 

[TP] For $(CH_3)_3CBr + {}^{-}OCH_3 \rightarrow (CH_3)_3COCH_3 + Br^{-}$ what is the value of $k_{for}$?

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

| $[(CH_3)_3CBr]$ | $[{}^{-}OCH_3]$ | Rate (M/s) |
|---|---|---|
| 0.0001 | 0.0001 | $2.8 \times 10^{-5}$ |
| 0.0002 | 0.0001 | $5.6 \times 10^{-5}$ |
| 0.0001 | 0.0002 | $2.8 \times 10^{-5}$ |

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0 of 0



# Lecture 34 CH102 A1 (MWF 9:05 am)

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 it own particular dependence.

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## Differential rate laws: rate vs concentration

In liquid methanol, $CH_3OH$, the following reaction occurs:

$(CH_3)_3CBr + {}^{-}OCH_3 \rightarrow (CH_3)_3COCH_3 + Br^{-}$

Write a rate law for this reaction.

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## Differential rate laws: rate vs concentration

In liquid methanol, $CH_3OH$, the following reaction occurs:

$(CH_3)_3CBr + {}^-OCH_3 \rightarrow (CH_3)_3COCH_3 + Br^-$

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

Measure rate for different combinations of reactant concentrations.

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## $(CH_3)_3CBr + {}^-OCH_3 \rightarrow (CH_3)_3COCH_3 + Br^-$

| $[(CH_3)_3CBr]$ | $[^-OCH_3]$ | Rate (M/s) |
|---|---|---|
| 0.0001 | 0.0001 | $2.8 \times 10^{-5}$ |
| 0.0002 | 0.0001 | $5.6 \times 10^{-5}$ |
| 0.0001 | 0.0002 | $2.8 \times 10^{-5}$ |

$rate_{for} \approx [(CH_3)_3CBr]^a$, $rate_{for} \approx [^-OCH_3]^b$

1. What is the order, $a$, in $(CH_3)_3CBr$?
2. What is the order, $b$, in $^-OCH_3$?
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 $(CH_3)_3CBr + {}^-OCH_3 \rightarrow (CH_3)_3COCH_3 + Br^-$ what is the order in $(CH_3)_3CBr$ ?

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

| $[(CH_3)_3CBr]$ | $[^-OCH_3]$ | Rate (M/s) |
|---|---|---|
| 0.0001 | 0.0001 | $2.8 \times 10^{-5}$ |
| 0.0002 | 0.0001 | $5.6 \times 10^{-5}$ |
| 0.0001 | 0.0002 | $2.8 \times 10^{-5}$ |

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[TP] For $(CH_3)_3CBr + {}^-OCH_3 \rightarrow (CH_3)_3COCH_3 + Br^-$ what is the order in $^-OCH_3$?

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

| $[(CH_3)_3CBr]$ | $[^-OCH_3]$ | Rate (M/s) |
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[TP] For $(CH_3)_3CBr + {}^-OCH_3 \rightarrow (CH_3)_3COCH_3 + Br^-$
what is the full differential rate law?

25% 1. rate = $k_{for}$ $[(CH_3)_3CBr]$ $[{}^-OCH_3]$
25% 2. rate = $k_{for}$ $[(CH_3)_3CBr]$
25% 3. rate = $k_{for}$ $[{}^-OCH_3]$
25% 4. Neither of the above

| $[(CH_3)_3CBr]$ | $[{}^-OCH_3]$ | Rate (M/s) |
|---|---|---|
| 0.0001 | 0.0001 | $2.8 \times 10^{-5}$ |
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| 0.0001 | 0.0002 | $2.8 \times 10^{-5}$ |

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[Quiz] For $(CH_3)_3CBr + {}^-OCH_3 \rightarrow (CH_3)_3COCH_3 + Br^-$
what is the value of $k_{for}$?

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

| $[(CH_3)_3CBr]$ | $[{}^-OCH_3]$ | Rate (M/s) |
|---|---|---|
| 0.0001 | 0.0001 | $2.8 \times 10^{-5}$ |
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| 0.0001 | 0.0002 | $2.8 \times 10^{-5}$ |

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0 of 0



 

## Making sense of rate vs concentration

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

$(CH_3)_3CBr + {}^-OCH_3 \rightarrow (CH_3)_3COCH_3 + Br^-$

is

rate = $k_{for}[(CH_3)_3CBr]$

Shouldn't the rate depend on $[{}^-OCH_3]$ too?

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## Making sense of rate versus […]

$(CH_3)_3CBr + {}^-OCH_3 \rightarrow (CH_3)_3COCH_3 + Br^-$

rate = $k\,[(CH_3)_3CBr]$

What reaction mechanism could account for rate not depending on $[{}^-OCH_3]$?

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## $(CH_3)_3CBr + {}^{-}OCH_3 \rightarrow (CH_3)_3COCH_3 + Br^-$

A possible mechanism that accounts for rate not depending on $[{}^{-}OCH_3]$ is …

(1) $(CH_3)_3CBr \rightarrow (CH_3)_3C^+ + Br^-$ , slow

(2) $(CH_3)_3C^+ + {}^{-}OCH_3 \rightarrow (CH_3)_3COCH_3$ , fast

Show that this accounts for the observed rate law.

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## Making sense of rate constants

The mechanism is

(1) $(CH_3)_3CBr \rightarrow (CH_3)_3C^+ + Br^-$, slow

(2) $(CH_3)_3C^+ + {}^{-}OCH_3 \rightarrow (CH_3)_3COCH_3$ , fast

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

$NO_2(g) + CO(g) \rightarrow NO(g) + CO_2(g)$

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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