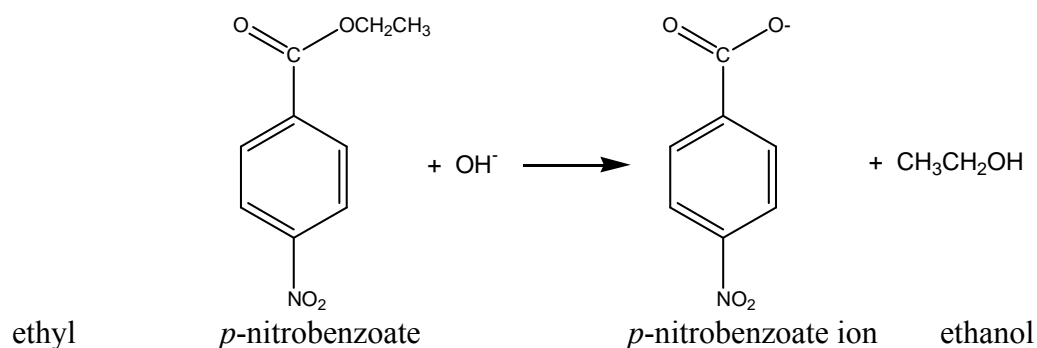


**Supplemental Questions
for
Kinetics**

1a. The reaction between ethyl *p*-nitrobenzoate (ENB) and hydroxide ion, shown below, was studied by monitoring the disappearance of the ENB. The data in Table 1 represent the concentration of ENB as a function of time for various hydroxide ion concentrations. In each experiment the initial concentration of ENB was 1.00×10^{-4} M and the temperature was maintained at 25.0°C.



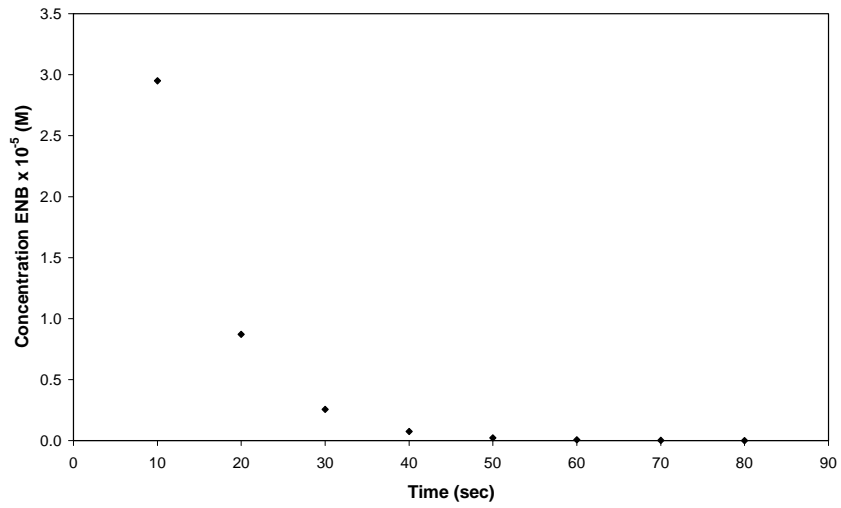
[OH ⁻] Time (sec)	[OH ⁻] = 0.500 M [ENB] (M)	[OH ⁻] = 0.250 M [ENB] (M)	[OH ⁻] = 0.100 M [ENB] (M)	[OH ⁻] = 0.0100 M [ENB] (M)
10	2.95×10^{-5}	5.45×10^{-5}	7.83×10^{-5}	9.76×10^{-5}
20	8.72×10^{-6}	2.97×10^{-5}	6.13×10^{-5}	9.52×10^{-5}
30	2.57×10^{-6}	1.62×10^{-5}	4.80×10^{-5}	9.29×10^{-5}
40	7.60×10^{-7}	8.80×10^{-6}	3.75×10^{-5}	9.07×10^{-5}
50	2.24×10^{-7}	4.80×10^{-6}	2.94×10^{-5}	8.85×10^{-5}
60	6.62×10^{-8}	2.61×10^{-6}	2.30×10^{-5}	8.64×10^{-5}
70	1.95×10^{-8}	1.42×10^{-6}	1.80×10^{-5}	8.43×10^{-5}
80	5.77×10^{-9}	7.75×10^{-7}	1.41×10^{-5}	8.23×10^{-5}

Table 1. Concentration of ENB as a function of time at different [OH⁻].

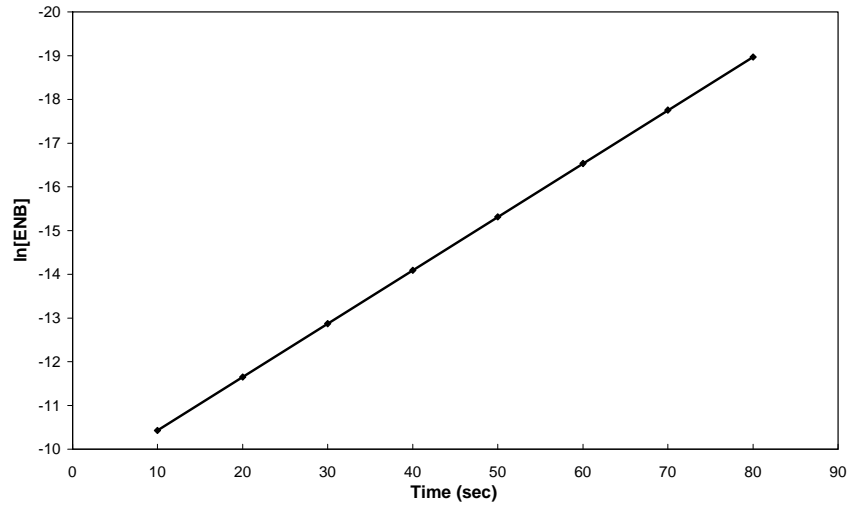
a. Using the data obtained at [OH⁻] = 0.500 M, determine the order of the reaction with respect to ENB. You will need to prepare three separate graphs in Excel to do this.

The graph of ln[ENB] as a function of time is linear. Therefore, the reaction is first order with respect to ENB.

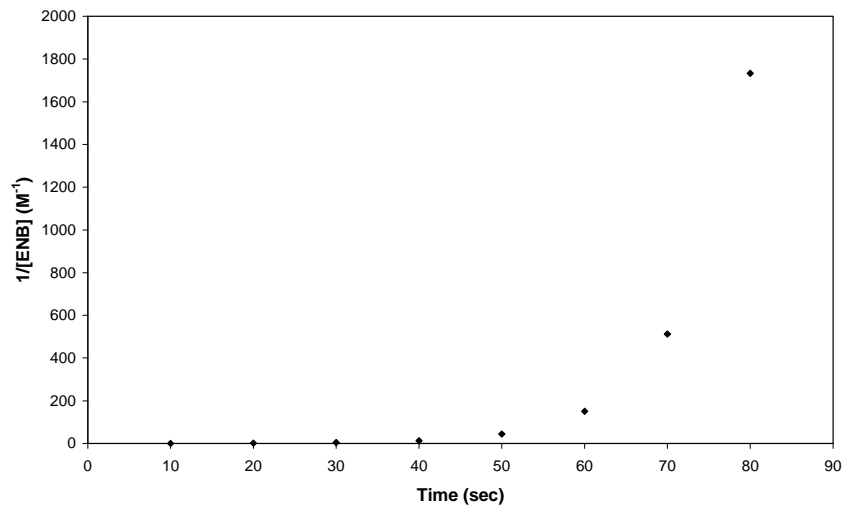
Concentration of ENB as a Function of Time
(linear for 0th order reaction)



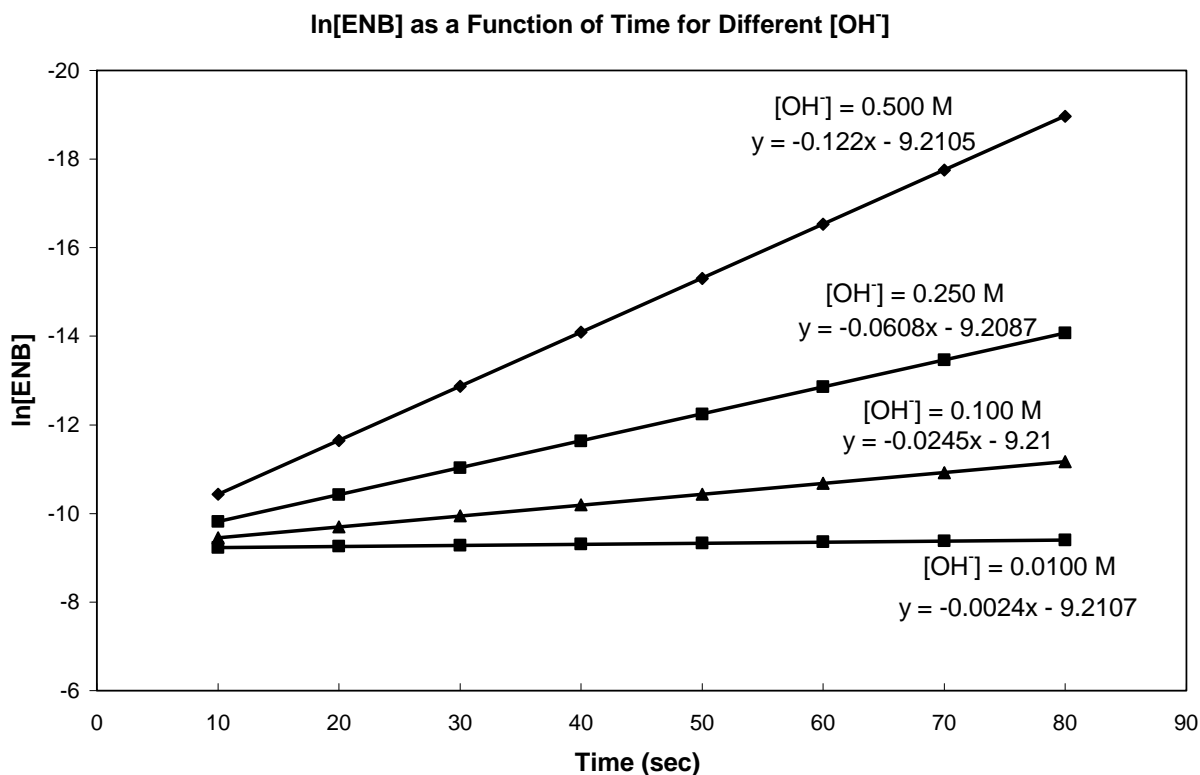
\ln [ENB] as a Function of Time
(linear for 1st order reaction)



1/[ENB] as a Function of Time
(linear for 2nd order reaction)

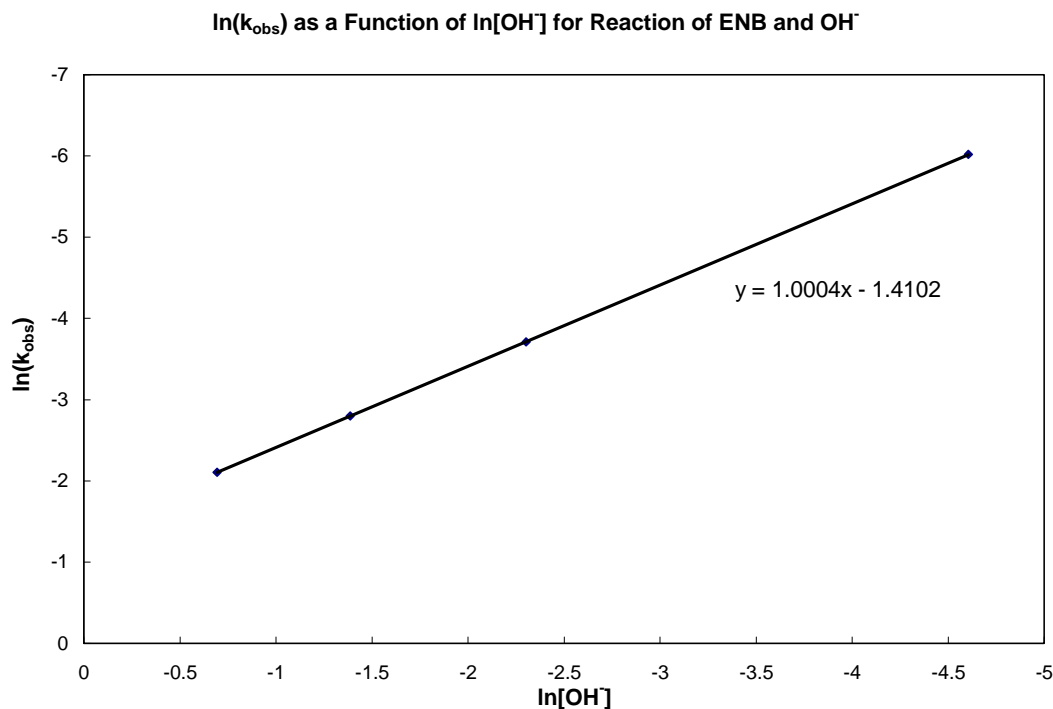


b. Prepare a graph in Excel showing the $[\text{ENB}]$ as a function of time at different $[\text{OH}^-]$ (use the method from part *a* that gave a straight line, and use different symbols to differentiate the data at different $[\text{OH}^-]$). Tabulate the observed rate constant, k_{obs} , as a function of $[\text{OH}^-]$.



$[\text{OH}^-]$ (M)	k_{obs} (s^{-1})
0.500	0.122
0.250	0.0608
0.100	0.0245
0.0100	0.0024

d. Prepare a graph using the k_{obs} at different $[\text{OH}^-]$ to determine the order of the reaction with respect to OH^- .



The slope of the ln(k_{obs}) as a function of ln[OH⁻] is 1.0004. Therefore, the order of the reaction with respect to OH⁻ is first order.

e. Give the overall rate law for this reaction.

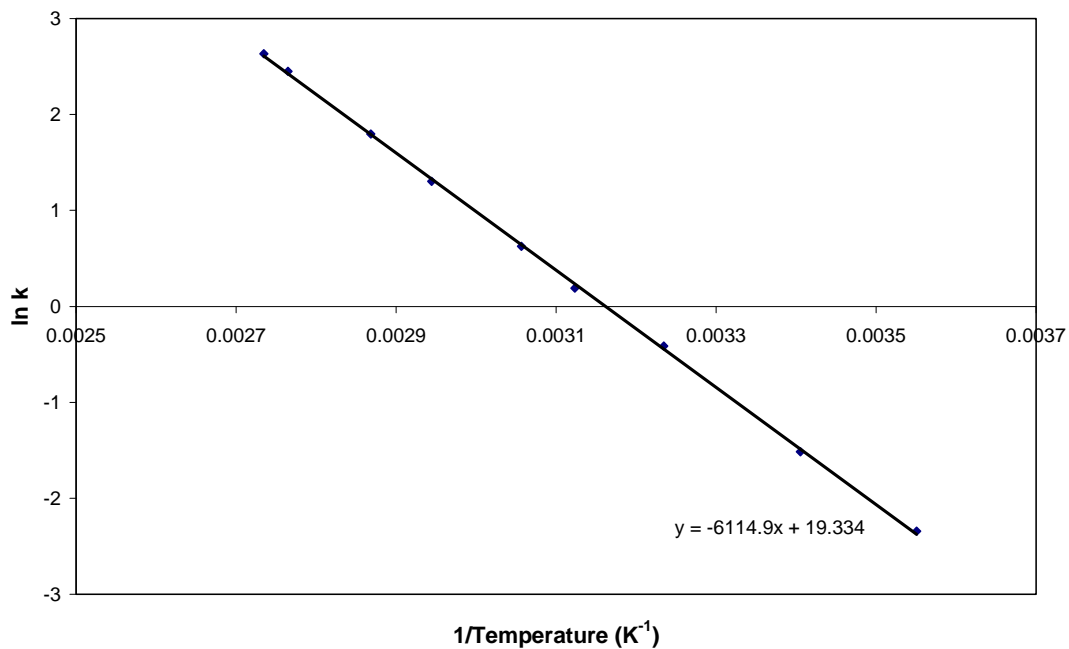
The overall rate law is: rate = k [OH⁻][ENB].

f. The temperature dependence of the rate constant was investigated at the temperatures shown in Table 2. Prepare a graph of these data and from it determine the activation energy for this reaction in kJ/mole.

Temperature (°C)	k (M·s ⁻¹)
8.5	0.096
20.5	0.22
36.0	0.66
47.0	1.21
54.0	1.87
66.5	3.68
75.5	6.02
88.5	11.59
92.5	13.89

Table 2. Dependence on temperature for the rate constant for the reaction between ENB and OH⁻.

In k for the Reaction of ENB with OH- as a Function of 1/Temperature

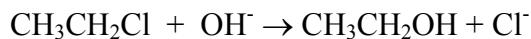


Start with the Arrhenius equation, $\ln k = \ln A - \frac{E_a}{RT}$. A graph of $\ln k$ as a function of $1/T$ has a slope equal to $-E_a/R$.

$$-\frac{E_a}{R} = -6114.9K$$
$$E_a = (6114.9K)(8.314510J \cdot K^{-1} \cdot mole^{-1})$$
$$E_a = 50.842kJ \cdot mole^{-1}$$

The activation energy for this reaction is 50.842 kJ/mole.

2. Chloroethane, $\text{CH}_3\text{CH}_2\text{Cl}$, reacts with OH^- according to the chemical equation:



a. From the following initial rate data, determine the rate law for this reaction.

$[\text{CH}_3\text{CH}_2\text{Cl}]$ (M)	$[\text{OH}^-]$ (M)	Initial Rate ($\text{M}\cdot\text{s}^{-1}$)
0.100	0.200	5.8×10^{-7}
0.100	0.100	3.1×10^{-7}
0.200	0.100	6.0×10^{-7}

Compare experiment 1 and experiment 2.

$$\frac{[\text{OH}^-]_1}{[\text{OH}^-]_2} = \frac{0.200}{0.100} = 2.00$$
$$\frac{\text{Rate}_1}{\text{Rate}_2} = \frac{5.8 \times 10^{-7}}{3.1 \times 10^{-7}} = 1.9$$

When the $[\text{OH}^-]$ doubles, the rate doubles. Therefore, the reaction is first order with respect to OH^- .

Compare experiment 2 and experiment 3.

$$\frac{[\text{OH}^-]_3}{[\text{OH}^-]_2} = \frac{0.200}{0.100} = 2.00$$
$$\frac{\text{Rate}_3}{\text{Rate}_2} = \frac{6.0 \times 10^{-7}}{3.1 \times 10^{-7}} = 1.9$$

When the $[\text{CH}_3\text{CH}_2\text{Cl}]$ doubles, the rate doubles. Therefore, the reaction is first order with respect to $\text{CH}_3\text{CH}_2\text{Cl}$.

b. What is the rate law for this reaction?

Rate law for the reaction is: $\text{rate} = k[\text{OH}^-][\text{CH}_3\text{CH}_2\text{Cl}]$

c. What is the rate constant for this reaction?

Solving for k in each experiment by substituting values of the initial rate and the reactant concentration gives the values shown below. Then calculate average and estimated standard deviation to get final value of k .

Experiment Number	k ($M^{-1}\cdot s^{-1}$)
1	2.9×10^{-5}
2	3.1×10^{-5}
3	3.0×10^{-5}

The rate constant is $3.0(1) \times 10^{-5} M^{-1}\cdot s^{-1}$.

d. Give the expression for the rate in terms of the rate of change of $[CH_3CH_2Cl]$. Give the expression for the rate in terms of the rate of change of $[CH_3CH_2OH]$.

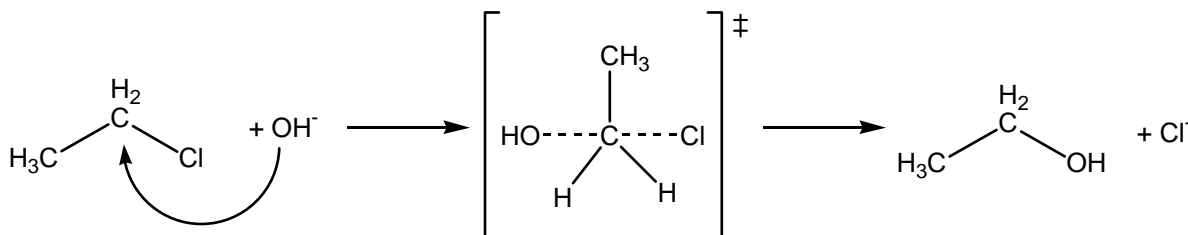
The rate in terms of $[CH_3CH_2Cl]$ is

$$rate = -\frac{d[CH_3CH_2Cl]}{dt}$$

The rate in terms of $[CH_3CH_2OH]$ is

$$rate = \frac{d[CH_3CH_2OH]}{dt}$$

e. The following mechanism has been proposed for this reaction.



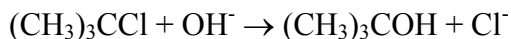
What does the symbol ‡ on the second species shown indicate?

It is a transition state.

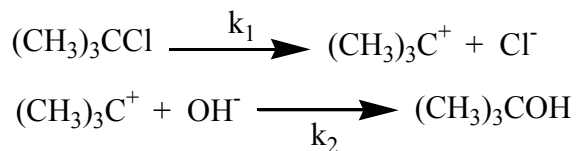
d. How many steps are there in this mechanism?

There is only one step in this mechanism.

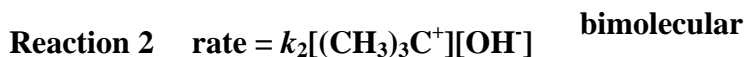
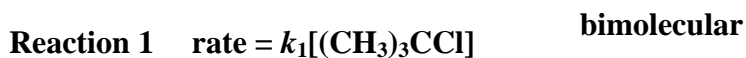
3. *t*-Butyl chloride, $(\text{CH}_3)_3\text{CCl}$, reacts with OH^- according to the following equation:



The proposed mechanism for this reaction is as follows:



a. Write the rate expressions (laws) for the elementary reactions in this mechanism, and give their molecularity.



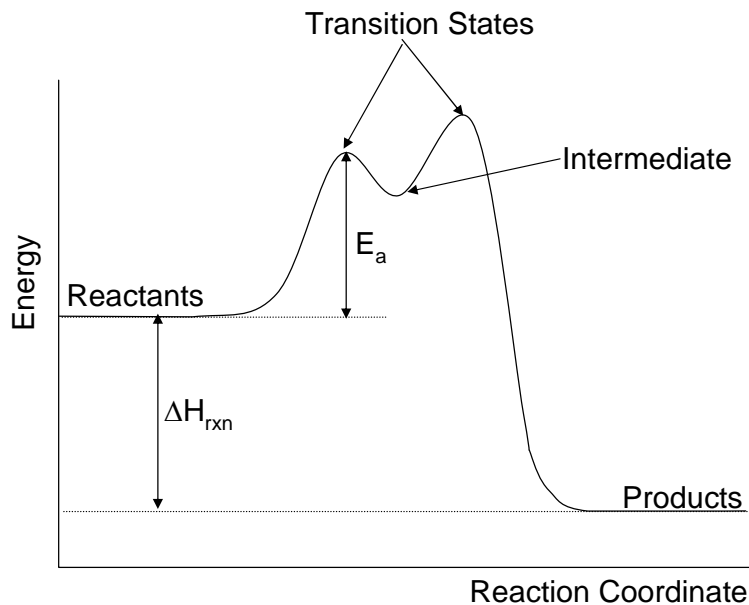
b. If the first step is much slower than the second ($k_1 \ll k_2$). Give the rate law for this reaction.

The rate law is: $\text{rate} = k_1[(\text{CH}_3)_3\text{CCl}]$.

c. What is the species $(\text{CH}_3)_3\text{C}^+$ an example of?

This species is an intermediate.

d. The reaction of *t*-butyl chloride with OH^- is exothermic. With this information and the information in parts *a* and *b*, qualitatively sketch the potential energy diagram for the reaction. Label the important features of the diagram.



e. The rate law was determined experimentally under conditions where the $[\text{OH}^-]$ was very high relative to the $[(\text{CH}_3)_3\text{CCl}]$. The graph of $\ln[(\text{CH}_3)_3\text{CCl}]_t$ as a function of time was linear. What is the order of the reaction with respect to $(\text{CH}_3)_3\text{CCl}$?

The reaction is first order with respect to $(\text{CH}_3)_3\text{CCl}$.

f. The experiment was performed at several different $[\text{OH}^-]$, and the rate of reaction remained unchanged. What is the order of the reaction with respect to the second reactant? Why?

Changing the $[\text{OH}^-]$ had no effect on the rate of reaction, so the reaction is zeroth order with respect to OH^- .

4. (Do questions 2 and 3 before trying to answer this one!). Questions 2 and 3 were both concerned with the reaction of a halogenated hydrocarbon with OH^- .

The rate law for chloroethane was found to be $rate = k[\text{OH}^-][\text{CH}_3\text{CH}_2\text{Cl}]$, while the rate law for *t*-butylchloride was found to be $rate = k[(\text{CH}_3)_3\text{CCl}]$.

a. What does it mean when similar compounds, like these are, have different rate laws for the same reaction?

Even though they are similar, they react differently.

b. Based on the mechanism in questions 2 and 3, which reaction do you expect to have the larger ΔS^\ddagger ? Why?

$\text{CH}_3\text{CH}_2\text{Cl}$ has the larger (more negative) ΔS^\ddagger because in the transition state two particles have come together to form one particle. With $(\text{CH}_3)_3\text{CCl}$ there is only one particle present in the transition state.