Fall 2011-12

Chemistry 217
Quiz 3

Name: _____KEY_____

Signature: _____

Helpful constants to know for this exam:

Boltzmann's constant: $k_B = 2.94 \times 10^{-24}$ cal K^{-1} = 1.38×10^{-23} J K^{-1}

Gas constant: $R = 1.99$ cal K^{-1} mol^{-1} = 8.314 J K^{-1} mol^{-1}

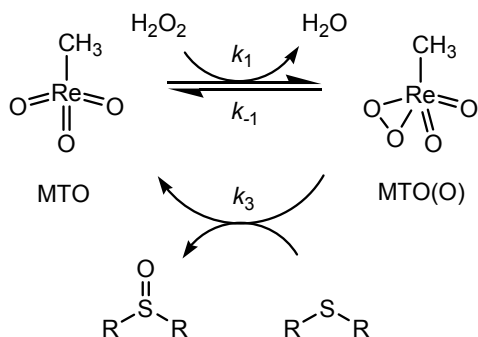Planck's constant: $h = 1.58 \times 10^{-34}$ cal sec = 6.626×10^{-34} J sec

$e = 2.718$

For a unimolecular reactions:

$$k = e\frac{k_B T}{h}e^{\Delta S\ /R}e^{-E_a/RT}$$

For a bimolecular reactions:

$$k = e^2\frac{k_B T}{h}e^{\Delta S\ /R}e^{-E_A/RT}$$

1) The complex methyltrioxorhenium (MTO) catalyzes the oxidation of sulfides to sulfoxides by H_2O_2 according to the mechanism shown below.

This reaction is run in H_2O, so $[H_2O]$ can be considered constant (55.6 M, in significant excess) for any rate expression that contains it.

a) Assuming that the complex MTO(O) is a *steady-state* intermediate, derive the rate law for sulfoxide formation via the mechanism above. Because the total concentration of rhenium catalyst species does not change over the course of the reaction, you should express your law in terms of $[Re]_T = [MTO] + [MTO(O)]$.

> (a) We first write the expression for the steady state concentration of MTO(O), and then use the relation $[Re]_T = [MTO] + [MTO(O)]$ to express that concentration in terms of $[Re]_T$. The rate law then follows:

$$[MTO(O)] = \frac{k_1[H_2O_2][MTO]}{k_{-1} + k_3[RSR]}$$

$$[MTO] = \frac{[MTO(O)](k_{-1} + k_3[RSR])}{k_1[H_2O_2]}$$

$$[Re]_T = [MTO] + [MTO(O)] = \frac{[MTO(O)](k_{-1} + k_3[RSR])}{k_1[H_2O_2]} + [MTO(O)]$$

$$[MTO(O)] = \frac{k_1[H_2O_2][Re]_T}{k_{-1} + k_3[RSR] + k1[H_2O_2]}$$

$$Rate = k_3[MTO(O)][RSR]$$

$$Rate = \frac{k_1k_3[Re]_T[H_2O_2][RSR]}{k_{-1} + k_3[RSR] + k_1[H_2O_2]}$$

b) Derive the rate law for sulfoxide formation in terms of $[Re]_T$ assuming that k_3 is rate-determining and that there is a rapid *pre-equilibrium* between MTO and MTO(O).

$$K_{eq} = \frac{k_1}{k_{-1}} = \frac{[MTO(O)]}{[H_2O_2][MTO]}$$

$$Rate = k_3[MTO(O)][RSR]$$

$$[MTO] = \frac{k_{-1}[MTO(O)]}{k_1[H_2O_2]}$$

$$Rate = \frac{k_1 k_3 [Re]_T [H_2O_2][RSR]}{k_{-1} + k_1[H_2O_2]}$$

$$[Re]_T = [MTO] + [MTO(O)] = \frac{k_{-1}[MTO(O)]}{k_1[H_2O_2]} + [MTO(O)]$$
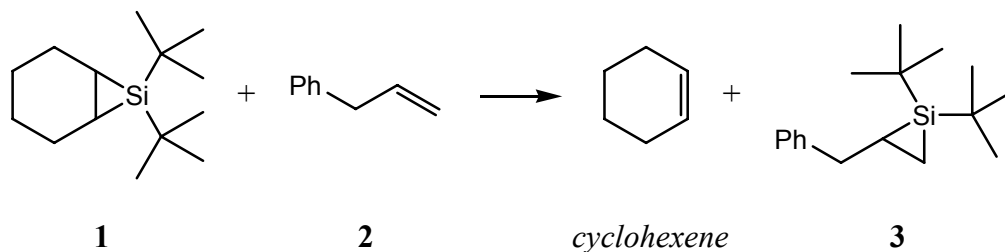
$$[MTO(O)] = \frac{k_1[H_2O_2]\{Re\}_T}{k_{-1} + k_1[H_2O_2]}$$

c) The rate laws for situations (a) and (b) should be different. How would you experimentally determine which rate law is correct? What experiment(s) would you perform, and under what conditions? What would be the anticipated results, and how would you analyze them?
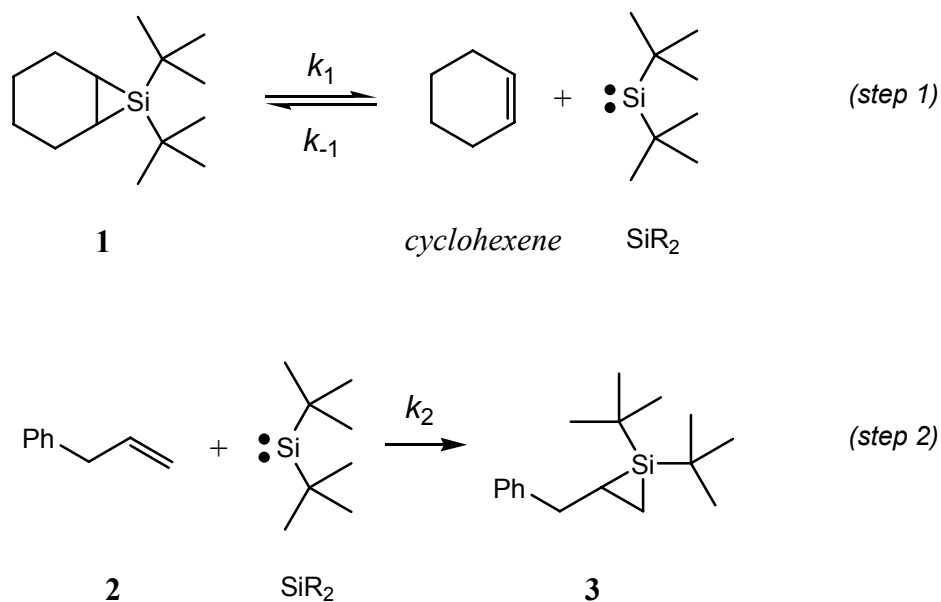
The key difference between the two rate laws is the presence or absence, respectively, of a [RSR] term in the denominator. In (a), the dependence of the rate on [RSR] follows saturation kinetics, whereas in (b) the dependence is simply first-order. Experimentally, then, one needs to simply measure the rate as a function of [RSR]. Although not necessary, it would simplest to use an excess of $[H_2O_2]$, so that the rate laws simplify a bit (i.e., $k_1[H_2O_2] >> k_{-1}$). Then one measures the pseudo first-order rate constant (k_{obs}) under conditions of excess [RSR] (and a constant excess of $[H_2O_2]$), and repeats the experiment varying [RSR] (making sure to go to quite high concentrations). Analysis of the data (to solve for k_{obs}) would proceed using the integrated rate expression for a first order reaction. A plot of the resulting k_{obs} values versus [RSR] will provide the answer. If that plot is linear, then the rate law in (b) is indicated, but if rate law (a) is operative, the plot should show saturation (start linear but then curve over to reach a saturation slope of zero).

2) Driver and Woerpel[1] found that the dialkylsilyl fragment of silacyclopropane **1** spontaneously migrated to allylbenzene **2** to form the new benzylsilacyclopropane **3.** Based on kinetic observations, these investigators proposed a two-step mechanism in which SiR_2 dissociates from **1** as a silylene (SiR_2).

Overall reaction:

| **1** | **2** | *cyclohexene* | **3** |

Proposed Mechanism:

| **1** | | *cyclohexene* | SiR_2 | *(step 1)* |

| **2** | SiR_2 | **3** | *(step 2)* |

The proposed SiR_2 intermediate, however, was never observed. Because step 2 and the reverse of step 1 both represent the addition of SiR_2 to a double bond, the authors assumed that k_2 and k_{-1} were similar in magnitude.

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[1] Driver, T. G.; Woerpel, K. A. *J. Am. Chem. Soc.* **2003,** *125,* 10659-10663.

a) Derive **an appropriate rate law** for the appearance of product **3** ($\partial[3]/\partial t$) in terms of measurable quantities. If you use any assumptions or approximations in your derivation, name them and briefly (in one sentence or less) justify them.

$$\frac{\partial[3]}{\partial t} = k_2[2][SiR_2]$$

[SiR$_2$] can't be measured, so we have to substitute for it. The problem states that k_2 and k_{-1} are of roughly the same magnitude, and I took that to mean that SiR$_2$ is created at roughly the same rate that it's destroyed. In this situation, the **steady-state approximation** is most appropriate:

$$\frac{\partial[SiR_2]}{\partial t} = 0 = k_1[1] - k_{-1}[\text{cyclohexene}][SiR_2] - k_2[2][SiR_2]$$

$$[SiR_2] = \frac{k_1[1]}{k_{-1}[\text{cyclohexene}] + k_2[2]}$$

Substituting this into the rate law, for $\partial[3]/\partial t$,

$$\frac{\partial[3]}{\partial t} = \frac{k_1 k_2[1][2]}{k_{-1}[\text{cyclohexene}] + k_2[2]}$$

b) Driver and Woerpel performed kinetic experiments under the assumption that the overall reaction was first-order in **1**, such that

$$\frac{\partial[3]}{\partial t} = k_{obs}[\mathbf{1}]; \quad [\mathbf{1}]_t = [\mathbf{1}]_0 e^{-k_{obs}t}.$$

Using the method of initial rates, the authors determined k_{obs} for different starting concentrations of allylbenzene (2). Using the data shown below, **calculate k_1 for the reaction.** Make sure to include units in your answer.

$k_1 =$

$[\mathbf{1}]_0 = 0.05$ mM
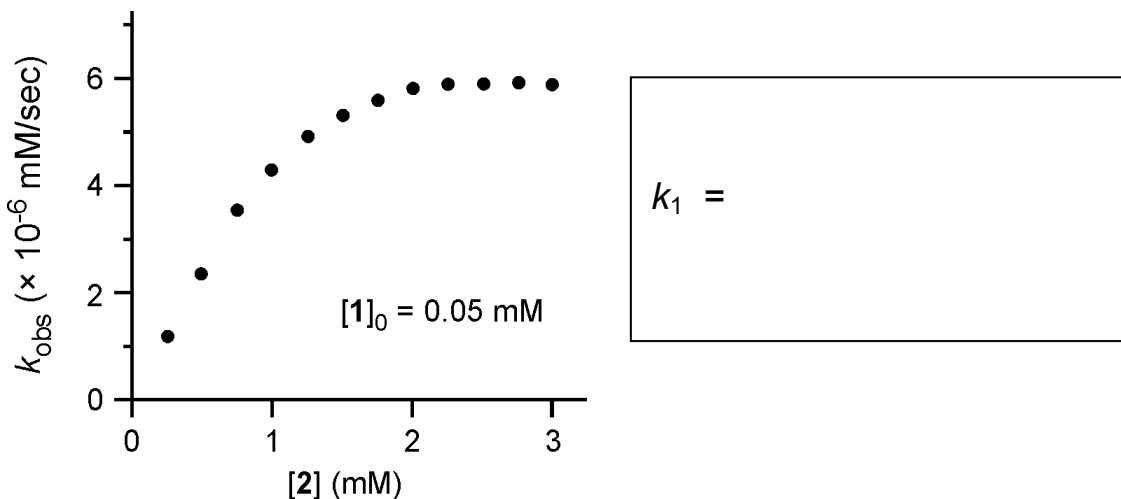
Calculations:

b. Adapting the answer to part (a) to the first-order expression in the problem,

$$k_{obs} = \frac{k_1 k_2 [\mathbf{2}]}{k_{-1}[\text{cyclohexene}] + k_2[\mathbf{2}]}$$

The graph shows that the rate of the reaction exhibits saturation kinetics at very high concentrations [**2**]. This is consistent with the expression above; as $k_2[\mathbf{2}]$ becomes much larger than $k_{-1}[\text{cyclohexene}]$,

$$k_{obs} \rightarrow \frac{k_1 k_2 [\mathbf{2}]}{k_2[\mathbf{2}]} = k_1.$$

The graph levels off at $k_{obs} = k_1 = 6 \times 10^{-6}$ mM/sec. The units on the vertical axis of the graph aren't correct—they should be /sec.

c) The investigators also constructed an Eyring plot, with the goal of determining activation parameters for the reaction:

slope = -1.11×10^4 K
intercept = 16.3

y-axis: $\ln(k_{obs}/T)$
x-axis: $1/T\ (\times\ 10^{-3}\ K^{-1})$
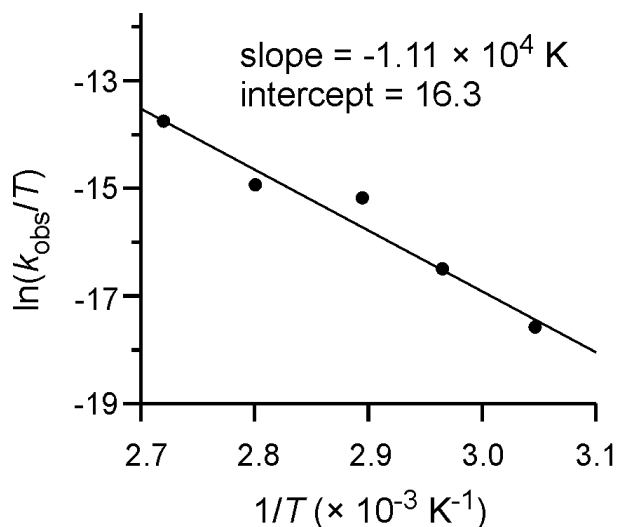
Calculate $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ and the activation energy E_a for the reaction from this plot.

$$\ln\left(\frac{k_{rxn}}{T}\right) = \left(\ln\frac{k_B}{h} + \frac{\Delta S^{\ddagger}}{R}\right) - \frac{\Delta H^{\ddagger}}{R}\left(\frac{1}{T}\right)$$
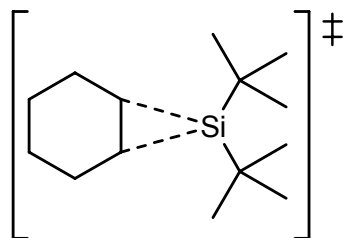
$slope = -\Delta H^{\ddagger}/R$
$intercept = \ln(k_B/h) + \Delta S^{\ddagger}/R$

$\Delta H^{\ddagger} = -(slope)(R)$
   $= -(-1.11 \times 10^4\ K)(1.99\ cal\ mol^{-1}\ K^{-1})$
   $= \textbf{22.1 kcal/mol} = \textbf{92.4 kJ/mol}$

$\Delta S^{\ddagger} = (R)[(intercept) - \ln(k_B/h)]$
   $= (1.99\ cal\ mol^{-1}\ K^{-1})[(16.3) - \ln(2.94 \times 10^{-24}\ cal\ K^{-1}/1.58 \times 10^{-34}\ cal\ sec)]$
   $= \textbf{-14.6 cal mol}^{-1}\ \textbf{K}^{-1} = \textbf{-61.1 J mol}^{-1}\ \textbf{K}^{-1}$

d) Propose a transition state for the reaction in **step 1**. Is $\Delta S^{\ddagger}$ you calculated consistent with **step 1** being rate-limiting? Explain

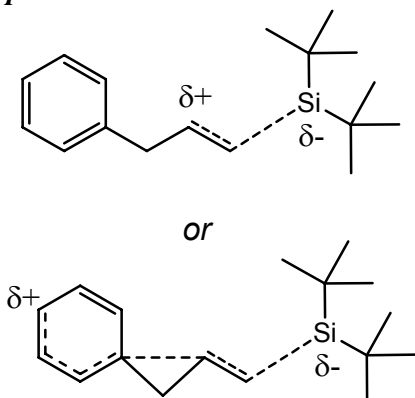**No**

Bonds are in the process of breaking in the transition state, and one molecule is becoming two molecules. You would expect positive $\Delta S\ddagger$ for this process, which is not consistent with the observed negative $\Delta S^{\ddagger}$.

e) Propose a transition state for the reaction in **step 2**. Is $\Delta S^{\ddagger}$ you calculated consistent with **step 2** being rate-limiting? Explain

Step 2 *transition state*

or

Yes or No, both are correct

$\Delta S^{\ddagger}$ refers to the difference in entropy between this TS and the starting material for the first step. Although SiR2 is in the process of binding to an alkene in either of the transition states shown above, there is still more disorder than in the already-bound starting material. So I would again positive $\Delta S^{\ddagger}$ for this process. BUT, in the second transition state above, closure of the cyclopropane ring constrains the system and increases order. So, $\Delta S^{\ddagger}$ could conceivably be negative for the cyclopropyl transition state only.