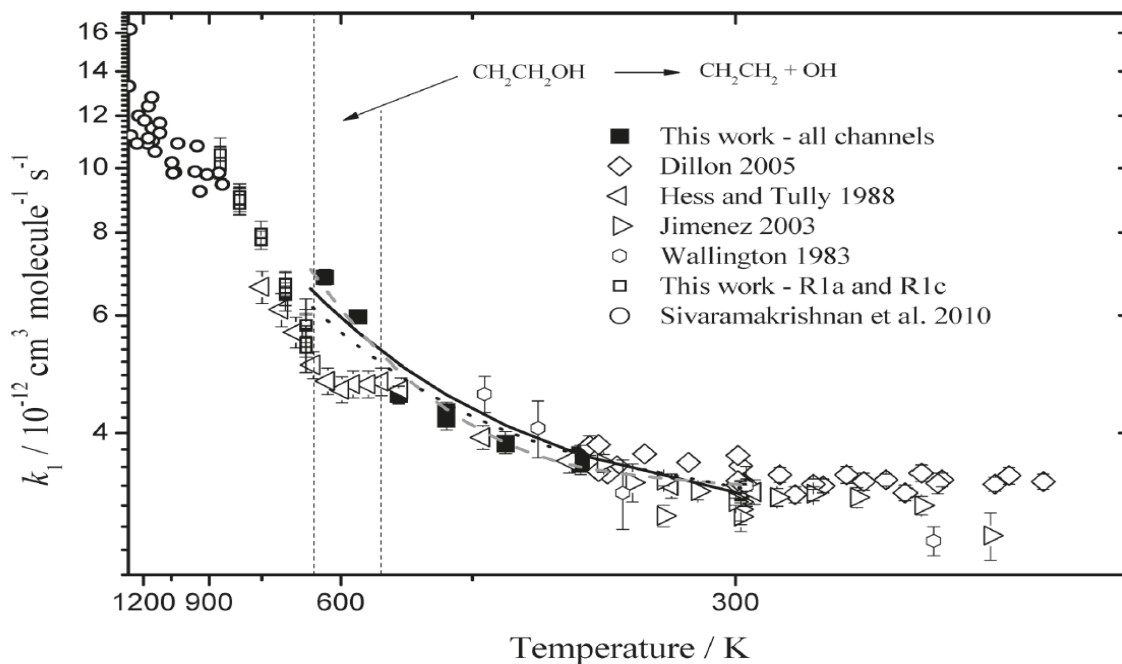


UMass Boston Department of Chemistry  
July 2011 Written Qualifying Exam  
Paper: "Site-Specific Rate Coefficients for Reaction of OH with Ethanol  
from 298 to 900 K" by Carr, *et al.*

1. What are the authors attempting to learn from this experiment? Why do they believe that the scientific question is important? Provide an answer both in the context of ethanol's use as a fuel *and* in the context of general physical chemistry. (2 points)
2. The authors obtain reaction rates for this system using pseudo-first order kinetics. What does this mean? Why do they make this decision – that is, what obstacles are overcome by using this technique? What are the advantages and disadvantages of this decision? (2 points)
3. Describe how the two reactants (i.e., OH and 'alcohol') in this experiment are introduced into the flow system, including the impact of different precursor mixtures. Describe how the reagent concentrations are monitored. (2 points)
4. The following three questions refer to Figure 4, below, which shows the rate constant for reaction 1.1 as a function of temperature. (2 points)



**Figure 4.** Arrhenius plot of the kinetic data obtained for reaction R1.1 in this study and in previous literature. Solid squares are the total rate coefficient for reaction R1.1. Empty squares are reduced by the rate of recycling OH. Error bars are the quoted  $2\sigma$  values. Lines are fits of eqs E5 (black solid,  $AT^2 \exp(B/T)$  fit to our data), E6 (dotted line,  $AT^2 \exp(B/T)$  from IUPAC), and E7 (dashed line,  $AT^n \exp(B/T)$  fit to our data).

- The usual means of displaying the temperature dependence of a rate constant is to use an “Arrhenius plot”. What is the Arrhenius equation? How does an Arrhenius plot “normally” behave?
- What is the **graphical** evidence that this is not “normal” Arrhenius behavior? Note: there is definitely more than one answer to this question. Give **at least two** examples.
- Identify the chemical reason for **two** of your examples of non-Arrhenius behavior in b).

5. Equation two (E2) is reproduced below:

$$\begin{pmatrix} 1 & 1 & 1 \\ z_{1a}^{-1} & 1 & 1 \\ 1 & z_{1b}^{-1} & 1 \\ z_{1a}^{-1} & z_{1b}^{-1} & 1 \\ 1 & 1 & z_{1c}^{-1} \\ z_{1a}^{-1} & z_{1b}^{-1} & z_{1c}^{-1} \end{pmatrix} \begin{pmatrix} k_{1a} \\ k_{1b} \\ k_{1c} \end{pmatrix} = \begin{pmatrix} k_{1.1} \\ k_{1.2} \\ k_{1.3} \\ k_{1.4} \\ k_{1.5} \\ k_{1.6} \end{pmatrix} \quad (\text{E2})$$

- Identify all the terms in this equation. Which are directly measured in this experiment and which are the solved unknowns?
- Explain how the authors reduced this equation to (E3).
- Explain how the authors used this equation to obtain their site-specific rate constants for the title reaction.

5. (Green Chemistry, 2 points) Draw each of the possible radicals produced by the title reaction. Which of these radicals is the most stable? In Chem 671, we argued that the most stable radical product generally determined the overall reaction yield. Why was this a good assumption in the context of the course? Why is it not such a good assumption in the context of the use of ethanol as fuel?