University of Massachusetts Boston
Department of Chemistry
Chemistry Doctoral Program
Green Chemistry Track
Written Qualifying Exam
June 18, 2007

Physical Chemistry II

Questions are directly related to the paper:

> "Atmospheric Chemistry of a Model Biodiesel Fiel, $CH_3C(O)O(CH_2)_2OC(O)CH_3$: Kinetics, Mechanisms, and Products of Cl Atom and OH Radical Initiated Oxidation in the Presence and Absence of NO_x" M. D. Hurley, J. C. Ball, T. J. Wallington, A. Toft, O. J. Nielsen, S. Bertman, and M. Perkovic. *Journal of Physical Chemistry A*, **2007**, 111(13), 2547-2554.

1. What are the authors attempting to learn from this experiment? Do they succeed? Why did they choose this molecule for study?

2. The authors obtain reaction rates for this system using the method of relative rates.
   a) What does this mean?
   b) Why do they make this decision – that is, what obstacles are overcome by using this technique?
   c) What are the advantages and disadvantages of this decision?

3. The authors extract rate constants from their data using the following equation:

$$\mathrm{Ln}\left(\frac{[\text{reactant}]_0}{[\text{reactant}]_t}\right) = \frac{k_{\text{reactant}}}{k_{\text{reference}}} \times \mathrm{Ln}\left(\frac{[\text{reference}]_0}{[\text{reference}]_t}\right)$$

   a) Identify the terms in this expression, and explain how they are obtained *in this experiment.*
   b) Sketch a plot of $\mathrm{Ln}([\text{reactant}]_0/[\text{reactant}]_t)$ versus $\mathrm{Ln}([\text{reference}]_0/[\text{reference}]_t)$ and explain how you would extract the rate constant from the graph. What characteristics of the plot can be used to assess the quality of the data?
   c) Derive the above expression, starting from the rate law for first order kinetics.
   d) Both the reaction to be studied and the reference reaction are in fact bimolecular. Is your derivation in c), above, legitimate?

4. Shown are two plots of product yields vs. partial pressure of O_2 for the Cl-initiated reactions, representing results in the presence and in the absence of NO_x.

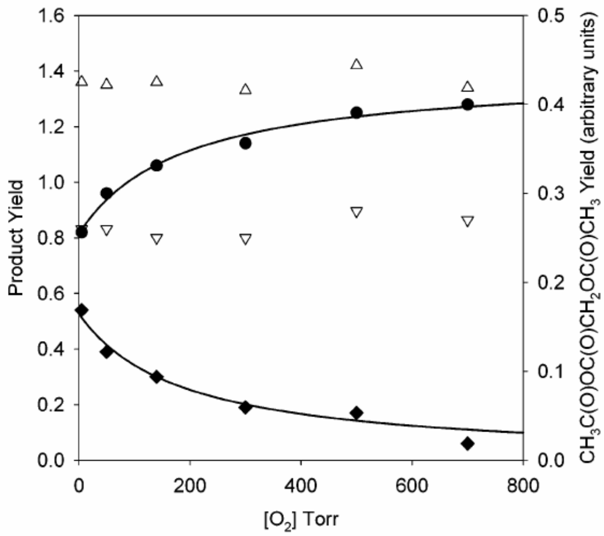

Figure 6. Yields of $CH_3C(O)OC(O)H$ (circles), $CH_3C(O)OH$ (diamonds), $CH_3C(O)OC(O)CH_2OC(O)CH_3$ (triangles down), and the combined yield of $CH_3C(O)OC(O)H$ and $CH_3C(O)OH$ (triangles up) versus the O_2 partial pressure following the UV irradiation of $CH_3C(O)O(CH_2)_2OC(O)CH_3/Cl_2/N_2/O_2$ mixtures at 700 Torr total pressure and 296 ± 1 K. Curves are the least-squares fits of expressions II and III to the data. See text for details.

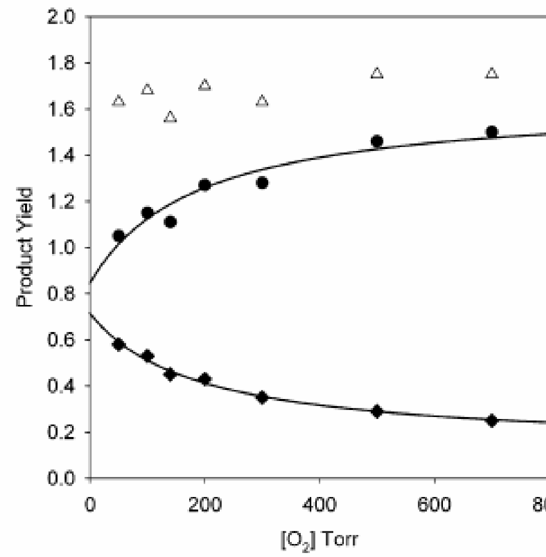

Figure 8. Yields of $CH_3C(O)OC(O)H$ (circles), $CH_3C(O)OH$ (diamonds), and the combined yield of $CH_3C(O)OC(O)H$ and $CH_3C(O)$-OH (triangles) versus the O_2 partial pressure following the UV irradiation of $NO/CH_3C(O)O(CH_2)_2OC(O)CH_3/Cl_2/N_2/O_2$ mixtures at 700 Torr total pressure and 296 ± 1 K. Curves are the least-squares fits of expressions II and III to the data. See text for details.

a) Explain why the product yields of these systems depend on the partial pressure of O_2.

b) Explain why one of the products observed in Figure 6 is not observed in Figure 8.

c) Is this a result of a kinetic or thermodynamic difference between the two pathways?

d) Which mechanism is likely to be more significant in the real atmosphere?

5. Shown below is the FTIR data obtained from the product study of the Cl-initiated reaction in air in the absence of NO_x.

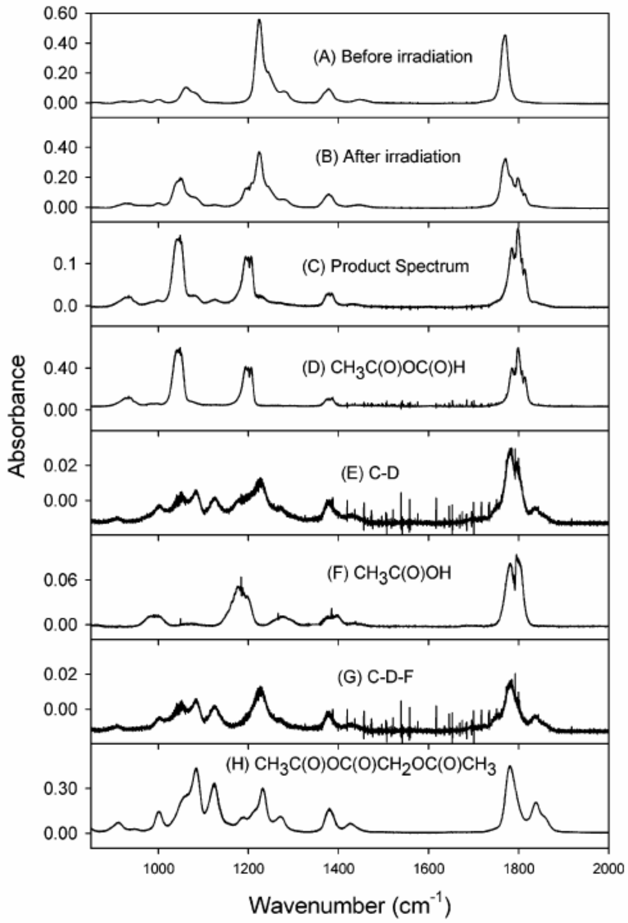

Figure 3. IR spectra obtained before (A) and after (B) a 15 s irradiation of 3.9 mTorr of $CH_3C(O)O(CH_2)_2OC(O)CH_3$ and 92 mTorr of Cl_2 in 700 Torr air. (C) shows the IR product spectrum. (E) shows the product spectrum after the subtraction of features due to $CH_3C(O)OC(O)H$. (G) shows the product spectrum after the subtraction of features due to $CH_3C(O)OC(O)H$ and $CH_3C(O)OH$.

a) Explain the sequence of panels in the figure and what they reveal about the reaction mechanism.

b) What might you expect to be different about these figures in the reaction conducted in the presence of NO_x?

c) Briefly describe how the authors can produce a complete reaction mechanism from this seemingly limited experimental data.

6. (Green Chemistry) The authors are investigating the chemistry of a "model" biodiesel fuel.

a) What is biodiesel? What distinguishes biodiesel from traditional diesel fuel?
b) Why are they using a model compound rather than a "real" biodiesel fuel?
c) Assuming a complete combustion in an internal combustion engine, what products would you expect to obtain from burning the model biodiesel studied in this paper?
d) What is the environmental benefit of using biodiesel fuels to replace traditional fuels?