❖ Rice-Herzfeld Mechanism of Organic Molecules Decomposition (Acetaldehyde)

In 1934, Frank O. Rice and Karl F. Herzfeld performed an extensive study on the chain reactions and developed special mechanics to account the observed rate laws. In the honor of researchers, this mechanism is popularly known as Rice-Herzfeld mechanism. The conceptual foundation of this mechanism can easily be understood by taking the example of an organic compound, acetaldehyde.

The pyrolysis of acetaldehyde is a typical case of stationary type chain reactions (n = 1) for which the overall reaction can be written as given below.

$$\mathrm{CH_3CHO \longrightarrow CH_4 + CO} \tag{210}$$

Furthermore, the elementary steps for the same can be proposed as

$$Initiation: \qquad \mathrm{CH_3CHO} \xrightarrow{k_1} \mathrm{{}^{\cdot}CH_3 + {}^{\cdot}CHO} \tag{211}$$

$$Propagation: \qquad \mathrm{{}^{\cdot}CH_3 + CH_3CHO} \xrightarrow{k_2} \mathrm{CH_4 + {}^{\cdot}CH_2CHO} \tag{212}$$

$$\mathrm{{}^{\cdot}CH_2CHO} \xrightarrow{k_3} \mathrm{{}^{\cdot}CH_3 + CO} \tag{213}$$

$$Termination: \qquad \mathrm{{}^{\cdot}CH_3 + {}^{\cdot}CH_3} \xrightarrow{k_4} \mathrm{CH_3CH_3} \tag{214}$$

The net rate of formation of CH_4 must be equal to the sum of the rate of formation and the rate of disappearance of the same i.e.

$$\frac{d[\mathrm{CH_4}]}{\mathrm{dt}} = k_2[\mathrm{{}^{\cdot}CH_3}][\mathrm{CH_3CHO}] \tag{215}$$

Now, in order to obtain the overall rate expression, we need to apply the steady-state approximation on the $[\mathrm{{}^{\cdot}CH_3}]$ and $[\mathrm{{}^{\cdot}CH_2CHO}]$ first i.e.

$$\frac{\mathrm{d}[\mathrm{{}^{\cdot}CH_3}]}{\mathrm{dt}} = 0 = k_1[\mathrm{CH_3CHO}] - k_2[\mathrm{{}^{\cdot}CH_3}][\mathrm{CH_3CHO}] + k_3[\mathrm{{}^{\cdot}CH_2CHO}] - 2k_4[\mathrm{{}^{\cdot}CH_3}]^2 \tag{216}$$

Similarly,

$$\frac{\mathrm{d}[\mathrm{{}^{\cdot}CH_2CHO}]}{\mathrm{dt}} = 0 = k_2[\mathrm{{}^{\cdot}CH_3}][\mathrm{CH_3CHO}] - k_3[\mathrm{{}^{\cdot}CH_2CHO}] \tag{217}$$

Taking negative both side of equation (217), we have

$$-k_2[\mathrm{{}^{\cdot}CH_3}][\mathrm{CH_3CHO}] + k_3[\mathrm{{}^{\cdot}CH_2CHO}] = 0 \tag{218}$$

Using the above result in equation (216), we get

$$k_1[\mathrm{CH_3CHO}] + 0 - 2k_4[^{\cdot}\mathrm{CH_3}]^2 = 0 \tag{219}$$

$$[^{\cdot}\mathrm{CH_3}] = \left(\frac{k_1}{2k_4}\right)^{1/2}[\mathrm{CH_3CHO}]^{1/2} \tag{220}$$

After putting the value of $[^{\cdot}\mathrm{CH_3}]$ from equation (220) in equation (215), we have

$$\frac{d[\mathrm{CH_4}]}{\mathrm{dt}} = k_2\left(\frac{k_1}{2k_4}\right)^{1/2}[\mathrm{CH_3CHO}]^{1/2}\,[\mathrm{CH_3CHO}] \tag{221}$$

$$\frac{d[\mathrm{CH_4}]}{\mathrm{dt}} = k_2\left(\frac{k_1}{2k_4}\right)^{1/2}[\mathrm{CH_3CHO}]^{3/2} \tag{222}$$

Now consider a new constant as

$$k = k_2\left(\frac{k_1}{2k_4}\right)^{1/2} \tag{223}$$

Using in equation (222), we get

$$\frac{d[\mathrm{CH_4}]}{\mathrm{dt}} = k[\mathrm{CH_3CHO}]^{3/2} \tag{224}$$

The kinetic chain length for the same can be obtained by dividing the rate of formation of the product by rate of initiation step i.e.

$$Kinetic\ chain\ length = \frac{R_p}{R_i} \tag{225}$$

Where R_p and R_i are the rate of propagation and rate of initiation respectively. Now since the rate of propagation is simply equal to the overall rate law i.e. equation (224), the rate of initiation can be given as

$$R_i = k_1[\mathrm{CH_3CHO}] \tag{226}$$

After using the values of R_p and R_i from equation (224, 226) in equation (225), we get the expression for kinetic chain length as

$$Kinetic\ chain\ length = \frac{k[\mathrm{CH_3CHO}]^{3/2}}{k_1[\mathrm{CH_3CHO}]} \tag{227}$$

or

$$Kinetic\ chain\ length = \frac{k}{k_1}[\mathrm{CH_3CHO}]^{1/2} \tag{228}$$

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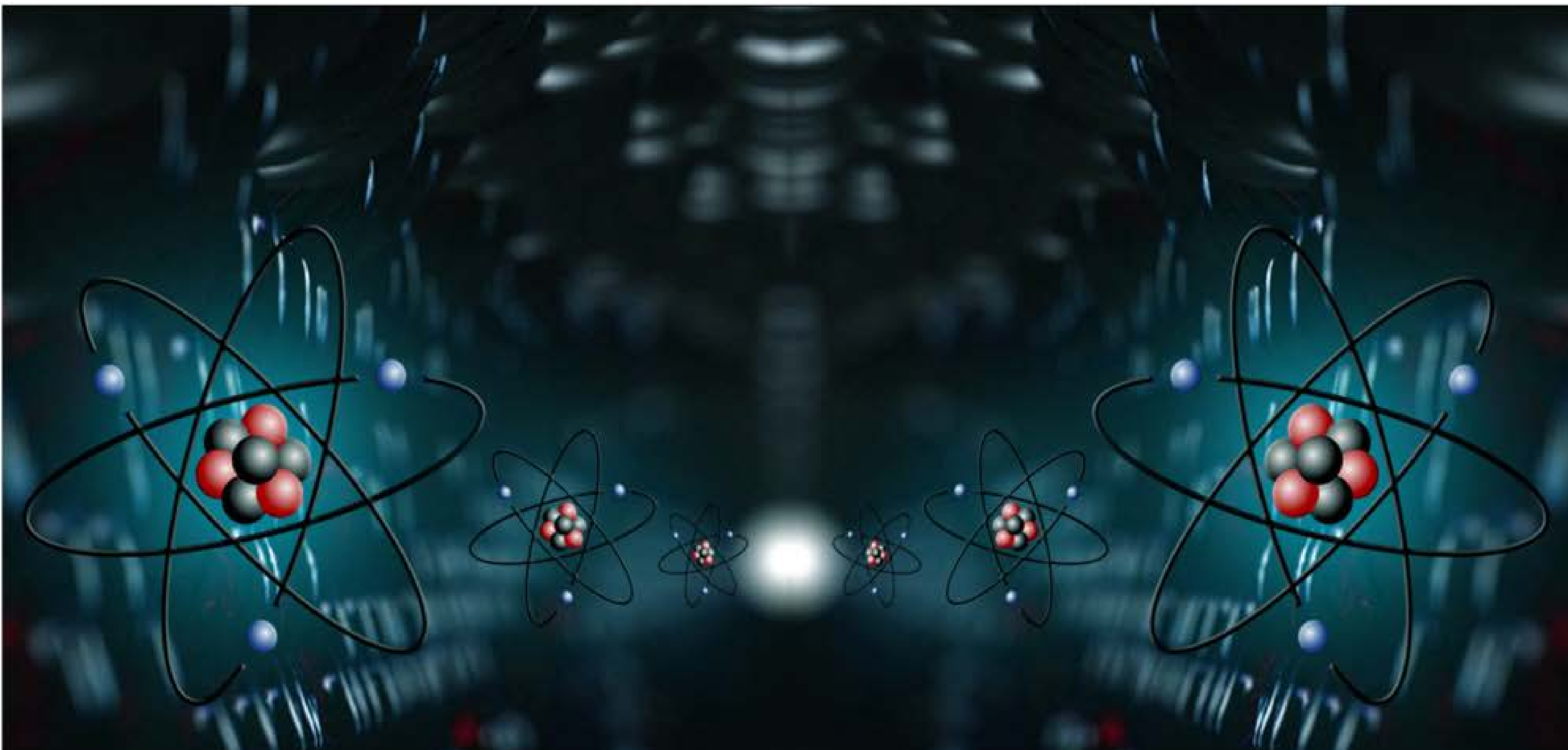

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ISBN: 978-81-938720-1-7
MRP: Rs 800.00

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