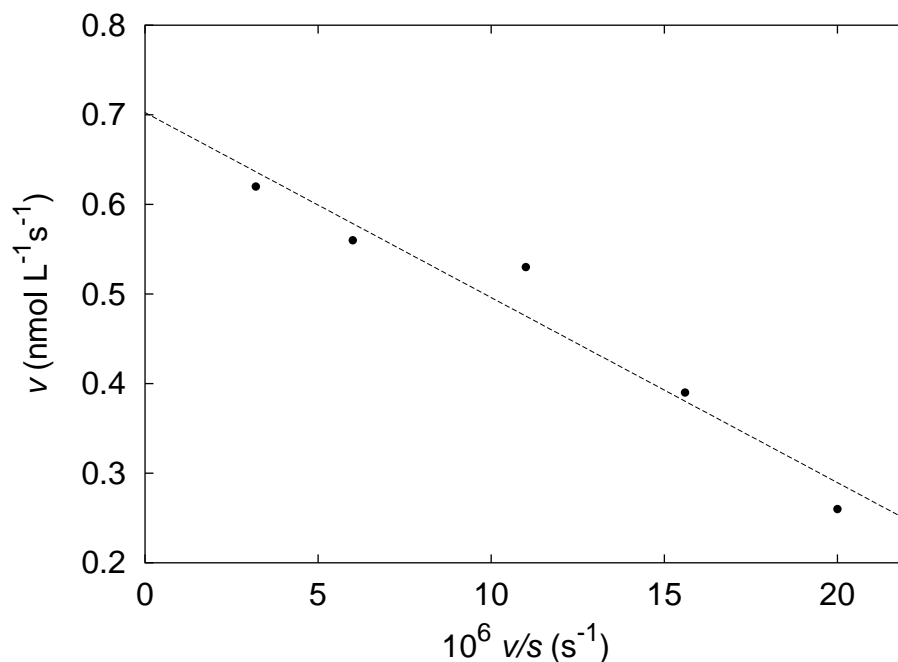# Chemistry 2710 Spring 2001 Assignment 4 Solutions

1. We construct an Eadie-Hofstee plot. Let $s = [\text{simazine}]$.

| v/s (s^{-1})	2.00×10^{-5}	1.56×10^{-5}	1.10×10^{-5}	6.02×10^{-6}	3.20×10^{-6}
v (nmol L^{-1}s^{-1})	0.26	0.39	0.53	0.56	0.62

The slope of the plot is $-21\,\mu\text{mol/L}$ so $K_M = 21\,\mu\text{mol/L}$. The intercept ($v_{\max}$) is $7.0 \times 10^{-10}\,\text{mol}\,\text{L}^{-1}\text{s}^{-1}$ so the specific activity is

$$\tilde{v}_{\max} = \frac{7.0 \times 10^{-10}\,\text{mol}\,\text{L}^{-1}\text{s}^{-1}}{400 \times 10^{-6}\,\text{g}} = 1.8\,\mu\text{mol}\,\text{L}^{-1}\text{s}^{-1}\text{g}^{-1}.$$

2. (a) We get the activation energy and preexponential factor by linear regression of $\ln k$ vs $1/T$. While we don't really need an Arrhenius plot, it's gratifying to see the data plotted in this form anyway. Here are the raw data for my Arrhenius plots:

	$\ln k$ for different substituents X				
T^{-1} (K^{-1})	-H	-CH$_3$	-OCH$_3$	-Cl	-NO$_2$
0.0022566	-10.815	-10.554	-10.272	-10.845	-11.128
0.0021591	-9.216	-8.948	-8.686	-9.257	-9.531
0.0020698	-7.702	-7.429	-7.149	-7.722	-8.004
0.0019875	-6.084	-5.826	-5.532	-6.092	-6.401

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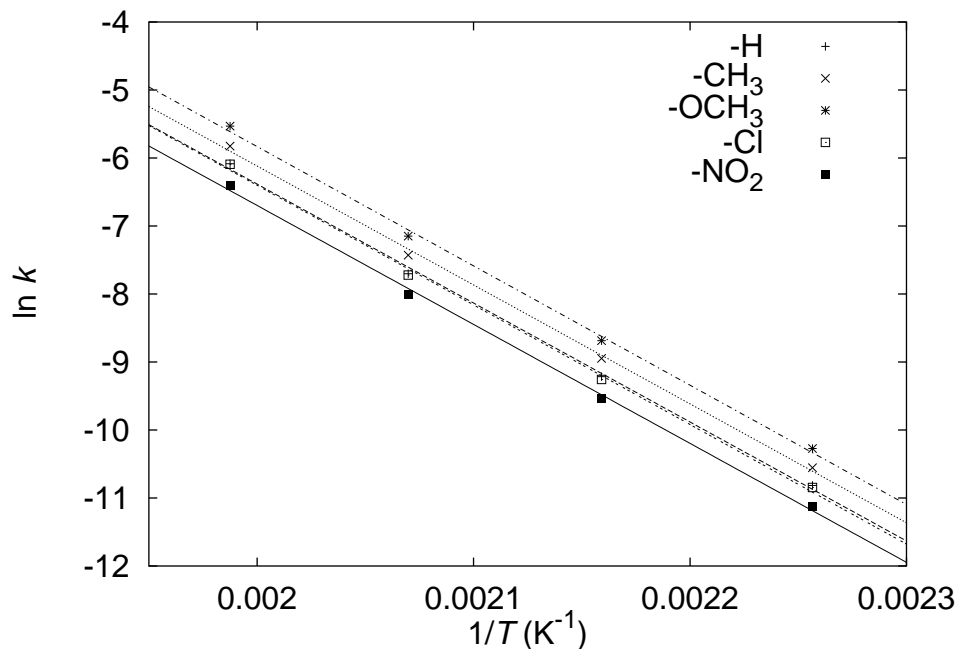
The activation energy is the slope of the Arrhenius plot multipled by $-R$. The preexponential factor k_∞ is the exponential of the intercept:

Substituent	slope (K)	intercept	$\bar{E}_a$ (kJ/mol)	k_∞ (s^{-1})
-H	-17492	28.60	145.44	2.63×10^{12}
-CH$_3$	-17489	28.86	145.42	3.41×10^{12}
-OCH$_3$	-17546	29.26	145.89	5.09×10^{12}
-Cl	-17586	28.77	146.22	3.13×10^{12}
-NO$_2$	-17494	28.29	145.45	1.93×10^{12}

(b) Since the reaction occurs in solution, the enthalpy and entropy of activation are calculated as follows:

$$\Delta \bar{H}^{\ddagger} = \bar{E}_a - RT.$$
$$\Delta \bar{S}^{\ddagger} = R\left[\ln\left(\frac{hk_\infty}{k_B T} \right) - 1 \right].$$

The results for the five reactions are

Substituent	$\Delta \bar{H}^{\ddagger}$ (kJ/mol)	$\Delta \bar{S}^{\ddagger}$ (J K^{-1}mol^{-1})
-H	141.50	-19.30
-CH$_3$	141.48	-17.14
-OCH$_3$	141.95	-13.82
-Cl	142.29	-17.84
-NO$_2$	141.52	-21.86

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There is very little variation in the enthalpy of activation. This means that the amount of energy required to reach the transition state is nearly independent of the substituents. On the other hand, there is significant variation in the entropy of activation. Since $\Delta \bar{S}^{\ddagger} = \bar{S}_{\text{TS}} - \bar{S}_{\text{reactant}}$, this can either be due to a significant variation in the "looseness" of the transition state, or to different degrees of disorganization in the reactant. The former seems unlikely. The triangular transition state is probably quite similar in all cases. (The approximate constancy of the activation energy suggests this.) However, it may be that the isocyanide group is either more or less mobile in the reactant depending on substituent effects.