

CHAPTER-IV

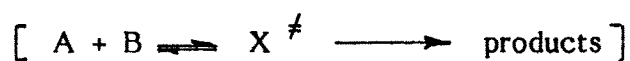
DISCUSSION

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Chemical kinetics attained a new meaning when Arrhenius¹ 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 collisions between energised molecules, was considered by Evans and Polanyi² Eyring³ and 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 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 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.

As far as oxidation reactions are considered, it was found that these are multistep reactions but are complicated due to simultaneous occurrence of a number of steps, some of them are relatively fast or slow. Each step is preferably accompanied by single electron transfer.⁴ The slowest step in given reaction is the rate determining step.

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



The expression for the rate constant $[k_r]$ of reaction, on the basis of absolute reaction rate theory, can be put in the following form

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

where 'Q' terms refer to the partition functions, 'K' is the Boltzmann constant, 'E₀' is the energy of activation referred to the zero point energy and 'h' is the plank's constant. Since the equilibrium constant 'K[‡]' for the formation of the activated complex is given by,

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

the above equation (1) reduces as follows

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

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

Where $[\Delta G^\ddagger]$ is the free energy of activation i.e. the change in Gibbs free energy in passing from the initial state to the activated state and it can be expressed as

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

or

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

where $[\Delta S^\ddagger]$ and $[\Delta H^\ddagger]$ are the entropy and enthalpy changes involved in the formation of the activated complex.

Since the experimental energy of activation $E'_{(expt)}$ is related to $[\Delta H^\ddagger]$ by expression

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

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

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

In case of bimolecular reactions.⁵

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

Thus equations (8) and (9) can be used to evaluate the energy of activation.

The results, that are obtained in the oxidation of hydrazides by chloramine-T, are shown in the following table.

TABLE
ACTIVATION PARAMETER VALUES OF THE OXIDATION OF
HYDRAZIDES BY CHLORAMINE-T

Parameters	Values in case of SAH	Values in case of O-CBAH
1) Energy of activation (Ea)	10.41 Kcal/Mole	14.70 Kcal/Mole
2) Frequency Factor (A)	$7.31 \times 10^3 \text{ Sec}^{-1}$	$2.68 \times 10^6 \text{ Sec}^{-1}$
3) Entropy [ΔS^\ddagger]	- 42.13 e.u.	- 30.40 e.u.
4) Enthalpy [ΔH^\ddagger]	9.78 Kcal/Mole	14.08 Kcal/Mole
5) Free Energy [ΔG^\ddagger]	22.97 Kcal/Mole	23.60 Kcal/Mole
Graphical Values		
1) Energy of activation (Ea)	10.46 Kcal/mole	14.64 Kcal/Mole
2) Enthalpy [ΔH^\ddagger]	9.98 Kcal/Mole	13.73 Kcal/Mole

In this reaction, the fairly high positive values of free energy of activation [ΔG^\ddagger] and enthalpy of activation [ΔH^\ddagger] indicate that the transition state is highly solvated, while the large negative value of entropy of activation [ΔS^\ddagger] suggests the formation of a rigid transition state.

Another prominent effect on the reaction rates in solutions is the influence of ionic strength. Bronsted,⁶ Bjerrum⁷ and Christiansen⁸ 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 reactants whether ions or polar molecules, may be altered by the added electrolytes which is known as primary salt effect. In the second case, the effective concentration of a reactants or a catalytic ions coming from a weak electrolyte, may be decreased due to the decrease in the ionisation of the electrolyte because of the added salt. It is known as secondary salt effect.

The primary salt effect can be subdivided into the following two heads -

i) The primary exponential salt effect, and ii) the primary linear salt effect.

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

$$\ln k = \ln k_0 + 2 \cdot \frac{Z_A \cdot Z_B \alpha \sqrt{\mu}}{1 + \beta a \sqrt{\mu}}$$

For very dilute solution, where ' μ ' is small, it reduces to

$$\ln k \approx \ln k_0 + 2 Z_A Z_B \alpha \sqrt{\mu}$$

where Z_A and Z_B are charges of the reacting ions forming the activated complex, ' μ ' is the ionic strength of the medium, ' a ' is the mean

distance of the closest approach of ions, ' α ' and ' β ' are the Debye-Huckel constants, and ' k ' and ' k_0 ' are the 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 chloramine-T, indicates the participation of neutral species in the rate determining step of the reaction.

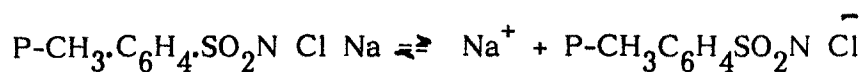
A solvent effect on the oxidation of hydrazides was studied in methanol and it was found that the reaction rate decreases with increase in methanol percentage in water/methanol mixture.

In order to discuss the possible mechanism, of the oxidation of salicylic acid hydrazide and ortho-chloro benzoic acid hydrazide by chloramine-T, it is necessary to summarise the results obtained. The investigations are epitomised as under -

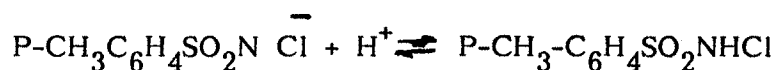
- (1) The oxidation of salicylic acid hydrazide and ortho-chloro benzoic acid hydrazide is first order (Tables 3.1.2 and 3.2.2) with respect to chloramine-T.
- (2) The oxidation of these hydrazides by chloramine-T is first order with respect to salicylic acid hydrazide and ortho-chloro benzoic acid hydrazide.
- (3) The fairly high positive values of free energy of activation $[\Delta G^\ddagger]$ and enthalpy of activation $[\Delta H^\ddagger]$ indicate that the transition state is highly solvated, while the large negative value of entropy of activation $[\Delta S^\ddagger]$ suggests the formation of a rigid transition state.

- (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 product analysis shows the presence of p-toluene-sulphonamide, bis-hydrazide (R.CO.NH.NH.CO.R) and nitrogen gas. The presence of P-toluene-sulphonamide was detected by paper chromatographic method and bis-hydrazide was detected by TLC method. The evolution of nitrogen gas is identified by lime test.⁹

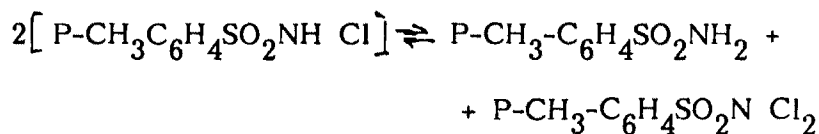
Chloramine-T behaves like a strong electrolyte¹⁰ in aqueous solution and dissociates as -



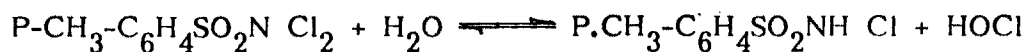
The anion then picks up a proton to form the free acid.



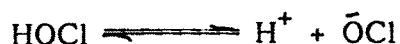
The free acid has not been isolated but the evidence for existence has been reported.¹⁰ The free acid then gives rise to p-toluene-sulphonamide and dichloramine-T.



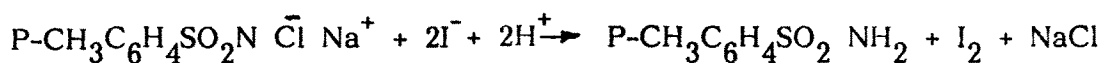
The dichloramine-T and the free acid hydrolyse to give hypochlorous acid.



finally HOCl ionizes as -



It liberates iodine with acidified KI solution

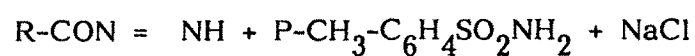
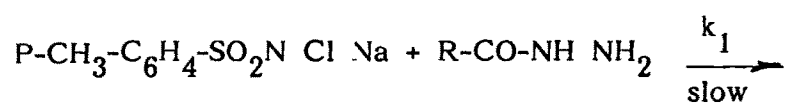


Therefore, the possible oxidising species obtained from chloramine-T in alkaline solution are N-chloro p-toluene-sulphonamide, hypochlorite ion and chloramine-T itself. The rate of oxidation of hydrazides by chloramine-T is independent of alkali concentration. Therefore, the possibility of N-chloro p-toluene-sulphonamide as the oxidising species has been ruled out. Similar type of alkali independence of the reaction rate has been observed by many authors.^{11,12,13}

It is also investigated that added P-toluene-sulphonamide has no effect on the rate of oxidation reaction of aromatic acid hydrazides by chloramine-T. The hypochlorite ion may not be involved in the reaction, otherwise reaction would have been immeasurably fast. Since the addition of sodium chloride does not change the rate of this reaction, the formation of molecular chlorine as an intermediate is also ruled out. So it is believed that the chloramine-T itself is an oxidising species in the oxidation of hydrazides. Similar observation was reported by Radhakrishnamurti,¹⁴

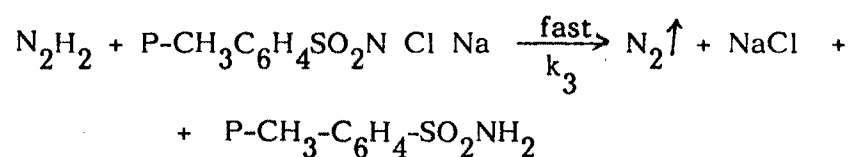
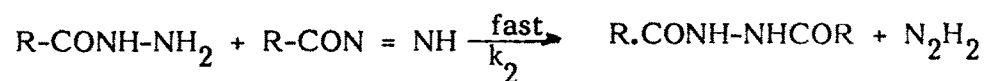
Krishna Rao¹³ and Mahadevappa^{15,19} where they have reported that the chloramine-T, itself is an oxidising species.

Thus, on the basis of the foregoing evidences, the following sequence of reactions is proposed -

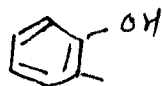


acyldi-imide

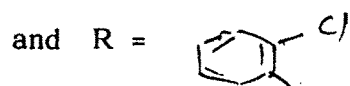
It is slowest and rate determining step.



whereas R =



In case of salicylic acid hydrazide.



in case of ortho-chloro benzoic acid hydrazide.

It can be proposed that the rate determining step involves reaction between hydrazide and chloramine-T. The chloramine-T reacts with hydrazide giving acyldi-imide as an intermediate in the slow and rate determining step. The acyldi-imide species is known to be a good acylating agent which further reacts with excess of hydrazide giving bis-hydrazide (R-CONH-NHCOR) as the oxidation product in the next step. The bis-hydrazide was also found to be a major oxidation product of hydrazides with selenium,¹⁶ lead tetra acetate¹⁷ and halogens.¹⁸

On the basis of observed kinetics of oxidation of hydrazides by chloramine-T, the following rate law is proposed.

$$\frac{-d [\text{CAT}]}{dt} = k_1 [\text{CAT}] [\text{hydrazide}]$$

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