

Answer Key for CYL110 Minor 2

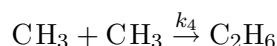
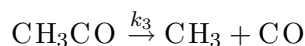
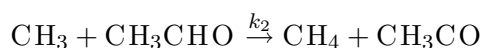
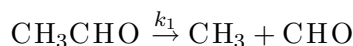
Date: Oct. 11, 2009

Narayanan Kurur

1. STATE whether the following statements are true or false. [5 × 2]

- (a) Knowledge of the rate law of a reaction allows us to decide unambiguously what the mechanism is. FALSE.
- (b) If the partial orders are equal to the corresponding coefficient in the balanced reaction, the reaction must be elementary. FALSE.
- (c) A two step reaction $A \xrightarrow{k_1} I \xrightarrow{k_2} P$ can be distinguished from a one step reaction $A \xrightarrow{k_1} P$ kinetically, if $k_1 \gg k_2$. TRUE
- (d) In a continuous flow method, the solution ages with time. FALSE.
- (e) The number of positive terms in the rate law is the number of independent, parallel pathways. TRUE

2. (a) The mechanism of the pyrolysis of acetaldehyde at 520 °C and 0.2 bar is



Apply the steady state approximation to the intermediates and obtain an expression for the rate law of this reaction. [20]

We setup the rate of change of the concentration of the two intermediates, the methyl and acetyl radicals. They are respectively

$$\frac{d[\text{CH}_3]}{dt} = k_1[\text{CH}_3\text{CHO}] - k_2[\text{CH}_3][\text{CH}_3\text{CHO}] + k_3[\text{CH}_3\text{CO}] - 2k_4[\text{CH}_3]^2, \quad (5 \text{ marks})$$

$$\frac{d[\text{CH}_3\text{CO}]}{dt} = k_2[\text{CH}_3][\text{CH}_3\text{CHO}] - k_3[\text{CH}_3\text{CO}] \quad (3 \text{ marks})$$

Adding these two expressions and setting them to zero (steady state approximation) we obtain

$$k_1[\text{CH}_3\text{CHO}] - 2k_4[\text{CH}_3]^2 = 0$$

which implies that

$$[\text{CH}_3] = \frac{k_1}{2k_4} \sqrt{[\text{CH}_3\text{CHO}]} \quad (5 \text{ marks})$$

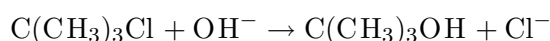
The rate of the reaction is

$$-\frac{d[\text{CH}_3\text{CHO}]}{dt} = k_1[\text{CH}_3\text{CHO}] + k_2[\text{CH}_3][\text{CH}_3\text{CHO}] \quad (3 \text{ marks})$$

Substituting the steady state $[\text{CH}_3]$ concentration obtained from the SSA into the above expressions yields the rate law to be

$$-\frac{d[\text{CH}_3\text{CHO}]}{dt} = k_1[\text{CH}_3\text{CHO}] + \frac{k_2 k_1}{2k_4} [\text{CH}_3\text{CHO}]^{3/2} \quad (4 \text{ marks})$$

(b) Suggest a plausible mechanism for the reaction: [15]



if the observed rate law is

$$-\frac{d[\text{C}(\text{CH}_3)_3\text{Cl}]}{dt} = \frac{k[\text{C}(\text{CH}_3)_3\text{Cl}][\text{OH}^-]}{k'[\text{Cl}^-] + k''[\text{OH}^-]}$$

If $k' \gg k''$ then the rate of the reaction reduces to

$$\text{Rate} = r = \frac{k[\text{C}(\text{CH}_3)_3\text{Cl}][\text{OH}^-]}{k'[\text{Cl}^-]}$$

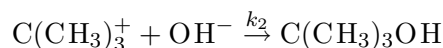
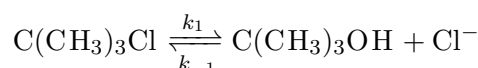
with a stoichiometry $\text{C}_4\text{H}_{10}\text{O}$. (3 marks)

At the other limit when $k'' \gg k'$ on the other hand we find that

$$\text{Rate} = r = \frac{k[\text{C}(\text{CH}_3)_3\text{Cl}][\text{OH}^-]}{k''[\text{OH}^-]}$$

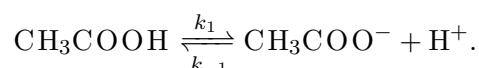
with a stoichiometry of $\text{C}_4\text{H}_9\text{Cl}$. (3 marks)

This suggests the mechanism

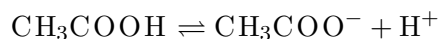


BY applying the steady state approximation to the *t*-butyl carbocation we obtain the observed rate of the reaction with $k' = k_1$, $k'' = k_2$, and $k = k_1 k_2$. (9 marks)

3. Relaxation studies at 25 °C yielded k_1 and k_{-1} values of $7.8 \times 10^5 \text{ s}^{-1}$ and $4.5 \times 10^{10} \text{ L mol}^{-1} \text{ s}^{-1}$, respectively, for the reaction



Determine the relaxation time for 1M acetic acid solution. [15] The concentration of acetate ions and proton (x let us say) in a 1M solution of acetic acid may be obtained from the equilibrium



where the equilibrium constant $K_a = \frac{k_1}{k_{-1}} = \frac{x^2}{1-x}$. From this relation we obtain x to be

$$x \approx \sqrt{K_a} = \sqrt{\frac{7.8 \times 10^5}{4.5 \times 10^{10}}} = 4.16 \times 10^{-3}. \quad (5 \text{ marks})$$

The relaxation time τ for a reaction $\text{A} \rightleftharpoons \text{B} + \text{C}$ is

$$\tau = \frac{1}{k_{-1}([\text{A}_{\text{eq}}] + [\text{B}_{\text{eq}}]) + k_1} = \frac{1}{2xk_{-1} + k_1}, \quad (5 \text{ marks})$$

which evaluates to

$$\tau = 2.67 \times 10^{-9} \quad (5 \text{ marks})$$

4. Consider a particle confined to move in the region $-a/2 \leq x \leq a/2$ and whose wavefunction is $\Psi(x, t) = \cos(\pi x/a) \exp(-i\omega t)$. [8 × 5]

- (a) Find the potential $V(x)$ and hence write the Hamiltonian.

$$i\hbar \frac{\partial}{\partial t} \Psi(x, t) = \left(-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x) \right) \Psi(x, t)$$

$$\hbar\omega \Psi(x, t) = \left(-\frac{\hbar^2}{2m} - \frac{\pi^2}{a} + V(x) \right) \Psi(x, t)$$

$$V(x) = 0. \quad (3 \text{ marks})$$

$$\hat{\mathcal{H}} = \hat{T} + \hat{V} = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2}. \quad (2 \text{ marks})$$

- (b) What is the probability of finding the particle in the region $-a/6 \leq x \leq a/6$?

$$P(-a/6 \leq x \leq a/6) = \frac{2}{a} \int_{-a/6}^{a/6} \Psi^*(x, t) \Psi(x, t) dx = \frac{2}{a} \int_{-a/6}^{a/6} \cos^2\left(\frac{\pi x}{a}\right) dx \quad (3 \text{ marks})$$

$$P(-a/6 \leq x \leq a/6) = 0.608 \quad (2 \text{ marks}).$$

- (c) What is the expectation for the energy of the particle in this state? The straightforward way is to observe that $\Psi(x, t)$ is an energy eigenfunction so that

$$\hat{\mathcal{H}}\Psi(x, t) = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \Psi(x, t) \quad (2 \text{ marks})$$

$$\frac{\hbar^2}{2m} \left(\frac{\pi}{a}\right)^2 \Psi(x, t) \quad (2 \text{ marks})$$

and so the expectation for the energy is the eigenvalue or in other words

$$\langle E \rangle = E = \frac{\hbar^2}{8ma^2} \quad (1 \text{ mark}).$$

$$\langle E \rangle = \frac{2}{a} \int_{-a/2}^{a/2} \Psi^*(x, t) \hat{\mathcal{H}}\Psi(x, t) dx = \frac{2}{a} \int_{-a/2}^{a/2} \Psi^*(x, t) \left(-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \right) \Psi(x, t) dx \quad (3 \text{ marks})$$

$$\langle E \rangle = \frac{\hbar^2}{2m} \left(\frac{\pi}{a}\right)^2 = \frac{\hbar^2}{8ma^2} \quad (2 \text{ marks})$$

- (d) What is the uncertainty in the energy measurement?

The uncertainty in the energy, ΔE , is 0 because $\Psi(x, t)$ is an energy eigenfunction. (5 marks)

Alternatively you could show that

$$\Delta E = \sqrt{\langle \hat{\mathcal{H}}^2 \rangle - \langle \hat{\mathcal{H}} \rangle^2} \quad (1 \text{ mark})$$

$$= \frac{2}{a} \int_{-a/2}^{a/2} \Psi^*(x, t) \left(-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \right)^2 \Psi(x, t) dx - \left(\frac{2}{a} \int_{-a/2}^{a/2} \Psi^*(x, t) \left(-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \right) \Psi(x, t) dx \right)^2$$

After a lot of completely mindless algebra, which is unnecessary as is seen from the first solution given above, one can show that!

$$\Delta E = 0 \quad (2 \text{ marks})$$

- (e) An operator $\hat{\mathcal{P}}$ is defined as $\hat{\mathcal{P}}\psi(x) = \psi(-x)$. Show that $\hat{\mathcal{P}}$ is an acceptable quantum mechanical operator.

Verify that

$$\hat{\mathcal{P}}(c_1\Psi_1 + c_2\Psi_2) = c_1\hat{\mathcal{P}}\Psi_1 + c_2\hat{\mathcal{P}}\Psi_2 \quad (2 \text{ marks})$$

and

$$\int \Psi(x, t)^* \hat{\mathcal{P}}\Psi(x, t) d\tau = \int (\hat{\mathcal{P}}\Psi(x, t))^* \Psi d\tau \quad (3 \text{ marks})$$

- (f) Is $\Psi(x, t)$ an eigenfunction of $\hat{\mathcal{P}}$? If so, what is its eigenvalue?

$$\hat{\mathcal{P}}\psi(x) = \psi(x) \quad (3 \text{ marks})$$

Hence $\Psi(x, t)$ is an eigenfunction of $\hat{\mathcal{P}}$ with an eigenvalue of 1. (2 marks)

- (g) Decide whether $\hat{\mathcal{P}}$ commutes with the Hamiltonian.

Because $\Psi(x, t)$ is an eigenfunction of both $\hat{\mathcal{P}}$ and $\hat{\mathcal{H}}$, it implies that $[\hat{\mathcal{P}}, \hat{\mathcal{H}}] = 0$. (5 marks)

Alternatively, one has to show that if $\hat{\mathcal{P}}$ and $\hat{\mathcal{H}}$ commute then it implies that

$$[\hat{\mathcal{P}}, \hat{\mathcal{H}}] = 0 \quad (2 \text{ marks})$$

$$[\hat{\mathcal{P}}, \hat{\mathcal{H}}]\Psi(x, t) = (\hat{\mathcal{P}}\hat{\mathcal{H}} - \hat{\mathcal{H}}\hat{\mathcal{P}})\Psi(x, t) = 0 \quad (3 \text{ marks})$$

- (h) If another wavefunction of the particle is $\Psi'(x, t) = \sin(2\pi x/a) \exp(-i\omega t)$, determine whether $\Psi(x, t)$ and $\Psi'(x, t)$ are orthogonal.

Orthogonality implies that

$$\int_{-a/2}^{a/2} \Psi(x, t)^* \Psi'(x, t) dx = 0 \quad (2 \text{ marks}).$$

$$\int_{-a/2}^{a/2} \sin(2\pi x/a) \cos(\pi x/a) dx = 0. \quad (3 \text{ marks}).$$