CHM 331

PHYSICAL CHEMISTRY III

PART B

MAXWELL – BOLTZMAN'S STATISTICS

Boltzmann distribution represents the most probable configuration of energy for a molecular system at equilibrium. It is used to derive important thermodynamics properties of the system. The distribution of energy associated with the dominant configuration is known as Boltzmann distribution.

Introduction

Configuration is a general arrangement of total energy available to the system available to the system.

A microstate is a specific arrangement of energy that describes the energy contained by each individual oscillator. Microstates are equivalent to permutations.

Energy levels for oscillators are given by

$$E_\nu = h\nu (n + \tfrac{1}{2}), \quad n = 0, 1, 2 \text{ ---- } \infty \qquad (i)$$

ν = oscillator frequency
n = quantum number associated with a given energy level of the oscillator.
A modified version of the harmonic oscillator is given as

$$E_n = h\nu n, \qquad n = 0, 1, 2 \text{ ---- } \infty \qquad (ii)$$

For a ground state energy n = 0

Microstates and Configurations

By extending the concept of probability theory to chemical systems, the configurations with the largest number of corresponding permutations is the most probable configuration.

$$P_E = E/ N,$$

Where, P_E = probability of the configuration trial outcome
E = number of permutation associated with the event of interest.
N = total number of possible permutations
The most likely configurationally outcome for a trial is the configuration the greatest number of associated permutations.

$$\text{Number of microstates} = \frac{N!}{a_0! a_1! a_2! --- a_n!} = \frac{N!}{\prod a_n!} \qquad (iii)$$

a_n = occupational number , it describes the number of units occupying a given energy level e.g. in the configuration 3, 0, 0, $a_0 = 2$, $a_3 = 1$, and all other $a_n = 0$ which is 0!, = 1.
The probability of observing a configuration is given as

$$\text{Pi} = \frac{Wi}{W1 + W2 + \cdots + WN} = \frac{Wi}{\sum_{j=1}^{N} Wj} \qquad \text{(iv)}$$

Configuration with the largest weight is called the predominant configuration.

Dominant configuration = dln W/d X = 0   (v)

The sum of all probabilities is unity

$$P1 + P2 + \cdots + Pm = \sum_{i=1}^{m} Pi = 1 = Ptotal \qquad \text{(vi)}$$

Pi = 1/n , n = total number of variables

$$P_E = 1/N = 1/N + \cdots + \frac{1}{N} = J/N = E/N \qquad \text{(vii)}$$

For a series of manipulations M1, M2... Mj having nj ways to perform the entire series manipulations, the total number of ways to perform the entire series of manipulations (total M) is
$$\text{Total M} = (n1)(n2)...(nj) \qquad \text{(viii)}$$

Total number of permutation = n! of n objects.

P (n, j) represents the number of permutations possible using a subset of j objects from the total group of n,

$$P (n, j) = n (n-1)\ldots (n-j+1) = \frac{n\,(n-1)\ldots(1)}{(n-j)(n-j-1)\ldots(1)} = \frac{n!}{(n-j)!} \qquad \text{(ix)}$$

Configuration is an unordered arrangement of objects manipulated = n
Subset of objects = j

Configuration is $C (n, j) = P (n, j)/ j! = \frac{n!}{j(n-j)!}$ (x)

Stirling's Approximation

- Provides a simple method of calculating the natural log of N! It is written as

$$\ln N! = N \ln N - N \qquad \text{(xi)}$$
it is derived as follows;
$$\ln N! = \ln [(N) (N-1) (N-2)\cdots(2)(1)] = \ln [(N) + \ln (N-1) + (N-2) + \cdots + \ln(2) + \ln (1)]$$
$$= \sum_{n=1}^{N} \ln n = \int_1^N \ln(n)\, dn = N \ln N - N - (1\ln 1 - 1) = N \ln N - N$$
      (xii)

Derivation of Boltzmann distribution
$$\text{Dominant configuration} = \frac{dln\ W}{dX} = 0$$
$$\ln W = \ln N! - \ln \prod_n an! = N \ln N -$$

By differentiation,

$$\frac{d\ln W}{dan} = \frac{dN}{dan}\ln N + N\frac{d\ln N}{dan} - \sum d(an\ln an)/da$$

$$N = \sum an$$

Applying this to the energy spacing;

$$BD = e^{-\beta En} = e^{-\beta\left(\frac{n}{\beta}\right)} = e^{-n} \qquad (1)$$

The partition function is the summation over the energy levels

$$q = \sum_{n=0}^{\infty} e^{-n} = 1 + e^{-1} \qquad +e^{-2} + \cdots = \frac{1}{1-e^{-1}} = 1.58 \qquad (2)$$

$$\text{For } x < 1, \qquad \frac{1}{1-x} = 1 + x + x^2 + \ldots$$

The probability of an oscillator occupying the first three levels 0, 1, 2, is

$$P0 = \frac{e^{-\beta E0}}{q} = e^{-0} / 1.58 = 0.633$$

$$P1 = \frac{e^{-\beta E1}}{q} = e^{-1} / 1.58 = 0.233$$

$$P2 = \frac{e^{-\beta E2}}{q} = e^{-2} / 1.58 = 0.086$$

Partition function provides a measure of the number of energy levels of that are occupied for a given value of β. Atomic and molecular systems have degenerate energy levels

$$q = \sum_n gn e^{-\beta En}$$

$$Pi = \frac{gi e^{-\beta E1}}{q}$$

The canonical partition function is defined as

$$Q = \sum_i e^{-\beta Ei}$$

$$Q = \sum_n e^{-\beta En} = \sum_n e^{-\beta(EAn + EBn)}$$

E_{An} and E_{Bn} are energy levels associated with unit B respectively

Assuming that the levels are quantized,

$$Q = \sum_n e^{-\beta(EAn+EBn)} = e^{-\beta(EAo+EBo)} + e^{-\beta(EAo+EB1)} + e^{-\beta(EAo+EB2)} + ... +$$
$$e^{-\beta(EA1+EBo)} + e^{-\beta(EA1+EB1)} + e^{-\beta(EA1+EB2)} + ... + e^{-\beta(EA2+EBo)} + e^{-\beta(EA2+EB1)} +$$
$$e^{-\beta(EA2+EB2)} + ...$$

$$= (e^{-\beta Eo} + e^{-\beta EA1} + e^{-\beta EA2} + ... \chi e^{-\beta EB0} + e^{-\beta EB1} + e^{-\beta EB2} + ...) = (q_A)(q_B) = q^2$$

$$Q = q^N \text{ for N distinguishable units}$$

The quantized energy levels of the molecular/atomic system are embedded in the molecular partition function, q, and this partition function can be used to define the partition function for the ensemble Q which can be directly related to the thermodynamic properties of the ensemble.

$$Q = q^N/N! \text{ For N indistinguishable units}$$

$$P(Ei) = Wi \ \frac{e^{-\beta E1}}{Q}$$

gn represents the number of states present at a given energy level i.e. the degeneracy of the levels.

β is defined as;

$$d \ln W = \beta dE$$

β is the proportionality constant in the above relationship, the unit β is the inverse energy

if β_x and β_y are β values associated with the initial ensembles x and y. dEx and dEy refer to the change in total energy for the individual assemblies.

$$dE_x + dE_y = 0$$

$$\text{if } dE_x \text{ is positive, then } \beta_x \geq \beta_y \ .$$

In thermodynamics, temperature is a measure of internal kinetic energy, therefore, an increase in the energy will be accompanied by an increase in temperature of assembly x so before equilibrium is established, thermodynamic consideration dictates that

$$T_y \geq T_x$$

β is inversely related to T.

$$\beta = 1/k \ T$$

k is Boltzmann's constant = 1.381 x 10^{-23} JK^{-1}

Physical meaning of the Boltzmann distribution law
- All microstates are equally probable; with a microstate associated with the dominant configuration.

- Configurations having a significant number of microstates are only infinitesimally different from the dominant configuration. The macroscopic properties of the system will be identical to that of the dominant configuration.
- The macroscopic state of the system is called the equilibrium state
- The equilibrium state is of the system is characterized by the dominant configuration
- The Boltzmann distribution law describes the energy distribution associated with a chemical system at equilibrium.

MOLECULAR ENERGY LEVELS

The molecular partition function can be evaluated by considering molecular energy levels. For polyatomic molecules, there are four energetic degrees of freedom to consider in constructing the molecular partition function:

- Translation
- Rotation
- Vibration
- Electronic

Assuming the energetic degrees of freedom are not coupled, the total molecular partition function that includes all of these degrees of freedom can be decomposed into a product of partition functions corresponding to each degree of freedom.
If ε_{total} represents the energy associated with a given molecular energy level. This energy will depend on the translational, rotational, vibrational, and electronic level energies as follows:
$\varepsilon_{total} = \varepsilon_T + \varepsilon_R + \varepsilon_V + \varepsilon_E$ Using the expression for the total energy and substituting into the expression for the partition function, the following expression is obtained:

$$q_{Total} = \Sigma \, g_{Total} \, e^{-\beta\varepsilon}{}_{Total}$$
$$= \Sigma \, (g_T \, g_R \, g_V \, g_E) e^{-\beta(\varepsilon_T + \varepsilon_R + \varepsilon_V + \varepsilon_E)}$$
$$= \Sigma \, (g_T{}^{e-\beta\varepsilon}{}_T) \, (g_R{}^{e-\beta\varepsilon}{}_T) \, (g_R{}^{e-\beta\varepsilon}{}_R) \, (g_V{}^{e-\beta\varepsilon}{}_V) \, (g_E{}^{e-\beta\varepsilon}{}_E)$$
$$= q_T \, q_R \, q_V \, q_E$$

The total molecular partition function is simply the product of partition functions for each molecular energetic degree of freedom. Using this definition for the molecular partition, the final relationships of interest are

$$Q_{Total} = q^N{}_{Total} \text{ (distinguishable)}$$
$$Q_{Total} = \frac{1}{N!} Q^N{}_{Total} \text{ (indistinguishable)}$$

Translational energy levels correspond to the translational motion of atoms or molecules in a container of volume V. By employing a one-dimensional model, from quantum mechanics, the energy levels of a molecule confined to a box were described by the "particle-in-a-box" model.

$$Q_{T, 1 D} = \sum_{n=1} e^{\frac{-\beta n^2 h^2}{8ma^2}}$$

The summation consists of an infinite number of terms. The spacing between energy translational energy states is considered. Because numerous translational energy levels are

accessible at room temperature, the summation, in the equation, above can be replaced by integration with negligible error:

$$Q_T = \sum e^{-\beta \alpha n2} = \int e^{-\beta \alpha n2} \, dn$$

In this expression, the following substitution was made to keep the collection of constant terms compact:

$$\propto = \frac{h^2}{8ma^2}$$

The integral in equation is evaluated as;

$$Q_T = \int e^{-\beta \alpha n2} \, dn = \frac{1}{2} \sqrt{\frac{\pi}{\beta \alpha}}$$

Substituting for α, the translational partition function in one dimension becomes

$$Q_{T,\,1D} = \left(\frac{2\pi m}{h^2 \beta}\right)^{1/2} \alpha$$

This expression can be simplified by defining the thermal de Broglie wavelength, or simply the thermal wavelength, as follows:

$$\Lambda = \left(\frac{h^2 \beta}{2\pi m}\right)^{1/2}$$

Such that

$$q_{T,\,1D} = \frac{a}{\Lambda} = (2\pi mkT)^{1/2}\frac{a}{h}$$

Referring to Λ as the thermal wavelength reflects the fact that the average momentum of gas particle, p, is equal to $(mkT)^{1/2}$. Therefore, Λ is defined as h/p or the deBroglie wavelength of the particle. The three-dimensional translational partition function is the product of one-dimensional partition functions for each dimension:

$$Q_{T,\,3.d} = Q_{Tx}\, Q_{Ty}\, Q_{Tz}$$
$$= \left(\frac{a_x}{\Lambda}\right)\left(\frac{a_y}{\Lambda}\right)\left(\frac{a_z}{\Lambda}\right)$$
$$= \left(\frac{1}{\Lambda}\right)^3 a_x\, a_y\, a_z$$
$$= \left(\frac{1}{\Lambda}\right)^3 v$$

Where v is volume and Λ is the thermal wavelength. The translation partition is a function of both V and T. The increase in q_T with volume reflects the fact that as volume is increased, the translational energy – level spacings decreased such that more states are available for population at a given T. Given the small energy spacings between translational energy levels relative to k T at room temperature, it is expected that at room temperature a significant number of translational energy states are accessible. The magnitude of the translational partition function

q_T in three dimension is written as; $\quad \dfrac{V}{\Lambda^3}$

$$\Lambda^3 = (h^2 \beta/2\pi m)^{3/2}$$

The translational contribution to the internal energy is given as;

$$U_T = 3/2 \ NkT = 3/2 \ Nrt$$

ROTATIONAL PARTITION FUNCTION FOR DIATOMIC MOLECULES
A diatomic molecule consists of two atoms joined by a chemical bond. In treating rotational motion of diatomic molecules, the rigid rotor approximation is employed. The bond length is assumed to be constant during rotational motion and centrifugal distortions are neglected.

E_j is dependent on the rotational quantum number J

$$E_j = BJ \ (J+1) \text{ for } J = 0, 1, 2,...$$

B is the rotational constant and is defined by
$$B = \frac{h}{8\pi^2 cI}$$

I is the moment of inertia is written as $I = \mu r^2$

$$\mu = \frac{m1m2}{m1+m2}$$

$$q_R = \sum_j g_j \ e^{-\beta hcBJ(J+1)}$$

$$q_R = \sum_j (2J+1) \ \ e^{-\beta hcBJ(J+1)}$$

By assuming that the rotational energy – level spacings are small relative to k T, the rotational partition function evaluated by integration over the rotational states;

$$q_R = \int_0^\infty (2J+1) \ e^{-\beta hcBJ(J+1)}$$
$$= \frac{d}{dJ} -\boldsymbol{\beta} hcB(2J+1) \ e^{-\beta hcBJ(J+1)}$$

The rotational partition function is written as;

$$q_R = \frac{1}{\beta hcB} = \frac{kT}{hcB}$$

To correct for over counting the symmetry number σ is incorporated into the expression of the rotational partition function

$$q_R = \frac{1}{\sigma \beta hcB} = \frac{kT}{\sigma hcB}$$

 Discuss how to calculate σ in class

Rotational temperature; $\square_R = \frac{hcB}{k}$

Therefore; $q_R = \dfrac{1}{\sigma\beta hcB} = \dfrac{kT}{\sigma hcB} = \dfrac{T}{\sigma\theta_R}$

The internal energy from rotation is given as;

$U_R = NkT = nRT$ for linear atomic polyatomic molecules

$U_R = 3/2\ nRT$ for non - linear polyatomic molecules

VIBRATIONAL PARTITION FUNCTION

The energy levels of the harmonic oscillator are as follows;

$$E_n = hc\,\bar{v}\,(n + \tfrac{1}{2})$$

The vibrational partition function is written as;

$$qv = \frac{e^{-\beta hc\bar{v}/2}}{1-e^{-\beta hc\bar{v}}} \quad \text{(with zero point energy)}$$

$$qv = \frac{1}{1-e^{-\beta hc\bar{v}}} \quad \text{(without zero point energy)}$$

Vibrational temperature; $\square v = \dfrac{hc\bar{v}}{k}$ is defined as the frequency of a given vibrational

degree of freedom divided by k. Thus the vibrational partition function is written as;

$$qv = \frac{1}{1-e^{-\beta hc\bar{v}}} = \frac{1}{1-e^{-\beta hc\bar{v}/kT}} = \frac{1}{1-e^{-\theta_V/T}}$$

$\square_\square$ becomes smaller as T and q_v increases. In the high temperature limit q_v becomes

$$qv = \frac{T}{\Theta_V}$$

The vibrational contribution to the average energy is;

$$U_V = \frac{Nhc\,\bar{v}}{e^{\beta hc\bar{v}} - 1}$$

$$U_V = N/\beta = NkT = nRT$$

ELECTRONIC PARTITION FUNCTION

$$En = \frac{-m_e\,e^4}{8\,\varepsilon^2\,h^2\,n^2} \quad (n = 1, 2, 3,..)$$

$$q_E = \sum_n gn\,e^{-\beta hcEn}$$

if the energy level is very large compared to kT, $q_E \approx g0$(the degeneracy of the ground state)

$$\Box_E = \frac{hcEn}{k}$$

Because electronic energy – level spacings are generally large compared to kT, the partition function is equal to the ground state degeneracy which is a constant, β is zero. Therefore,

$$U_g = 0$$

THE EQUIPARTITION THEOREM

This states that any term in the classical Hamiltonian that is quadratic with respect to momentum or position (p2 and x2) will contribute kT/2 to the average energy. i. e the change in energy associated with passing from one energy level to the other must be significantly less than kT. This true for translational and rotational degrees of freedom but not for vibrational degrees of freedom except at relatively high temperatures.
Classical Hamiltonian in one – dimension is given as

$$H = \frac{p^2}{2\mu} + \frac{1}{2}kx^2$$

HEAT CAPACITY

Heat capacity at constant volume $C_v = - k\, \beta^2 \left[\frac{\partial U}{\partial \beta}\right]_v$

Translational heat capacity at constant volume is;

$$(Cv)_T = \left(\frac{dU}{dT}\right)_v = 3/2\ Nk$$

The rotational heat capacity is;

$(CV)_R = Nk$ (linear molecules) and 3/2 Nk for non linear molecules
Vibrational heat capacity is given as;

$$(CV)_V = Nk\beta^2 (\, hc\, \beta^2\, \overline{v}\,)^2\ \frac{Nhc\ \overline{v}}{(e^{\beta hc\overline{v}} - 1)^2}$$

Q electronic is equal to g.s degeneracy, average energy is zero. Cv at constant volume is zero.

ENTROPY

Boltzmann formula for entropy is

$$S = k\ \ln W$$

Skipping several steps of derivation,

$$S = \frac{E}{T} + k \ln Q = \frac{U}{T} + \ln Q$$

$$S = \left(\frac{d}{dT} (kT \ln)Q \right)_v$$

Sackur – Tetrode equation

$$S = n \, R \ln \left(\frac{RTe^{5/2}}{\Lambda^3 P \, N_A} \right)$$

$$\Lambda^3 = \left(\frac{h^2}{2\pi mkT} \right)^{3/2}$$

For an isothermal expansion of an ideal monatomic gas from initial volume Vi to a final volume Vf;

$\Delta S = S_{final} - S_{initial} = nR \ln V_f/V_i$

At different temperatures T1 and T2 ;

$\Delta S = S_{final} - S_{initial} = 3/2 \, nR \ln \frac{T1}{T2} = n \, C_v \ln \frac{T1}{T2}$

INTRODUCTION TO QUANTUM CHEMISRTY

Quantum mechanics predicts that atoms and molecules can only have discrete energies and thereby provides a basis for understanding all spectroscopies.
It is useful for calculations of chemical properties of biologically important molecules that are useful in the design for specific applications before they are tsted in the laboratory.
Technology is increasingly based on QM e.g. quantum computation that describes a state by zero or one is an active area of research.

QUANTUM MECHANICS AND CLASSICAL PHYSICS

Experimental evidence has been presented for two properties that distinguish Qm from classical physics. They are as follows

- Quantization; energy at the atomic level is not a continuous variable, but comes in discrete packets called quanta
- Wave – particle duality. Light waves have particle – like properties, and atoms and subatomic particles such as electrons have wave – like properties.
- The experiments on blackbody radiation and the photo electric effects (photochemistry) describe the wave – particle duality of light.

Classical physics predicted the following on photoelectric effect

- Light is incident as a plane wave over the whole Cu plate and tit is absorbed by many electrons in the solid.
- Electrons are emitted for all light frequencies provided the intensity of light is sufficient
- The kinetic energy per electron increases with the intensity of light

The results of the experiment on photoelectric effect can be summarized as follows

- The number of emitted electrons is proportional to the intensity of light, their kinetic energy is independent of the intensity of light
- Electrons are emitted above the threshold frequency v_0 even at high intensities
- The kinetic energy of the emitted electrons depends on the frequency
- The law of conservation of energy holds

Energy of light is proportional to its frequency. Einstein equation is

$$E = \Phi \square , (\Phi \text{ is a constant known as the Planck's constant h})$$

$$E = h\square$$

Energy E_e of the electron is written as;

$$E_e = \Phi \square - \sigma, (\sigma \text{ is the work – function})$$

The result of the blackbody radiation is summarized as follows;

SEE U IN CLASS

Text/ further reading

Physical chemistry by Thomas Engel and Philip Reid
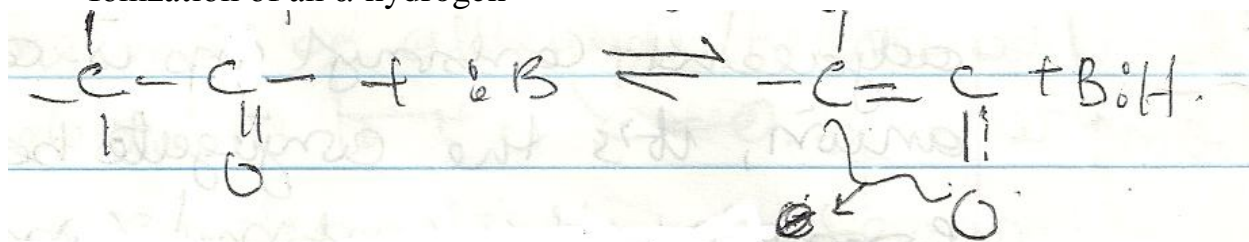Physical Chemistry by Pw Atkins

CHM 328

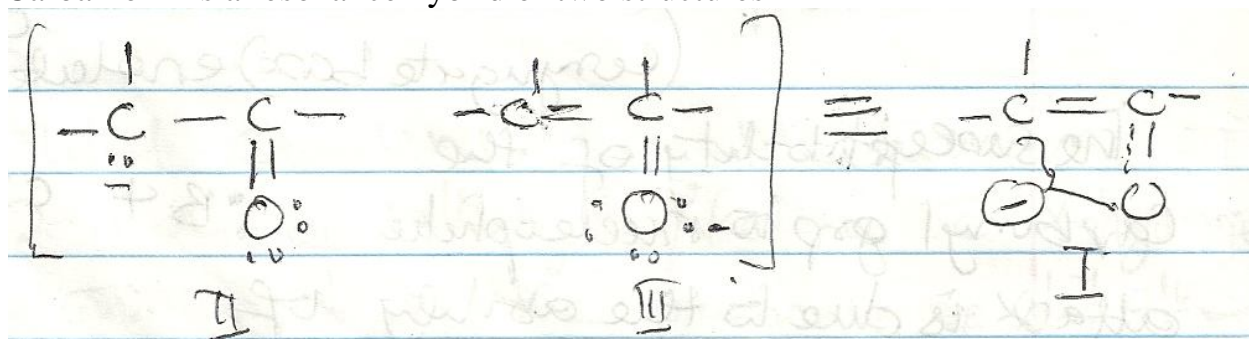# MECHANISM OF ORGANIC REACTIONS

CARBANIONS

The carbonyl can play the role as a functional group as well a substituent. The carbonyl group strengthens the acidity of the hydrogen atoms attached to the α-carbon and by doing this gives rise to a whole set of chemical reactions.
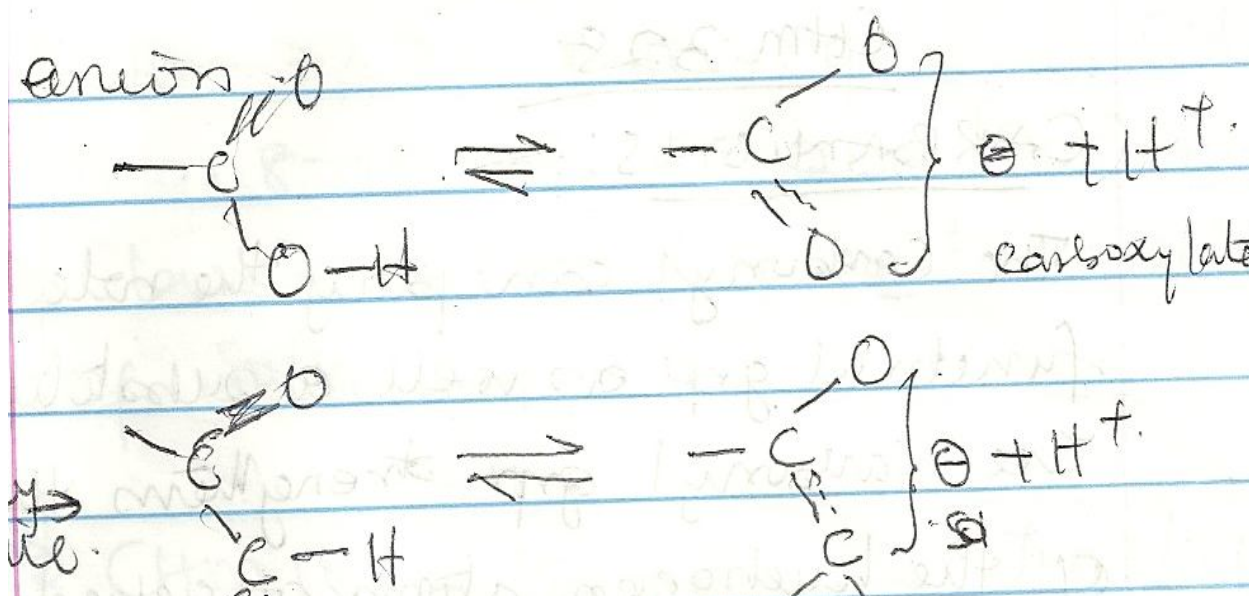
Ionization of an α-hydrogen

$$-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{\underset{O}{\parallel}}{C}}- \ + \ \overset{\ominus}{:}B \ \rightleftharpoons \ -\overset{|}{C}=\overset{|}{\underset{\parallel}{C}} \ + B:H.$$

[Conjugate base of a carbon acid which loses its proton from carbon
Carbanion I is a resonance hybrid of two structures

$$\left[\ -\overset{|}{\underset{:}{C}}-\overset{|}{\underset{\overset{\parallel}{O}:}{C}}- \quad -\overset{|}{C}=\overset{|}{\underset{\overset{\parallel}{O}:}{C}}- \ \right] \ = \ -\overset{|}{C}=\overset{|}{\underset{\overset{|}{\ominus}}{C}}{}^{-}$$

$$\text{I} \qquad\qquad \text{III} \qquad\qquad\qquad \text{I}$$

The carbonyl group effects the acidity of α-hydrogen in the same way it affects the acidity of carboxylic acids; by helping to accommodate the negative change on the anion.

anion

$$-\overset{\overset{O}{\parallel}}{C} \qquad \rightleftharpoons \qquad -\overset{\overset{O}{\parallel}}{C} \left\}\ \ominus + H^+ \right.$$
$$\overset{}{O}-H \qquad\qquad\qquad \overset{}{O} \qquad \text{carboxylate}$$

$$\overset{}{\underset{C-H}{\overset{N}{\parallel}O}} \qquad \rightleftharpoons \qquad -\overset{|}{\underset{C}{C}}\left\}\ \overset{O}{\ominus}+ H^+ \right.$$

Stability is due to the fact that most of the charge is carried by oxygen and not carbon.

A carbanion which is stabilized by an adjacent carbonyl group is called an enolate anion; it is the conjugate base of the keto form of the carbonyl compound and its enolate form also.

$$CH_3CCH_3 + :B \rightleftharpoons H:B + CH_2C \overline{} CH_2$$

$\rightleftharpoons: B + CH_3C (OH)= CH_2$
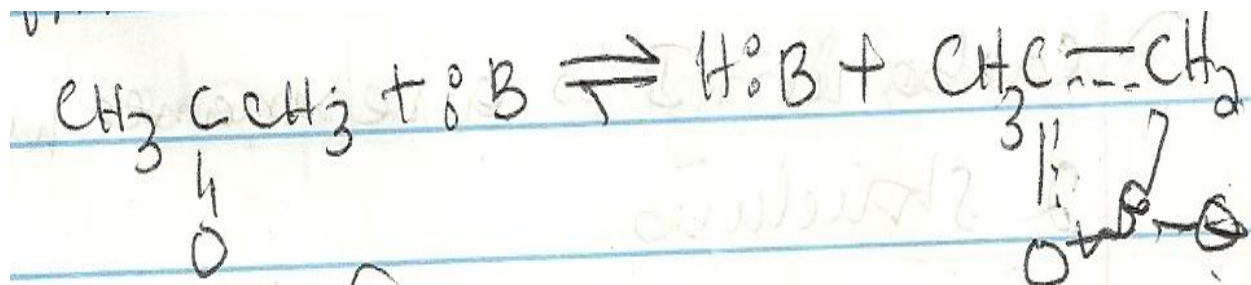
The susceptibility of the carbonyl group to nucleophilic attack is due to the ability of oxygen to accommodate the negative charge that develops as a result of the attack.

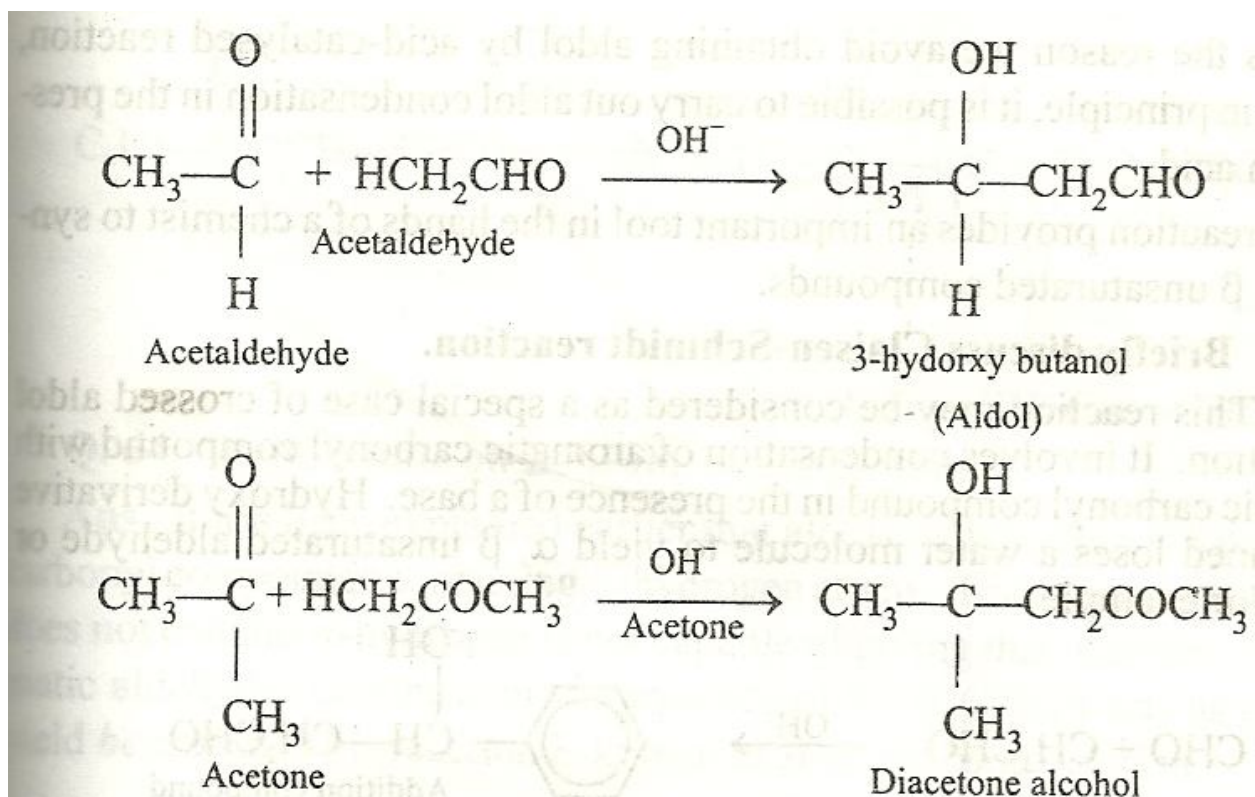$$Z: + C=O \rightarrow \left[-C \overline{} \overset{\delta-}{O} \right] \rightarrow -C-O^- $$
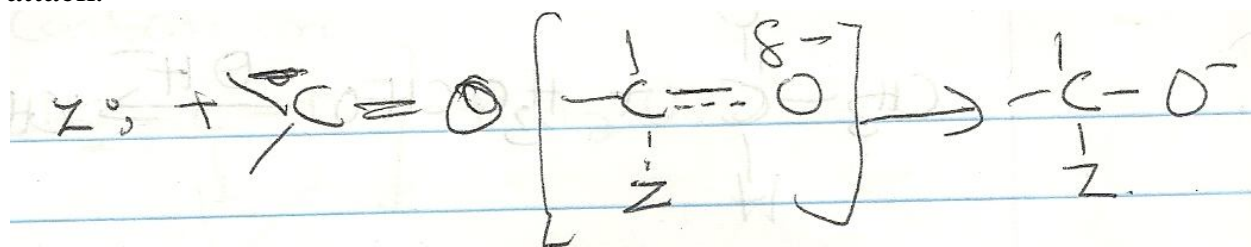
Reactions involving carbanions:
→ Carbanions are highly basic, so they behave as nucleophilic, thus they can attack carbon to form carbon-carbon bonds.
→Aldol condensation- carbanion generated from one molecule of aldehyde/ ketone add as a nucleophile to the RC=O of second molecule of a ketone/aldehyde
Mechanism of Aldol condensation:
→Two molecules of aldehyde/ ketone with α-hydrogen atoms react in the presence of dilute alkali to form β hydroxyl aldehyde or β hydroxyl ketone.

$$\underset{\substack{\text{Acetaldehyde}}}{\underset{\displaystyle \overset{\text{O}}{\underset{\displaystyle \overset{\displaystyle \|}{\text{CH}_3\text{—C}}}{\underset{\displaystyle |}{\underset{\displaystyle \text{H}}{}}}}}{} \;+\; HCH_2CHO \xrightarrow{\;OH^-\;} \underset{\substack{\text{3-hydorxy butanol} \\ \text{(Aldol)}}}{CH_3\text{—}\underset{\displaystyle \overset{\text{OH}}{|}}{\underset{\displaystyle |}{\underset{\displaystyle \text{H}}{\text{C}}}}\text{—}CH_2CHO}$$

Acetaldehyde

$$\underset{\substack{\text{Acetone}}}{\underset{\displaystyle \overset{\text{O}}{\underset{\displaystyle \overset{\displaystyle \|}{\text{CH}_3\text{—C}}}{\underset{\displaystyle |}{\underset{\displaystyle \text{CH}_3}{}}}}}{} + HCH_2COCH_3 \underset{\text{Acetone}}{\xrightarrow{\;OH^-\;}} \underset{\substack{\text{Diacetone alcohol}}}{CH_3\text{—}\underset{\displaystyle \overset{\text{OH}}{|}}{\underset{\displaystyle |}{\underset{\displaystyle \text{CH}_3}{\text{C}}}}\text{—}CH_2COCH_3}$$
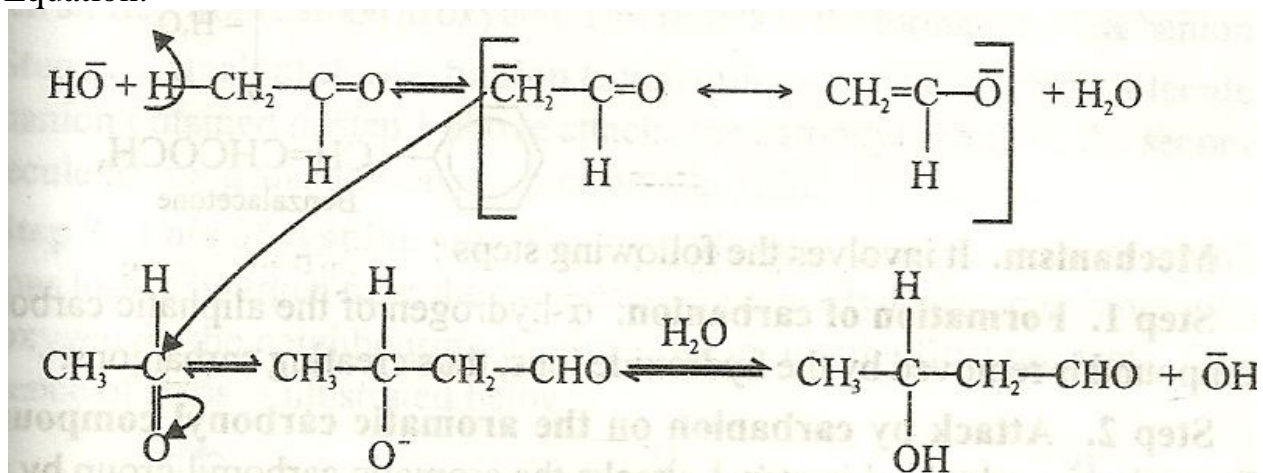
Step 1: Formation of carbanion-hydroxide from a base abstracts a proton from the α-carbon atom to a carbanion which is stabilized by resonance.

Step 2: Attack by the carbanion- the carbanion formed attacks the second molecule by nucleophilic addition mechanism to form an alkoxide ion.

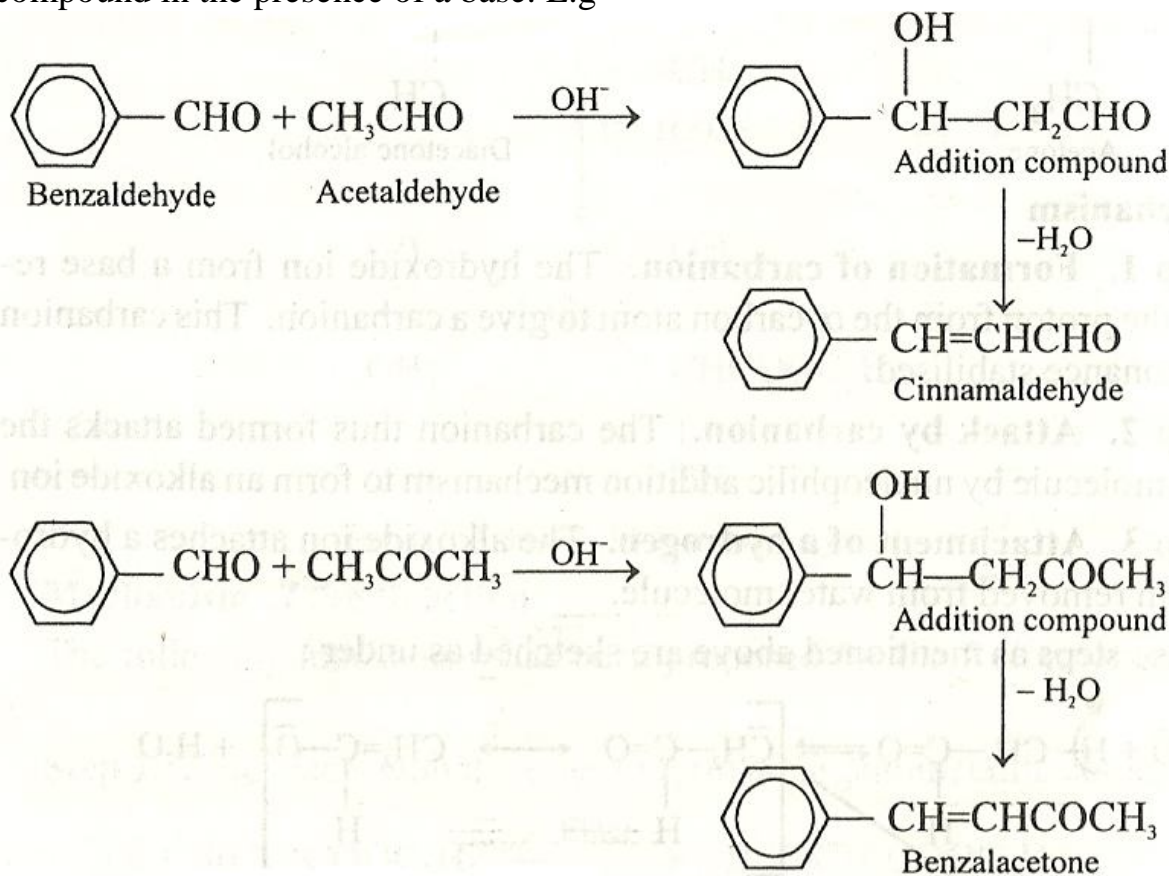Step 3: Attachment of a hydrogen:- the alkoxide ion attaches a hydrogen atom removed from H_2O molecule.

Equation:-

Claisen- Schmidt reaction

→a crossed aldol condensation; involving condensation of aromatic carbonyl compound in the presence of a base. E.g
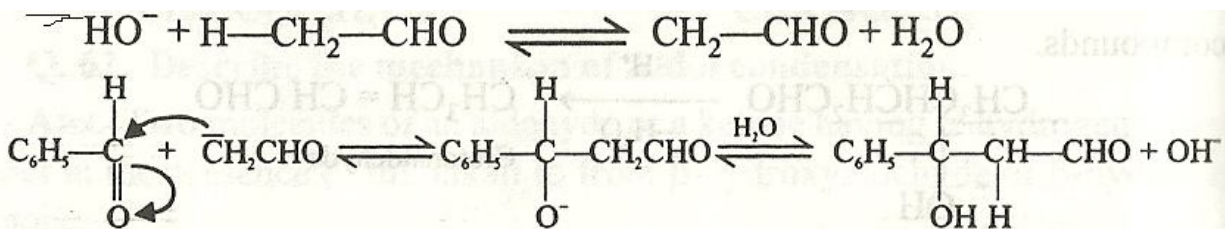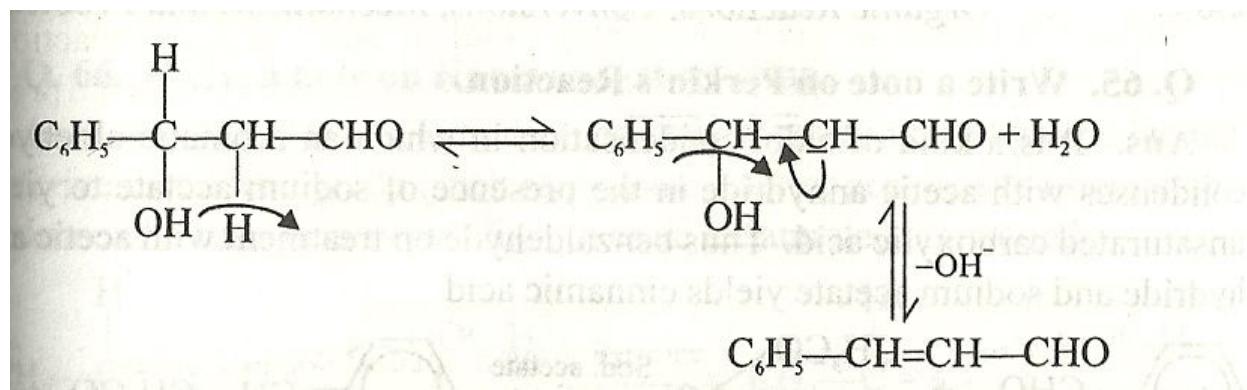

Mechanism:

Step 1: Formation of carbanion

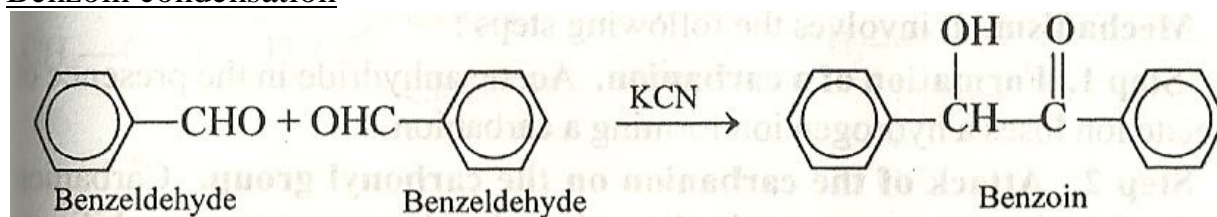Step 2: Attack by carbanion on the aromatic carbonyl compound to form alkoxide ion.

Step 3: Attachment of a proton

Step 4: α-H atom in the hydroxyl compound is removed by the base, followed by OH group and ultimately H_2O is removed

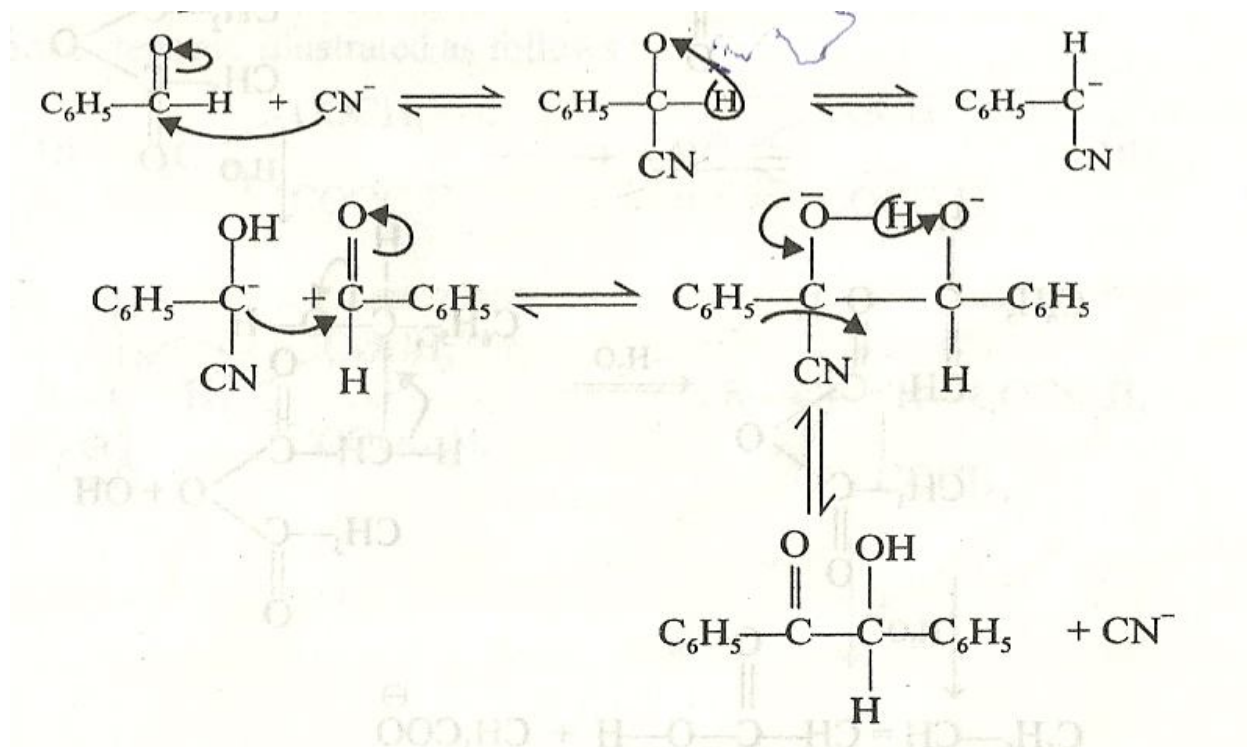$$C_6H_5-\underset{\underset{OH}{|}}{\overset{\overset{H}{|}}{C}}-\underset{\underset{H}{|}}{CH}-CHO \rightleftharpoons C_6H_5-\underset{\underset{OH}{|}}{CH}-CH-CHO + H_2O$$

$$\Big\updownarrow -OH^-$$

$$C_6H_5-CH=CH-CHO$$

Benzoin condensation

Benzeldehyde   Benzeldehyde   Benzoin

Step 1and 2 as in other condensation reactions.
Step 3, loss of CN⁻ ion

Perkins reaction
Step 1-2 as in others

Step 3: protonation of the alkoxide ion to form an aldol type compound.
Step 4: dehydration, the hydroxyl group and neighbouring hydrogen are removed as water.
Step 5: hydration

Benzaldehyde   Acetic Anhydride   Sod. acetate, 180°

$CH = CH\ COOH$
Cinnamic acid

$C_6H_5—CH = CH—C—O—H + CH_3COO^{\ominus}$
Cinnamic acid