

Lecture 34 CH102 A1 (MWF 9:05 am) Spring 2018 Copyright © 2017 Dan Dill dan@bu.edu

[TP] For $(\text{CH}_3)_3\text{CBr} + ^-\text{OCH}_3 \rightarrow (\text{CH}_3)_3\text{COCH}_3 + \text{Br}^-$
what is the value of k_{for} ?

25% 1. $2.8 \times 10^{-5} \text{ M s}^{-1}$
25% 2. $2.8 \times 10^{-1} \text{ s}^{-1}$
25% 3. $2.8 \times 10^{-1} \text{ M s}^{-1}$
25% 4. None of the above

$[(\text{CH}_3)_3\text{CBr}]$	$[^-\text{OCH}_3]$	Rate (M/s)
0.0001	0.0001	2.8×10^{-5}
0.0002	0.0001	5.6×10^{-5}
0.0001	0.0002	2.8×10^{-5}

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Friday, April 20, 2018

- Rate vs concentration from experiment
- Making sense of rate vs concentration: Reaction mechanism
- Making sense of rate constants: The Arrhenius relation

Next lecture: Complete: Making sense of rate constants: The Arrhenius relation. Rate versus temperature: E_a and A . Catalysis. Half-life.

Maxwell-Boltzmann kinetic energy distribution
<http://quantum.bu.edu/CDF/102/MaxwellBoltzmannEnergyDistribution.cdf>

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Rate versus concentration from experiment

We know how to define rate.

We also know that rate = $k \times$ concentration

So, we need to learn just how rate depends on concentration and what determines the rate constant, k .

We'll use data to learn how rate depends on concentration, the so-called **differential rate law**.

We'll see that each reaction will have its own particular dependence.

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Differential rate laws: rate vs concentration

In liquid methanol, CH_3OH , the following reaction occurs:

$$(\text{CH}_3)_3\text{CBr} + ^-\text{OCH}_3 \rightarrow (\text{CH}_3)_3\text{COCH}_3 + \text{Br}^-$$

Write a rate law for this reaction.

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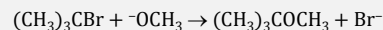
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Differential rate laws: rate vs concentration

In liquid methanol, CH_3OH , the following reaction occurs:



How can we know whether the predicted rate law is correct?

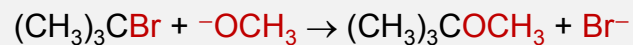
Measure rate for different combinations of reactant concentrations.



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$$\text{rate}_{\text{for}} \approx [(\text{CH}_3)_3\text{CBr}]^a, \text{rate}_{\text{for}} \approx [^-\text{OCH}_3]^b$$

1. What is the order, a , in $(\text{CH}_3)_3\text{CBr}$?
2. What is the order, b , in $^-\text{OCH}_3$?
3. What is the full differential rate law?
4. What is the value of the forward rate constant k_{for} ?



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[TP] For $(\text{CH}_3)_3\text{CBr} + ^-\text{OCH}_3 \rightarrow (\text{CH}_3)_3\text{COCH}_3 + \text{Br}^-$
what is the order in $(\text{CH}_3)_3\text{CBr}$?

1. 1
2. 2
3. Neither of the above
4. More info needed

$[(\text{CH}_3)_3\text{CBr}]$	$[^-\text{OCH}_3]$	Rate (M/s)
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Response
Counter

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[TP] For $(\text{CH}_3)_3\text{CBr} + ^-\text{OCH}_3 \rightarrow (\text{CH}_3)_3\text{COCH}_3 + \text{Br}^-$
what is the order in $^-\text{OCH}_3$?

1. 1
2. 2
3. Neither of the above
4. More info needed

$[(\text{CH}_3)_3\text{CBr}]$	$[^-\text{OCH}_3]$	Rate (M/s)
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[TP] For $(\text{CH}_3)_3\text{CBr} + ^-\text{OCH}_3 \rightarrow (\text{CH}_3)_3\text{COCH}_3 + \text{Br}^-$
what is the full differential rate law?

25% 1. $\text{rate} = k_{\text{for}} [(\text{CH}_3)_3\text{CBr}] [^-\text{OCH}_3]$

25% 2. $\text{rate} = k_{\text{for}} [(\text{CH}_3)_3\text{CBr}]$

25% 3. $\text{rate} = k_{\text{for}} [^-\text{OCH}_3]$

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[Quiz] For $(\text{CH}_3)_3\text{CBr} + ^-\text{OCH}_3 \rightarrow (\text{CH}_3)_3\text{COCH}_3 + \text{Br}^-$
what is the value of k_{for} ?

1. $2.8 \times 10^{-5} \text{ M s}^{-1}$

2. $2.8 \times 10^{-1} \text{ s}^{-1}$

3. $2.8 \times 10^{-1} \text{ M s}^{-1}$

4. None of the above

$[(\text{CH}_3)_3\text{CBr}]$	$[^-\text{OCH}_3]$	Rate (M/s)
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Making sense of rate vs concentration

From data, we have found that the differential rate law for

$$(\text{CH}_3)_3\text{CBr} + ^-\text{OCH}_3 \rightarrow (\text{CH}_3)_3\text{COCH}_3 + \text{Br}^-$$

is

$$\text{rate} = k_{\text{for}} [(\text{CH}_3)_3\text{CBr}]$$

Shouldn't the rate depend on $[^-\text{OCH}_3]$ too?

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Making sense of rate versus [...]

$$(\text{CH}_3)_3\text{CBr} + ^-\text{OCH}_3 \rightarrow (\text{CH}_3)_3\text{COCH}_3 + \text{Br}^-$$

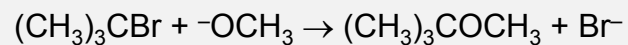
$$\text{rate} = k [(\text{CH}_3)_3\text{CBr}]$$

What reaction mechanism could account for rate **not depending** on $[^-\text{OCH}_3]$?

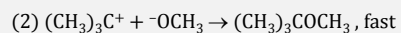
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A possible mechanism that accounts for rate **not depending** on $[\text{OCH}_3^-]$ is ...



Show that this accounts for the observed rate law.



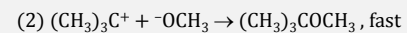
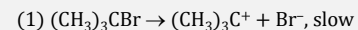
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Making sense of rate constants

The mechanism is



Reaction 1 is much slower than reaction 2 because ...

$k_{1,\text{for}}$ is **much smaller** than $k_{2,\text{for}}$

What determines the relative size of $k_{1,\text{for}}$ and $k_{2,\text{for}}$?



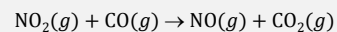
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Making sense of rate constants

To understand what determines the relative size of rate constants, let's begin by imagining how **enthalpy changes** as an **exothermic reaction**, such as



evolves as reactants, R, are transformed into products, P.

Sketch a diagram showing how enthalpy changes (vertical axis) as time passes (horizontal axis), starting with all reactants, R, and ending with all products, P.



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