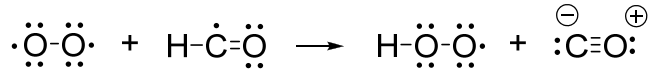
Environmental Chemistry
Problem Set 3
Due Thursday, November 12, 2009 (due by the start of class)

Report all final numerical results to the correct number of significant figures.

1. Some 130 Tg of C in the form of terpenes (all with molecular formula $C_{10}H_{16}$) are released from the earth's surface into the atmosphere each year.
   (a) Calculate the absolute concentration of terpenes (in molecule cm^{-3}) that would be present in the boundary layer due to one year's worth of emission if all the terpenes stayed in the boundary layer. Assume the earth's radius is 6380. km (four significant figures) and that the thickness of the boundary layer is 1 km. However, you should calculate the volume of the boundary layer differently from the approximate method we used in class. Take the difference of the volume of a sphere whose radius is = (earth's radius + thickness of the boundary layer), and the volume of a sphere whose radius is the earth's radius.
   (b) Calculate the absolute concentration of air (in molecule cm^{-3}) present in the boundary layer. Use atmospheric data at 0 km (not 1 km, as we did in class).
   (c) Calculate the mixing ratio, or relative concentration, of terpenes in ppb.
   (d) The two most common terpenes are α-pinene and β-pinene. The concentration of which alkene scavenger, OH, NO_3, or O_3, will be the most important in controlling the mixing ratio of these terpenes? You should justify your answer specifically, but a calculation is not necessary. (Hint: You can find the answer somewhere in your handouts.)

2. Use the data from Blanksby and Ellison's 2003 *Accounts of Chemical Research* paper to consider the ability of other free radicals to attack methane:
   (a) Bromine (Br), chlorine (Cl), and cyanide (CN) radical can all abstract a hydrogen atom from CH_4. Rank order the activation energies for these reactions. Justify your answer clearly and concisely, using bond dissociation energies as part of your reasoning.
   (b) Use bond dissociation energies to calculate $\Delta_r H^o$ for the reaction
   $$CH_4 + CN \rightarrow CH_3 + HCN$$
   (c) Based on your answer to part (b), it is clear that CN is far better than NO and O_2 at abstracting H atoms. Explain this difference qualitatively, using both the Lewis structure(s) of CN and the molecular orbital theory energy level diagram of CN.

3. A key step in the oxidation of both methane and ethene is the abstraction of H from formyl radical by O_2 (as shown below). But is it reasonable to assume that this reaction proceeds rapidly?



   Use bond dissociation energies to calculate $\Delta_r H^o$ for this reaction (in kcal/mol). Note the following:
   - Treat O_2 as if it had a single bond (that is, the way I have drawn its Lewis structure in the above reaction).

- Use the data from Blanksby and Ellison's 2003 *Accounts of Chemical Research* paper and Klotz and Rosenberg's *Chemical Thermodynamics* textbook.
- If a specific bond does not appear in one of the above sources, estimate the bond dissociation energy using a similar molecule. Clearly state what you are doing.

4. (Inspired by Baird and Cann Problem 5.4)
   (a) Write down the mechanism, and the overall reaction, by which H_2 will be oxidized in the troposphere. Assume that both ·OH and ·NO are available to participate in the oxidation mechanism. The only free radicals that may appear as products in the overall reaction are ·OH and $\cdot NO_2$.
   (b) Identify all catalysts and intermediates in your mechanism.
   (c) Explain how H_2 oxidization can contribute to ozone formation.

5. Terminal alkenes like 1-butene make up a significant component of urban air pollution. Let us consider its processing in the troposphere:
   (a) Calculate the activation entropy ($\Delta S^{\neq}$) (in cal mol^{-1} K^{-1}), the activation energy (E_a) (in kcal mol^{-1}) and the lifetimes for 1-butene reacting with OH, NO_3, and O_3 at 250. K. Please note the following:
      - Use the typical oxidant concentrations given in Atkinson and Arey's 2003 *Accounts of Chemical Research* paper.
      - Report the OH lifetime in hours, the NO_3 lifetime in hours, and the O_3 lifetime in days.
      - Write out your work for the OH reaction.
      - Please use a spreadsheet to recalculate your results for the OH reaction, and to do the calculations for the NO_3 and O_3 reactions. Turn in a printout of your spreadsheet as part of your work for this problem set.
   (b) What effect (if any) would increasing the temperature have on the three lifetimes?

6. (Inspired by Baird and Cann Problem 5.9)
   Write down the mechanism, and the overall reaction, by which propene ($CH_3CH_2CH_2$) is oxidized in the troposphere. Note the following:
      - Assume that oxidization is initiated by attack of ·OH, and that the attack forms a secondary radical.
      - The only free radicals that may appear as products in the overall reaction are ·OH and $\cdot NO_2$.
      - The only form of carbon that may appear as a product in the overall reaction is CO_2.
      - Assume any acetaldehyde that forms in the mechanism undergoes the following photolysis reaction: