

# Chemistry 2710 Spring 2001 Test 2 Solutions

1. (a) The high-energy intermediate  $\text{CH}_3\text{CH}_2\text{O}^*$  should be highly reactive so we should apply the SSA to this species.

$$\frac{d[\text{CH}_3\text{CH}_2\text{O}^*]}{dt} = k_1[\text{CH}_3\text{CH}_2\text{O}][\text{He}] - k_{-1}[\text{He}][\text{CH}_3\text{CH}_2\text{O}^*] - k_2[\text{CH}_3\text{CH}_2\text{O}^*] \approx 0.$$

$$\therefore [\text{CH}_3\text{CH}_2\text{O}^*] \approx \frac{k_1[\text{CH}_3\text{CH}_2\text{O}][\text{He}]}{k_{-1}[\text{He}] + k_2}.$$

The overall reaction is  $\text{CH}_3\text{CH}_2\text{O} \rightarrow \text{CH}_2\text{O} + \text{CH}_3$  so the rate of reaction is

$$v = \frac{d[\text{CH}_2\text{O}]}{dt} \approx \frac{k_1 k_2 [\text{CH}_3\text{CH}_2\text{O}][\text{He}]}{k_{-1}[\text{He}] + k_2}.$$

- (b) If the pressure of helium is sufficiently low, we can ignore the term  $k_{-1}[\text{He}]$  in the denominator of the rate expression. The rate becomes

$$v \approx \frac{k_1 k_2 [\text{CH}_3\text{CH}_2\text{O}][\text{He}]}{k_2} = k_1 [\text{He}][\text{CH}_3\text{CH}_2\text{O}].$$

Since the helium concentration is constant ( $d[\text{He}]/dt = 0$  in this mechanism), the observed rate at low helium pressure would be  $v \approx k_1' [\text{CH}_3\text{CH}_2\text{O}]$  where  $k_1' = k_1 [\text{He}]$ .

- (c) This is a gas-phase reaction, so we need the rate constant in units compatible with the standard state of 1 bar. From the ideal gas law,

$$\begin{aligned} \frac{n}{V} &= \frac{P}{RT} \\ &= \frac{100000 \text{ Pa/bar}}{(8.314510 \text{ J K}^{-1} \text{ mol}^{-1})(443.15 \text{ K})} \\ &= 27.14 \text{ mol m}^{-3} \text{ bar}^{-1} \\ &= 0.02714 \text{ mol L}^{-1} \text{ bar}^{-1}. \\ \therefore k_\infty &= 5.4 \times 10^{11} \text{ bar}^{-1} \text{ s}^{-1}. \end{aligned}$$

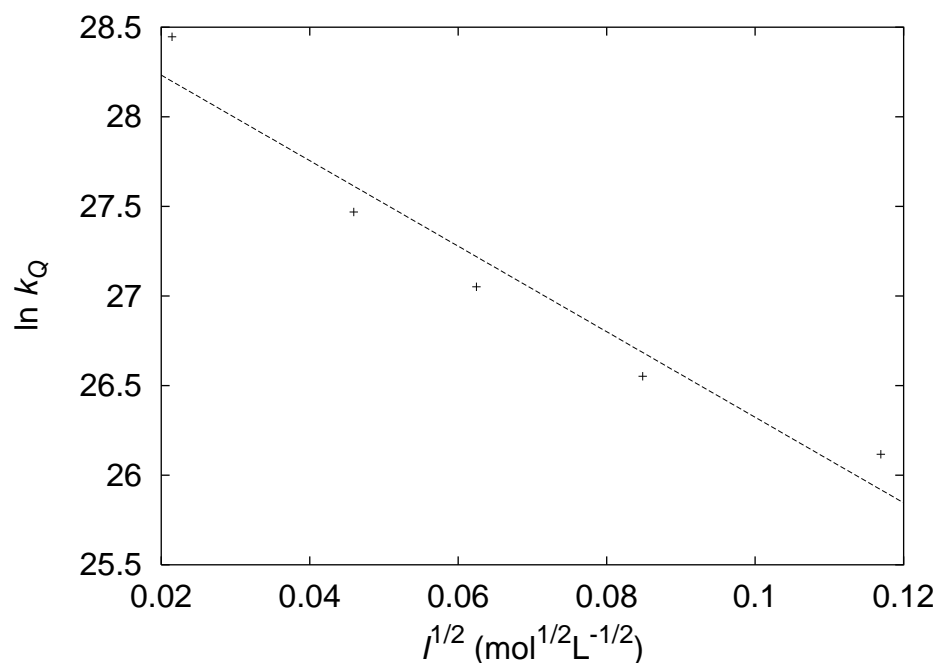
We also need  $\Delta \bar{n}^\ddagger$ . In order to transfer energy to the ethoxy radical, a helium atom will have to make close contact. I would therefore guess that  $\Delta \bar{n}^\ddagger$  would be about  $-1$ . The entropy change is then

$$\begin{aligned} \Delta \bar{S}^\ddagger &= R \left[ \ln \left( \frac{h k_\infty}{k_B T} \right) - 1 + \Delta \bar{n}^\ddagger \right] \\ &= (8.314510 \text{ J K}^{-1} \text{ mol}^{-1}) \left[ \ln \left( \frac{(6.626069 \times 10^{-34} \text{ J/Hz})(5.4 \times 10^{11} \text{ bar}^{-1} \text{ s}^{-1})}{(1.380658 \times 10^{-23} \text{ J/K})(443.15 \text{ K})} \right) - 1 - 1 \right] \\ &= -40 \text{ J K}^{-1} \text{ mol}^{-1}. \end{aligned}$$

The entropy change is not quite as large as would be the case if the transition state were a single molecule. It might therefore make more sense to use  $\Delta\bar{n}^\ddagger = 0$ . Repeating the above calculation, we find

$$\begin{aligned}\Delta\bar{S}^\ddagger &= (8.314510\text{JK}^{-1}\text{mol}^{-1}) \left[ \ln \left( \frac{(6.626069 \times 10^{-34}\text{J/Hz})(5.4 \times 10^{11}\text{bar}^{-1}\text{s}^{-1})}{(1.380658 \times 10^{-23}\text{J/K})(443.15\text{K})} \right) - 1 + 0 \right] \\ &= -32\text{JK}^{-1}\text{mol}^{-1}.\end{aligned}$$

2. A plot of  $\ln k_Q$  vs  $\sqrt{I}$  should be a straight line. Here is a plot of the data:

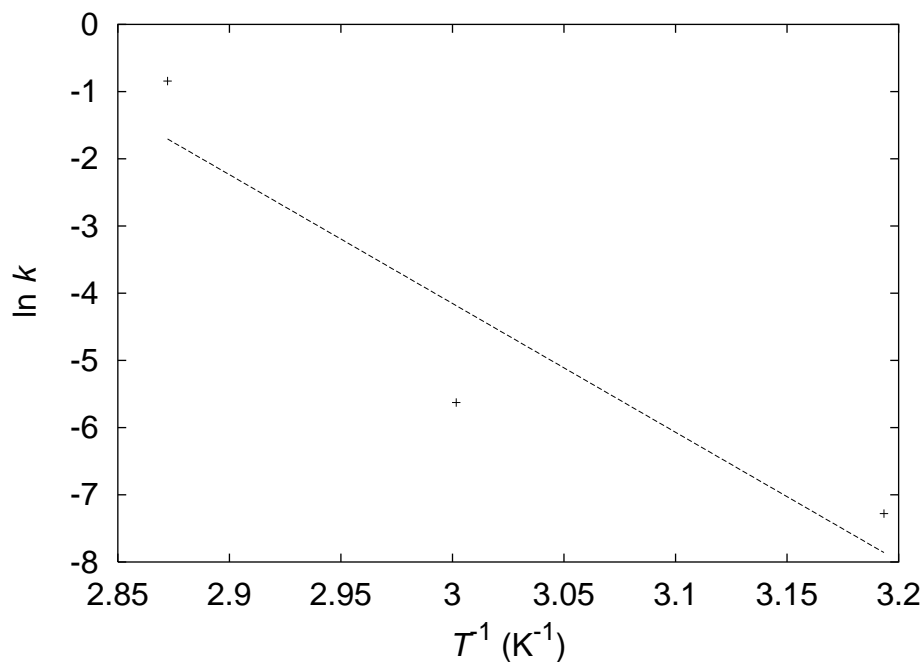


The data clearly do not fit a straight line so that Brønsted-Bjerrum theory is not adequate in this case. Brønsted-Bjerrum theory is based on Debye-Hückel theory, which assumes that charged particles in solution organize in a certain way. The arrangement may however be substantially different for large polymeric particles than it is for smaller solutes.

3. Here, it's a simple matter of doing a regression of  $\ln k$  vs  $1/T$ .

$1000T^{-1} (\text{K}^{-1})$	3.1934	3.0017	2.8723
$\ln k$	-7.2788	-5.6268	-0.8440

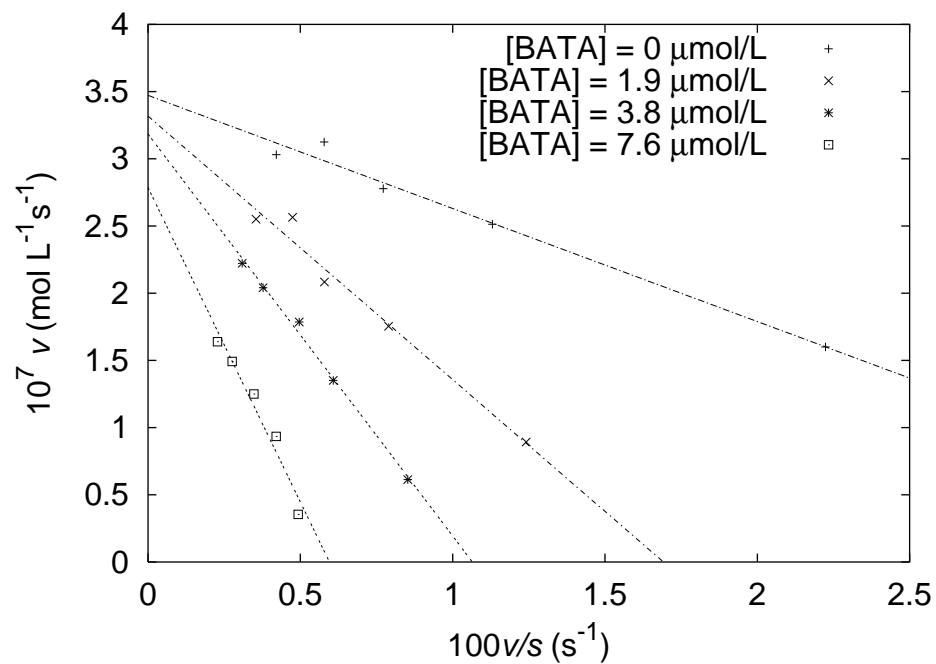
Although the graph is unnecessary, I like to look at the data, so here's my plot:



With only three points, it's impossible to say whether the scatter is just scatter, or whether there's something else going on. I would guess that it is just scatter. After all, working with hot, concentrated acids is quite difficult so one has to expect relatively large error bars on the measurements. The slope and intercept of the plot are, respectively,  $-19\,169\text{ K}$  and  $53.35$ . The activation energy and preexponential factor are therefore

$$\begin{aligned}\bar{E}_a &= -(8.314510\text{ J K}^{-1}\text{ mol}^{-1})(-19\,169\text{ K}) = 159\text{ kJ/mol.} \\ k_\infty &= e^{53.35} = 1.5 \times 10^{23}\text{ L mol}^{-1}\text{ s}^{-1}.\end{aligned}$$

4. In competitive inhibition,  $v_{\text{max}}$  (the intercept) is independent of the inhibitor concentration. In this case, all four curves have different intercepts, as we can see by drawing lines through the data:



Some of the points look like they were subject to significant experimental errors. However, even if we discard some of the points, the  $v_{\text{max}}$  values can't be brought into correspondence so this is *not* a competitive inhibitor. The use of a Lineweaver-Burk plot in this case encouraged an unwarranted conclusion about the data.