{-7}$ → $x = \sqrt{1.1 \times 10^{-5} \cdot 4.3 \times 10^{-7}}$

$= 2.2 \times 10^{-6}$

$pH = -\log[H^+] = -\log x = 5.66 = 5.7$

(ESSENTIALLY THE SAME RESULT WE GOT IN CLASS!) → SO "NO".