

Chemistry 2740 Spring 2016 Test 4 solutions

1. First order
2. The data give the percentage of TBP dimers dissociated, but to apply the first-order rate law, we need the percentage that remains. This is $100\% - \%$ dissociated:

t/min	0.9	5.4	10.3	30.4	60.1	70.2
% remaining	95	88	73	35	14	7

We can now generate a graph of $\ln(\%$ remaining) vs t (figure 1). The data are well fit by the line.

The slope of the line of best fit was obtained by linear regression. The slope is $-0.0363 \pm 0.0018 \text{ min}^{-1}$. (I use a program that gives a standard error on the slope. This allows me to determine how many significant figures the slope has using the rule of 3 and 30. Since you don't have access to such a program, you can simply report your slope to a reasonable number of digits.) Accordingly,

$$k_d = -(\text{slope}) = 0.0363 \text{ min}^{-1}.$$

- 3.

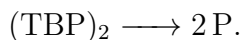
$$t_{1/2} = \frac{\ln 2}{k_d} = \frac{\ln 2}{0.0363 \text{ min}^{-1}} = 19.1 \text{ min}.$$

This is a surprisingly long time. These measurements, and others by the same group, have led to the suggestion that TBP dimer dissociation may be a rate-limiting step in transcription initiation.

4. We first write down the equilibrium condition:

$$\begin{aligned}k_d[(\text{TBP})_2] &= k_a[\text{TBP}]^2 \\ \therefore K_D &= \frac{[\text{TBP}]^2}{[(\text{TBP})_2]} = \frac{k_d}{k_a} \\ \therefore k_a &= \frac{k_d}{K_D} = \frac{0.0363 \text{ min}^{-1}}{4 \times 10^{-9} \text{ mol L}^{-1}} = 9 \times 10^6 \text{ L mol}^{-1} \text{ min}^{-1}.\end{aligned}$$

5. The overall reaction is obtained by doubling the second reaction and adding the two:



Thus,

$$v = \frac{1}{2} \frac{d[\text{P}]}{dt} = \frac{1}{2} k_x [\text{TBP}].$$

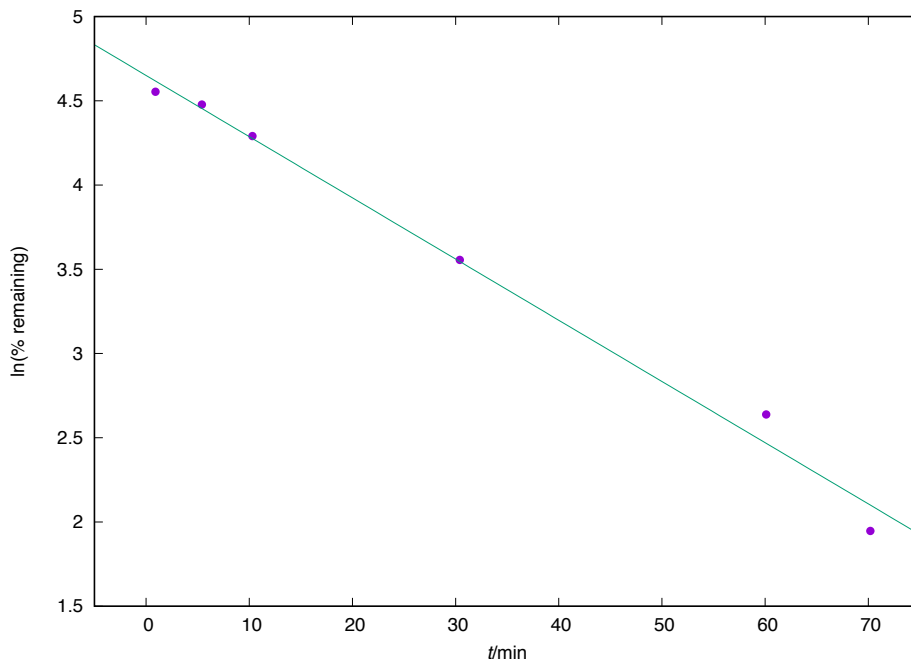


Figure 1: First-order plot for the TBP dissociation data.

Apply the equilibrium approximation to the first reaction:

$$\begin{aligned}
 k_d[(\text{TBP})_2] &\approx k_a[\text{TBP}]^2. \\
 \therefore [\text{TBP}] &\approx \sqrt{\frac{k_d}{k_a}[(\text{TBP})_2]}. \\
 \therefore v &\approx \frac{k_x}{2} \sqrt{\frac{k_d}{k_a}[(\text{TBP})_2]}.
 \end{aligned}$$

Note that, from question 4, $K_D = k_d/k_a$, so we could also write

$$v \approx \frac{k_x}{2} \sqrt{K_D[(\text{TBP})_2]}.$$

Bonus: Without the dimerization reaction, we would have

$$v_{\text{no dimer}} = k_x[\text{TBP}]. \quad (1)$$

Note that, since almost all of the TBP is in the form of TBP dimers, by stoichiometry, the concentration of TBP dimer is directly proportional to the total concentration of TBP: $[(\text{TBP})_2] \approx \frac{1}{2}[\text{TBP}]_{\text{total}}$, so that

$$v \approx \frac{k_x}{2} \sqrt{K_D[\text{TBP}]_{\text{total}}/2}. \quad (2)$$

In the case without dimerization, there is no distinction between $[\text{TBP}]$ and $[\text{TBP}]_{\text{total}}$. We can therefore compare the two rates, (1) and (2), directly. The two are plotted

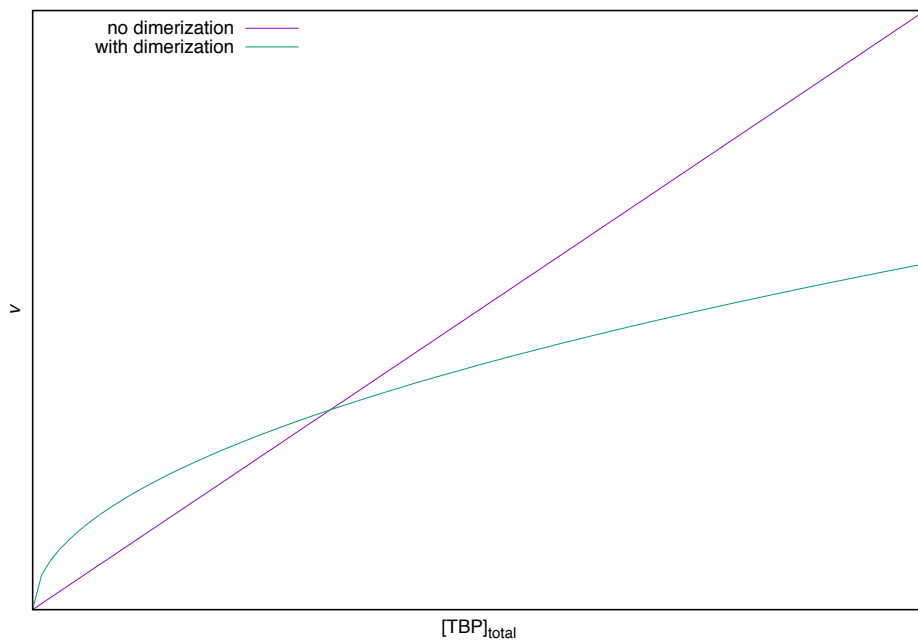


Figure 2: Rate of TBP degradation with and without dimerization

schematically in figure 2. Note that, provided $[\text{TBP}]_{\text{total}}$ is sufficiently large, the rate of TBP degradation is larger without dimerization than with. The small value of K_D means that this crossing will occur at small concentrations, in the nanomolar range.