CHEM 304 SPRING 2012

HW/Learning Goals #6: Tropospheric Chemistry: Photochemical Smog, Acid Rain, and Aerosol Formation

- 1. Oxidation of atmospheric CH₄:
 - a) Write a series of 5 reactions showing how CH₄ oxidation leads to tropospheric O₃ production.
 - b) Add two reactions to those in "a", thereby completing a series of reactions that depicts the oxidation of CH₄ to CH₂O (in which O₃ 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 CH₂O is ultimately converted to CO₂.
- 2. a) Following the "Generalized Hydrocarbon Oxidation Mechanism", write a series of reactions that shows how CH₃CH₃ (*ethane*, which is RCH₃ w/ R=CH₃) is oxidized to CH₃CHO (*acetaldehyde*), and also write the net reaction.
 - b) Write the additional reactions that show how "PAN" (*peroxyacetyl nitrate*, or CH₃CO-OO-NO₂) is formed from CH₃CHO 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 O₃ and other components 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 SO₂?
 - b) Write a series of 3 gas-phase reactions that shows how SO₂ is oxidized to this acid.
 - c) What subsequent reaction results in the formation of solid *ammonium sulphate*?
 - d) Write a reaction by which SO₂ is oxidized in the aqueous-phase.
- 6. What are the main (natural and human) sources of NO_x and SO₂ that "feed" the cycles in 4 & 5.
- 7. The natural acidity of rainwater comes primary from CO₂. Calculate the pH of rainwater that results from the current mixing ratio of CO₂ (370 ppm). Is this significantly more acidic than what results from "pre-industrial levels of CO₂ (280ppm) as we calculated in class?