

CHAPTER : IV

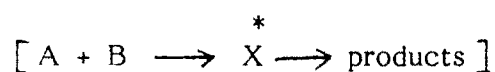
Discussion



DISCUSSION

Chemical kinetics attained a new meaning when Arrhenius⁸ put forward the concept of molecular activation as a prerequisite to a chemical reaction. This concept of activation is now universally accepted and forms the basis of all subsequent theories of chemical reactions. The nature of activated complex formed, as a result of molecular collision between energised molecules, was considered by Evans, Polanyi¹³², and Eyring.⁴ It was established that a chemical reaction involves, first the formation of an activated complex in a reversible process, which then decomposes and gives the final products of reaction. According to Eyring's point of view, it is necessary for the reacting atoms or molecules to approach each other to form the activated complex after collision and then pass over an energy barrier to give the products. The molecular species corresponding to the top of such energy barrier is referred to as an activated complex and the rate of the reaction is controlled by the rate at which this complex travels over the top of this energy barrier.

According to Evans, Eyring and polanyi, the reaction sequence for a bimolecular reaction is represented as



The expression for the rate constant (k_r) of such a reaction, on the bases of absolute reaction rate theory, can be written in the form

$$k_r = \frac{kT}{h} \cdot \frac{Q^*}{Q_A Q_B} \cdot e^{-E_0/RT} \quad (1)$$

where Q terms refer to the partition functions, 'k' is Boltzmann constant, 'h' is Planks constant and E₀ is the energy of activation referred to the zero point energy of both reactants and the activated complex. Since the

equilibrium K for the formations of the activated complex is given by

$$K = \frac{Q^*}{Q_A \cdot Q_B} \cdot e^{-E_a/RT} \quad (2)$$

hence the equation (1) reduces to

$$k_r = \frac{kT}{h} \cdot K \quad (3)$$

Equation (3) can also be expressed involving the entropy of activation and enthalpy of activation as

$$k_r = \frac{kT}{h} \cdot e^{-\Delta G^\ddagger/RT} \quad (4)$$

where ΔG^\ddagger is the free energy of activation.

As $\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger$, the equation (4) may be written as

$$k_r = \frac{kT}{h} \cdot e^{\Delta S^\ddagger/R} \cdot e^{-\Delta H^\ddagger/RT} \quad (5)$$

$$\text{or} \quad \ln \frac{k_r}{kT/h} = \frac{\Delta S^\ddagger}{R} - \frac{\Delta H^\ddagger}{RT} \quad (6)$$

where ΔS^\ddagger and ΔH^\ddagger are the entropy and enthalpy changes involved in the formation of the activated complex. Thus, a plot of $\ln \frac{k_r}{kT/h}$ against $\frac{1}{T}$ enables one to calculate ΔS^\ddagger and ΔH^\ddagger .

Since the experimental energy of activation E_{expt} is related to ΔH^\ddagger by the equation

$$E_{\text{expt}} = \Delta H^\ddagger - p\Delta V^\ddagger + RT \quad (7)$$

Equation (5) for unimolecular reactions or for the reactions in solution, in which ΔV^\ddagger is zero, reduces to

$$k_r = e \cdot \frac{kT}{h} \cdot e^{\Delta S^\ddagger/R} \cdot e^{-E_{\text{expt}}/RT} \quad (8)$$

In the case of bimolecular reactions

$$k_r = e^2 \cdot \frac{kT}{h} \cdot e^{\frac{\Delta S^\ddagger}{R}} \cdot e^{-E_{\text{expt}}/RT} \quad (9)$$

Thus equation (8) and (9) can be used to evaluate the energy of activation for a reaction by the study of the effect of temperature on the rate of the reaction.

The various Arrhenius parameters are calculated by using following equations

- 1) Energy of activation (E_a)

$$E_a = \log \frac{k_2}{k_1} \left[\frac{T_2 \times T_1}{T_2 - T_1} \right] 4.576 \quad (10)$$

where k_1 and k_2 are rate constants at temperatures T_1 and T_2

- 2) Frequency factor (A)

$$k_r = A e^{-E_a/RT}$$

$$\text{or} \quad \log A = \log k_r + \frac{E_a}{4.576 T} \quad (11)$$

- 3) Entropy of activation (ΔS^\ddagger)

$$\ln A = \ln \frac{kT}{h} + \frac{\Delta S^\ddagger}{R} + 1$$

$$\therefore \Delta S^\ddagger = R \left[\ln A - \ln \frac{kT}{h} - 1 \right] \quad (12)$$

- 4) Enthalpy (ΔH^\ddagger)

$$\Delta H^\ddagger = E_a - RT \quad (13)$$

- 5) Free energy (ΔG^\ddagger)

$$\Delta G^\ddagger = 4.576 \left[\log \frac{kT}{h} - \log k_r \right] T \quad (14)$$

Another prominent effect on the reaction rates in solutions is the influence of ionic strength, Bronsted, Bjerrum⁹ and Christainsen¹³⁴, have applied the Debye-Huckel theory to study the influence of neutral salts on the rate of reaction in the solution. These effects are of two kinds. In the first case, the activities of the reactions, whether ions or polar molecules, may be altered by the added electrolytes. This is the primary salt effect. In the second case, the effective concentration of a reactant or a catalytic ion coming from a weak electrolyte may be decreased due to a decrease in the ionisation of electrolyte because of the added salt. This is secondary salt effect, primary salt effect can be subdivided into following two heads:

- 1) Primary exponential salt effect and
- 2) Primary linear salt effect

The former for the dilute solutions is given by the Bronsted-Bjerrum equation,

$$\ln k = \ln k_0 + \frac{2 \cdot Z_A Z_B \cdot \infty \cdot \sqrt{\mu}}{1 + \beta a_i \sqrt{\mu}} \quad (15)$$

and for very dilute solution, where μ is small, it reduces to

$$\ln k \approx \ln k_0 + 2 \cdot Z_A Z_B \cdot \infty \cdot \sqrt{\mu} \quad (16)$$

where Z_A and Z_B are the charges of the reacting ions forming the activated complex, ' μ ' is the ionic strength of the medium, ' a_i ' is the mean distance of the closest approach of ions, and ∞ and β are the Debye - Huckel constants, while ' k ' and ' k_0 ' observed rate constants at ionic strength μ and the rate constant at zero ionic strength.

In the present study, the variation in the ionic strength of the medium does not influence the rate of oxidation of hydrazides by CAT,

indicates the participation of neutral species in the rate determining step of the reaction. If one of the reactants is a neutral molecule, so that Z_A or $Z_B = 0$, then no effect of ionic strength is observed.

In order to discuss the possible mechanism, of the oxidation of nicotinic acid hydrazide and isonicotinic acid hydrazide by CAT, it is necessary to summarise the results obtained. The investigations are epitomised as under.

- 1) The kinetics of oxidation of nicotinic acid hydrazide and isonicotinic acid hydrazide in alkaline medium by CAT are found to obey first order dependence each w.r.t. chloramine-T and hydrazides (NAH & INAH)
- 2) The rate of oxidation of hydrazides is independent of alkali (NaOH) concentration.
- 3) The variation in the ionic strength of the medium does not influence the rate of oxidation. This indicates the participation of neutral species in the rate determining step.
- 4) The various thermodynamic parameters determined are as follows.

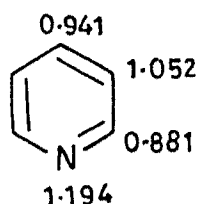
Parameters	Values in case of NAH	Values in case of INAH.
1) Energy of activation(Ea)	12.47 k.cals/mole 12.48 k.cals/mole (by graph.)	12.51 k.cals/mole 12.36 k.cals/mole (by graph)
2) Frequency factor (A)	$1.356 \times 10^6 \text{ sec}^{-1}$	$9.816 \times 10^5 \text{ sec}^{-1}$
3) Free energy ΔG^\ddagger	19.266 k.cals/mole	21.44 k.cals/mole
4) Entropy ΔS^\ddagger	-32.47 e.u.	-33.11 e.u.
5) Enthalpy change ΔH^\ddagger	11.97 k.cals/mole (by graph.)	12.21 k.cals/mole (by graph.)

The normal values of free energy of activation (ΔG^\ddagger) and enthalpy of activation (ΔH^\ddagger) indicate that the transition state is formed. The large negative value of entropy of activation (ΔS^\ddagger) and low value of frequency factor (A), suggest the formation of a rigid transition state.

5) The addition of chloride ions (NaCl) has no effect on the rate of the reaction. So there is no salt effect on the rate of oxidation of hydrazides.

6) The product analysis shows the presence of p-toluene sulfonamide, bishydrazide and nitrogen gas. The presence of p-toluene sulfonamide was detected by paper chromatographic method and bishydrazide was detected by TLC method. The evolution of nitrogen gas is identified by lime test¹³⁴

7) The rate of oxidation of NAH is slightly faster than that of INAH. This may be explained on the bases of molecular orbital calculations¹³⁰ which show that the electron density at position 3 of the pyridine ring is higher than that at position 4.



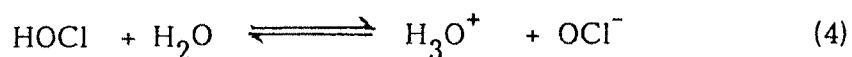
MECHANISM:

The mechanism of a chemical reaction is a mental model based on the experimental facts. Now a days knowledge of mechanism of chemical reaction has so advanced that, it is possible to explain the formation of final product which takes place through the number of intermediate steps in the reaction.

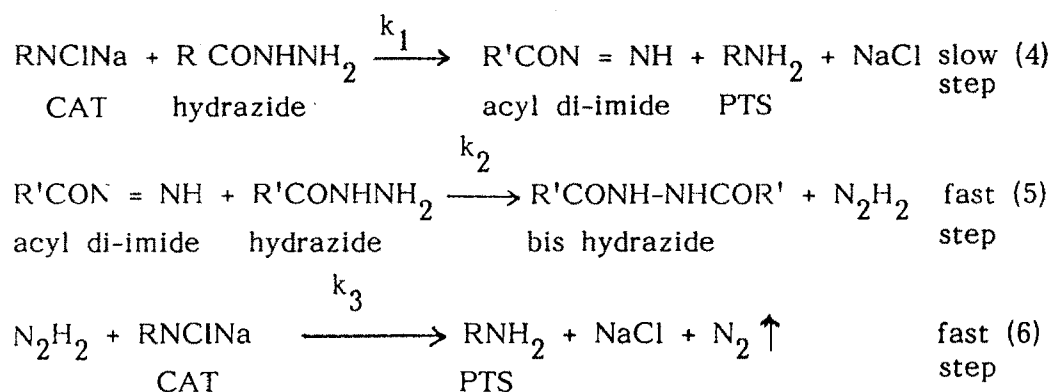
Chloramine-T behaves like a strong electrolyte¹³ in aqueous solution and dissociates. as



In aqueous solution chloramine-T is hydrolysed as follows:



Therefore the possible oxidising species in alkaline chloramine-T are²¹ N-chloro-p-toluene sulfonamide (RNHCl), hypochlorite ion (OCl⁻) and chloramine-T (RNCINa) itself. Since, the rate of oxidation of hydrazides by CAT is independent of alkali concentration, the possibility of RNHCl as the oxidising species has been ruled out. Similar type of alkali independence of the reaction rate has been observed by many authors.^{72,73,108} It is also investigated that the added p-toluene sulfonamide (RNH₂) has no effect on the oxidation rate, indicating that the hypochlorite ion (OCl⁻) may not be involved in the reaction. Moreover, with hypochlorite ion as the oxidising species, the oxidation is immeasurably fast. Since the addition of sodium chloride does not enhance the rate, the formation of molecular chlorine as an intermediate is also ruled out. So it is believed that the chloramine-T (RNCINa) itself is the oxidising species in the oxidation of hydrazides. Similar type of observation was reported by Radhakrishnamurti,¹³⁵ Krishna Rao,¹³⁶ Mahadevappa and Swami,¹⁰⁸ where chloramine-T itself is the oxidising species. Thus on the foregoing kinetic evidences the following sequence of reactions is proposed.



where R = p -CH₃-C₆H₄-SO₂⁻ and

R' = C₅H₄N (pyridine ring)

From the above scheme, it can be proposed that, the rate determining step(4) involves reaction between hydrazide and CAT resulting in to the formation of the product. The CAT reacts with hydrazide giving acyl di-imide as an intermediate in the slow and rate determining step. The acyl di-imide species is known to be good acylating agent, which reacts with excess of hydrazide giving bishydrazide as the oxidation product in the next step(5). The bishydrazide was also found to be a major oxidation product of hydrazide with selenium,¹³⁷ lead tetra acetate¹³⁸ and halogens.¹³⁹

On the basis of observed kinetics of oxidation of hydrazides by CAT, the following rate expression for the disappearance of CAT is derived by applying steady state principle on the basis of above reactions.

$$\begin{aligned}
 - \frac{d [\text{CAT}]}{dt} &= k_1 [\text{CAT}] [\text{Hydrazide}] + k_3 [\text{N}_2\text{H}_2] [\text{CAT}] \\
 &= [\text{CAT}] \left[k_1 [\text{Hydrazide}] + k_3 [\text{N}_2\text{H}_2] \right] \quad (8)
 \end{aligned}$$

Similarly applying steady state treatment for "acyl di-imide," the rate of formation of acyl di-imide can be equated with the rate of its consumption.

$$k_1 [\text{CAT}] [\text{Hydrazide}] = k_2 [\text{Acyl di-imide}] [\text{Hydrazide}]$$

$$\therefore [\text{Acyl di-imide}] = \frac{k_1}{k_2} [\text{CAT}] \quad (9)$$

Again the rate expression for $[\text{N}_2\text{H}_2]$ is represented as

$$[\text{N}_2\text{H}_2] = \frac{k_2}{k_3} \frac{[\text{Acyl di-imide}] [\text{Hydrazide}]}{[\text{CAT}]} \quad (10)$$

Substituting the value of $[\text{Acyl di-imide}]$ from equation (9) in equation (10), it becomes

$$[\text{N}_2\text{H}_2] = \frac{k_1}{k_3} [\text{Hydrazide}] \quad (11)$$

Now substituting $[\text{N}_2\text{H}_2]$ from equation (11), in equation (8),

$$\begin{aligned} - \frac{d [\text{CAT}]}{dt} &= [\text{CAT}] \left[k_1 [\text{Hydrazide}] + k_1 [\text{Hydrazide}] \right] \\ &= 2k_1 [\text{CAT}] [\text{Hydrazide}] \\ &= k [\text{CAT}] [\text{Hydrazide}] \end{aligned} \quad (12)$$

Thus the rate law is

$$- \frac{d [\text{CAT}]}{dt} = k [\text{CAT}] [\text{Hydrazide}]$$