

CHAPTER — IV.

DISCUSSION

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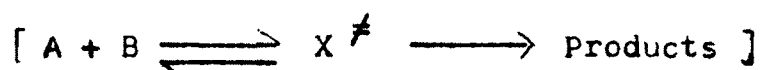
DISCUSSION

Kinetics of reaction is concerned with the analysis of the dynamics of chemical reactions. 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. The most rational approach of Arrhenius¹ for explaining the occurrence of a chemical reaction is the concept of molecular activation as a pre-requisite 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 and Polanyi,² Eyring³ and it was established that a chemical reaction involves first the formation of the activated complex in a reversible process, which then decomposes irreversibly to yield the final products of the 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 and then pass

over an energy barrier to give the products. The molecular species corresponding to the top of such energy barrier are referred to as activated complexes and the rate of the reaction is controlled by the rate at which complexes travel over the top of the barrier.

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



The expression for the rate constant for such a reaction, on the basis of absolute reaction rate theory, can be written in the form

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

Where Q terms refer to the partition functions, k is the Boltzman constant and E_0 is the energy of activation referred to the zero point energy, h Planck's constant. Since the equilibrium constant K^{\ddagger} for the formation of the activated complex is given by,

$$K^{\ddagger} = \frac{Q^{\ddagger}}{Q_A \times Q_B} \cdot e^{-E_0/RT} \quad \dots(2)$$

hence equation (1) reduces to,

$$k_r = \frac{kT}{h} K^{\ddagger} \quad \dots(3)$$

Therefore

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

Where ΔG^\ddagger is the free energy of activation i.e. the change in Gibbs free energy in passing from the initial state to the activated state or it can be expressed as

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

OR

$$\ln\left[\frac{k_r}{kT/h}\right] = \Delta S^\ddagger/R - \Delta H^\ddagger/RT \quad \dots(6)$$

where ΔS^\ddagger and ΔH^\ddagger are the entropy of activation and enthalpy of activation. Thus a plot of $\ln\left[\frac{k_r}{kT/h}\right]$ 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 expression

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

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

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

in the case of bimolecular reaction to

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

Thus, equations (8) and (9)⁴ 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.

For reactions occurring in solutions, the nature of the solvent used always plays an important role. For the solvent effects on ion-ion reactions, correlating the specific rate k_r with the dielectric constant of the medium ϵ_0 , Scatchard⁵ derived the expression.

$$\ln k_r = \ln k_0 - \frac{Z_A \cdot Z_B e^2}{k \cdot TrD} \quad \dots(10)$$

where k_r is the specific rate in a solvent of dielectric constant D for reactions between two ions of valency Z_A and Z_B , ' r ' is the radius of the activated complex and k_0 is the specific rate in a solvent of infinite dielectric constant. Equation (10) enables one to gain information about the nature of the reacting ions from a plot of $\log k_r$ Vs $1/D$. Unfortunately in the present study, the effect of dielectric constant could not be investigated due to the reactivity of the solvents methanol, ethanol, formamide and acetone with CAT.

The prominence effect for the reactions in solution is the influence of ionic strength Bronsted,⁶ Bjerrum⁷ and Christiansen⁸ have applied the Debye-Huckel theory to the influence of neutral salt on the rate of reaction in solution. These effects are of two kinds in the first case, the activities of reactants whether ions or polar molecules, may be altered by the added electrolyte, 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 in to 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.

$$\ln k = \ln k_0 + \frac{2 \cdot Z_A \cdot Z_B \cdot \alpha \sqrt{\mu}}{1 + \beta a_i \sqrt{\mu}} \quad \dots(11)$$

and for very dilute solutions, where μ is small, it reduced to

$$\ln k \approx \ln k_0 + 2 Z_A \cdot Z_B \alpha \sqrt{\mu} \quad \dots(12)$$

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 α 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 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 n-caproic acid hydrazide and n-Heptanoic acid hydrazide by CAT, it is necessary to summarise the results obtained. The investigations are summarised as under

- (1) The kinetics of oxidation of n-caproic and n-Heptanoic acid hydrazides in alkaline medium by CAT are found to obey first order dependence each w.r.t. CAT and hydrazides.
- (2) The various thermodynamic parameters determined are as follows :

Parameters	Values in case of n-CAH	Values in case of n-HAH
1) Energy of Activation (Ea)	13.88 K.Cals/mole 13.89 K.Cals/mole (by graph)	13.26 K.Cals/mole 14.08 K.Cals/mole (by graph)
2) Frequency Factor (A)	$5.90 \times 10^5 \text{ sec}^{-1}$	$6.48 \times 10^5 \text{ sec}^{-1}$
3) Free energy (ΔG^\ddagger)	23.48 K.Cals/mole	23.38 K.Cals/mole
4) Entropy (ΔS^\ddagger)	-32.26 e.u.	-32.07 e.u.
5) Enthalpy change (ΔH^\ddagger)	13.24 K.Cals/mole (by graph)	13.18 K.Cals/mole (by graph)

The fairly high positive values of free energy of activation ΔG^\ddagger and enthalpy of activation ΔH^\ddagger indicates that the transition state is highly solvated while the large negative value of entropy of activation ΔS^\ddagger suggest the formation of a rigid transition state.

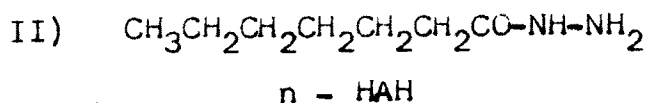
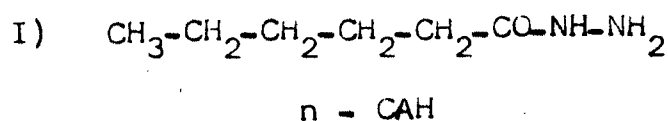
- (3) The rate of oxidation of hydrazide is independent of alkali (NaOH) concentration.

- (4) 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.
- (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 sulphonamide was detected by Paper Chromatographic method, and bishydrazide was detected by TLC method. The evolution of nitrogen gas is identified by lime test.⁹
- (7) The rate of oxidation of n-Caproic acid hydrazide is slightly faster than that of n-Heptanoic acid hydrazide

TABLE 4.1

Conf. of Hydrazide M x 10 ²	n-CAH		n-HAH	
	$-\frac{dc_o}{dt} \times 10^5$	k	$-\frac{dc_o}{dt} \times 10^5$	k
0.5	0.85	4.25	0.58	3.16
1.0	1.60	6.97	1.16	6.29
1.5	2.35	11.20	1.76	9.24
2.0	3.13	16.41	2.35	12.06
2.5	3.95	21.73	2.95	15.06

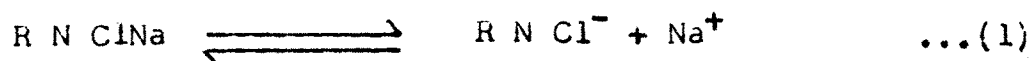
Results in the above table clearly shows that as the length of carbon chain is increased, the molecule becomes less reactive. Kinetics of oxidation of n-valeric and iso-valeric acid hydrazides is reported by Telwekar.¹⁰ The rate of oxidation of iso-valeric acid hydrazide is somewhat greater than that of n-valeric acid hydrazide. This difference in the reactivity indicates that the presence of branched chain in the iso-valeric acid hydrazide makes the molecule more reactive than its straight chain isomer. i.e. n-valeric acid hydrazide.



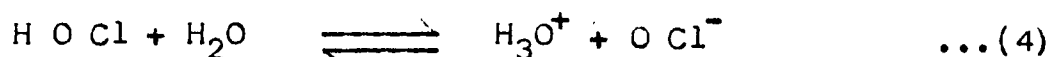
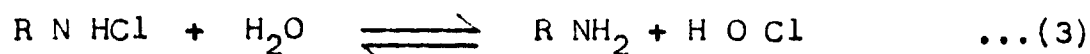
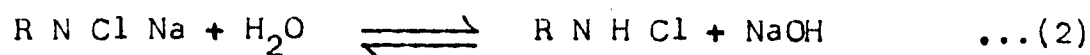
MECHANISM :

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 products which take place through the number of intermediate steps in the reaction.

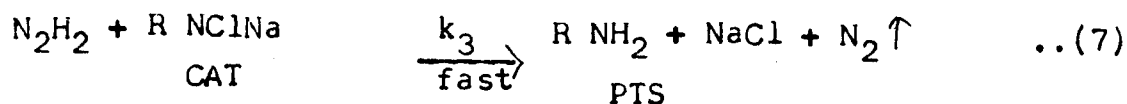
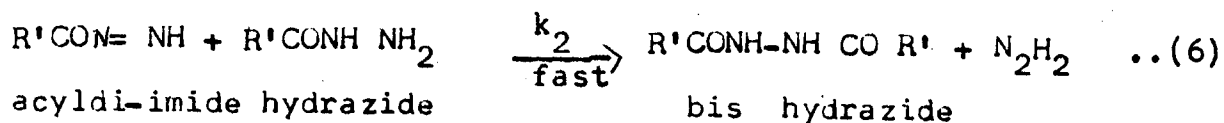
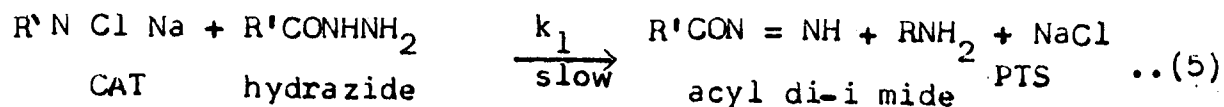
Chloramine-T behaves like strong electrolyte¹¹ in aqueous solution and dissociates as :



In aqueous solution chloramine-T hydrolysed as follows:



Therefore, the possible oxidising species in alkaline Chloramine-T solution are N-Chloro-p-toluene-sulfonamide, hypochlorite ion and Chloramine-T itself. Since, the rate of oxidation of hydrazides by Chloramine-T is independent of alkali concentration, the possibility of N-Chloro-p-toluene-sulfonamide as the oxidising species has been ruled out. Similar type of alkali independence of the reaction rate has been observed by many authors,^{12,13,14,15} It is also investigated that the added p-toluene sulfonamide has no effect on the oxidation rate, indicating that the hypochlorite ion 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, hence the formation of molecular chlorine as an intermediate is also ruled out. So it is believed that the Chloramine-T itself is the oxidising species in the oxidation of hydrazides. Similar type of observations were reported by Radhakrishnmurti,¹⁶ Krishn Rao¹⁵ Mahadevappa, Swami¹⁴ and Telwekar¹⁰ where Chloramine-T itself is the oxidising species. Thus, on the basis of the foregoing kinetic evidence, the following sequence of reaction is proposed :



where $\text{R} = \text{CH}_3\text{C}_6\text{H}_4\text{-SO}_2\text{-}$ and

$\text{R}' = \text{CH}_3\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-}$ in case of *n*-Caproic acid hydrazide and

$\text{R}' = \text{CH}_3\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-}$ in case of Heptanoic acid hydrazide

It can be proposed that the rate determining step involves reaction between hydrazide and Chloramine-T resulting in to the formation of product. On the basis of observed kinetics of oxidation of hydrazide, by Chloramine-T, following rate law is proposed, which accounts for the same i.e.

$$-\frac{d[\text{CAT}]}{dt} = k_1 [\text{CAT}] [\text{Hydrazide}] \quad \dots(8)$$

The Chloramine-T 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 bis-hydrazide ($R-CO-NH-NH-CO-R$) as the oxidation product in the next step. The bis-hydrazide was also found to be a major oxidation product of hydrazide with Selenium,¹⁷ lead tetra-acetate¹⁸ and halogens.¹⁹