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Class AP1,2,3

Kinetics II

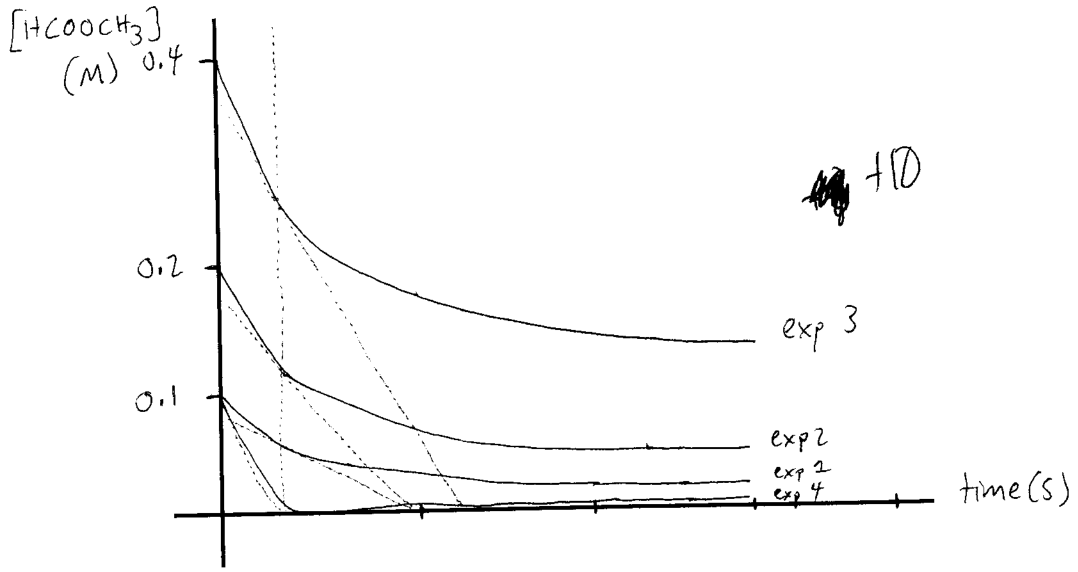
Consider the following rate table for the hydrolysis of methyl formate:

$$HC(O)OCH_3 + H_2O \rightarrow HCOOH + CH_3OH$$

| Exp | [HC(O)OCH$_3$] | [H2O] | Rate* | T (C) |
|---|---|---|---|---|
| 1 | 0.1 | 0.2 | $1.04 \times 10^{-3}$ | 15 |
| 2 | 0.2 | 0.2 | $2.08 \times 10^{-3}$ | 15 |
| 3 | 0.4 | 0.1 | $2.94 \times 10^{-3}$ | 15 |
| 4 | 0.1 | 0.3 | $6.64 \times 10^{-3}$ | 45 |

*The rate given is the rate of disappearance of methyl formate.

1. On the axes below, draw a rough plot of the concentration of methyl formate as a function of time for each of the experiments above. For full credit, you must:
   a) Label all axes with titles and units
   b) Indicate which curve goes with which experiment
   c) Indicate the initial concentration of methyl formate on each curve
   d) Use a dotted line (- - - - -) to indicate approximately how the initial rate was determined

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2. Calculate the order of the reaction with respect to each of the reactants, and determine the overall rate order.

$$\frac{r_2}{r_1} = \frac{k(15°C)[HCOOCH_3]_2^x[H_2O]_2^y}{k(15°C)[HCOOCH_3]_1^x[H_2O]_1^y}$$

$[H_2O]_2 = [H_2O]_1$

$$x = \ln(r_2/r_1) / \ln\left(\frac{[HCOOCH_3]_2}{[HCOOCH_3]_1}\right) = \frac{\ln(2.08\times10^{-3}/1.04\times10^{-3})}{\ln(0.2/0.1)} = 1$$

$$\frac{r_3}{r_2} = \frac{k(15°C)[HCOOCH_3]_3[H_2O]_3^y}{k(15°C)[HCOOCH_3]_2[H_2O]_2^y} \Rightarrow \frac{2.94\times10^{-3}}{2.08\times10^{-3}} = \frac{(0.4)(0.1)^y}{(0.2)(0.2)^y}$$

$y = 0.5$

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x = 1

y = 0.5

**overall order =** 1.5

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3. Write the rate law for the hydrolysis of methyl formate. Include the value of k at 15 C.

$$k = \frac{r}{[HCOOCH_3][H_2O]^{1/2}} = \frac{1.04\times10^{-3}}{(.1)(.2)^{1/2}} = 0.023\ M^{-1/2}\ s^{-1}$$

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$$r = k[HCOOCH_3][H_2O]^{1/2} = 0.023[HCOOCH_3][H_2O]^{1/2} = r$$

4. Calculate the activation energy for the hydrolysis of methyl formate (R = 8.314 J/mol K).

$$\frac{r_4}{r_1} = \frac{k(45°C)[HCOOCH_3]_4[H_2O]_4^{1/2}}{k(15°C)[HCOOCH_3]_1[H_2O]_1^{1/2}} \Rightarrow \frac{6.64\times10^{-3}}{1.04\times10^{-3}} = \frac{k(318K)(.1)(.3)^{1/2}}{k(288K)(.1)(.2)^{1/2}}$$

$$5.213 = \frac{k(318K)}{k(288K)} = \frac{Ae^{-Ea/318R}}{Ae^{-Ea/288R}}$$

$$5.213 = e^{-\frac{Ea}{R}\left(\frac{1}{318}-\frac{1}{288}\right)}$$

$$E_a = \frac{-R\ln(5.213)}{\left(\frac{1}{318}-\frac{1}{288}\right)} = 41.91\ kJ/mol$$

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**$E_a$ = 41.9 kJ/mol**

EC ~~5~~. If the concentration of water is high enough, we can assume it is constant (i.e., the reaction is first zero-order with respect to water). In this case, the concentration of methyl formate in water is given by the following expression

$$[\text{methyl formate}] = [\text{methyl formate}]_0 e^{-k_{eff}\times t}$$

where *[methyl formate]₀* is the concentration of methyl formate at the start of the reaction, $k_{eff}$ is the effective rate constant, and *t* is time.

Prove that the expression above agrees with the rate law you determined in question (3), and write an expression for $k_{eff}$ in terms of your *k* from question (3) and the concentration of water.

$$[\text{methyl formate}] = [\text{methyl formate}]_0 e^{-k_{eff}t}$$

$$r = -\frac{d}{dt}[\text{methyl formate}] = -[\text{methyl formate}]_0 \frac{d}{dt} e^{-k_{eff}t}$$

$$= -[\text{methyl formate}]_0 e^{-k_{eff}t}(-k_{eff})$$

$$= k_{eff}[\text{methyl formate}]_0 e^{-k_{eff}t}$$

$$r = k_{eff}[\text{methyl formate}]$$

$$r = k_{eff}[HCOOCH_3] \quad vs \quad r = k[HCOOCH_3][H_2O]^{1/2}$$

$$k_{eff} = k[H_2O]^{1/2}$$

The rate expressions agree, since both are first order with respect to $[HCOOCH_3]$.

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