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C H A P T E R - I V

DISCUSSION

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The mechanism of chemical reaction is a visualised picture of a reaction, which explains observed 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 takes place through the number of intermediate steps in the reaction. Now a days chemical kinetics attained a new meaning when Arrhenius[1] put forward the concept of molecular activation as a pre-requisite to chemical reaction. This concept of activation is now universely accepted and forms a 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 Polynyi,[2] Eyring[3] and it was established that a chemical reaction involves first with formation of an activated complex in a reversible process, which then decomposes irreversibly to yield the final products. According to Eyring for any chemical reaction to occur, the reacting atoms or molecules should approach one another and then pass over a free energy barrier. 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 these complexes travel over the top or hump of the barrier.

As far as oxidation reactions are considered, they do not takes place in single step. They are complicated due to simultaneous occurrance of a number of steps, of which some of them are relatively fast and some are slow. The kinetic study will be considerably simplified, if the rate determining steps are not more than one.

The order of the reaction with respect to the different reactions indicate whether the rate determining step involves one reactant or more than one. If the rate of the reaction depends upon the concentration of just one reactant, then in rate determining step, only that reactant is involved in given reaction. In the oxidation of hydrazides by chloramine-T it has been observed that the order of the reaction with respect to hydrazide is one and the concentration of chloramine-T has no effect on the rate of the reaction. Therefore, overall order of the reaction is one. The rate law can be given as

$$\frac{- d[CAT]}{dt} \quad \alpha \quad [\text{ Hydrazide }] \qquad \ldots \qquad (4.1)$$

i.e. $\frac{-d[CAT]}{dt} = k [\text{Hydrazide}][C-.] \qquad \ldots \qquad (4.2)$

Another prominent effect on reaction rates in solution is the influence of ionic strength. Bronsted[4], Bjarrum[5] and Christiansan[6] have applied the Debye-Huckel theory to study the influence of neutral salts on the rate of reaction in solution. The effects are of two kinds. The reactions in which ionic charge is created are faciliated by solvents having high dielectric constants and high ionic strength i.e. the activities of reactants whether ions or polar molecules

may be altered by added electrolytes. It is known as primary salt effect. In the number of reactions degree of ionization is increased by added salts by shifting the position of equilibrium, which is known as secondary salt effect. The relation between rate constant and ionic strength is given by the equation

$$\log k = \log k_o + 2. \; Z_A.Z_B \; \alpha \; \sqrt{\mu} \qquad \ldots \qquad (4.3)$$

where Z_A and Z_B are the charges of the reacting ions forming the activated complex

μ = Ionic strength of the medium

α = Debye-Huckel constant

k and k_o are the observed rate constant at ionic strength μ and the rate constant at zero ionic strength respectively.

In the above equation (4.3), if one of the reactant is neutral molecule then value of Z_A or Z_B will be zero. In such cases no effect of ionic strength is observed. In such a reactions variation in the ionic strength of the medium does not influence the rate of the reaction. In the oxidation of hydrazides by chloramine-T, variation in the ionic strength of the medium does not effect the rate of the reaction. This clearly indicates the participation of a neutral species in the rate determining step of the reaction.

Thermodynamic parameters are very important factors to be considered in proposing mechanism of the reaction. The rate

expression for the reaction is given by the equation (4.4)

$$k_r = \frac{KT}{h} e^{\Delta S/R} \cdot e^{-Ea/RT} \qquad \cdots \qquad (4.4)$$

where k_r =   Rate constant

K =   Boltzmann constant

h   =   Plank's constant

Ea   =   Energy of activation

ΔS =   Change in the entropy

T   =   Temperature

and

$$k_r = A. e^{-Ea/RT} \qquad \cdots \qquad (4.5)$$

where   A   is Frequency Factor

Hence

$$A = \frac{KT}{h} e^{S/R} \qquad \cdots \qquad (4.6)$$

$\frac{KT}{h} = 10^{13}$. Hence substituting values in equation (4.6),

$$\text{Frequency Factor } [A] = 10^{13} e^{S/R} \qquad \cdots \qquad (4.7)$$

It is evident that when (ΔS) i.e. change in entropy is positive, if frequency factor (A) is greater than 10^{13}. The positive change in entropy (ΔS) corresponds to less rigid activated complex and the reaction is faster. On the other hand if change in entropy (ΔS) is negative, the formation of activated complex is more rigid and the rate is slower. In

terms of frequency factor (A), it is found that for a reaction between ions of like charges it is greater than 10^{13} and for ions of unlike charges it is less than 10^{13}. The utility of these calculation i.e. increase or decrease of entropy has been well established by Moelwyn-Hughes, Frost and Pearson[7].

The results that are obtained in the oxidation of hydrazides by chloramine-T are shown in following table. The negative values of entropy of activation clearly indicate that rate of this reaction is slow.

TABLE

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

| Parameters		Values in case of 3-5 DNBH	Values in case of of P-MBH
Energy of Activation	(Ea)	11.36 K cal/mole	15.76 K cal/mole
Frequency factor	(A)	4.266×10^4 sec^{-1}	1.852×10^7 sec^{-1}
Entropy	(ΔS^*)	− 30.40 e.u.	− 18.44 e.u.
Enthalpy	(ΔH^*)	10.94 K cal/mole	15.14 K cal/mole
Free Energy	(ΔG^*)	20.98 K cal/mole	20.91 K cal/mole

In this reaction fairly high positive values (in the above table) of free energy of activation, enthalpy indicates that the transition state is highly solvated, while the large value of entropy activation (ΔS^*) suggests the formation of rigid transition state.

With considering the above all experimental facts the mechanism for the oxidation of aromatic hydrazides by chloramine-T can be interpreted as fllows
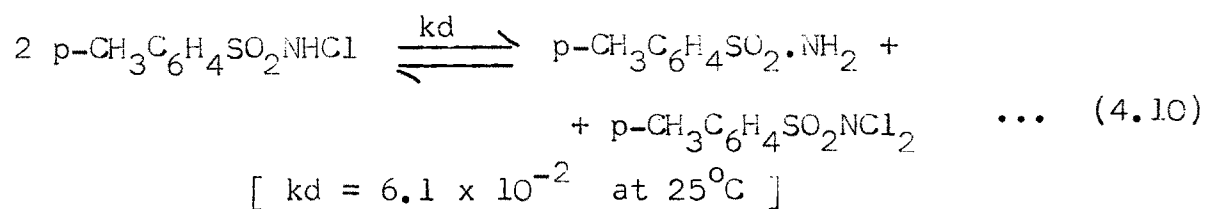
Chloramine-T behaves like strong electrolyte[8] in aqueous solution and dissociates as
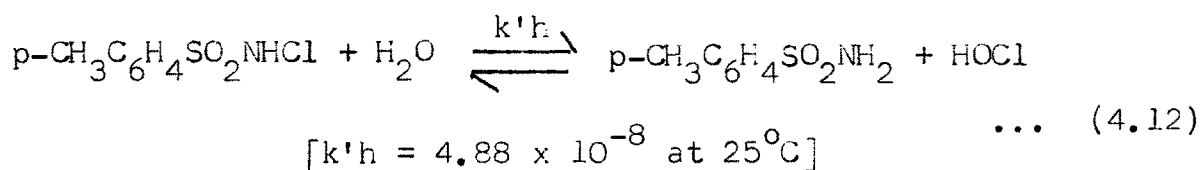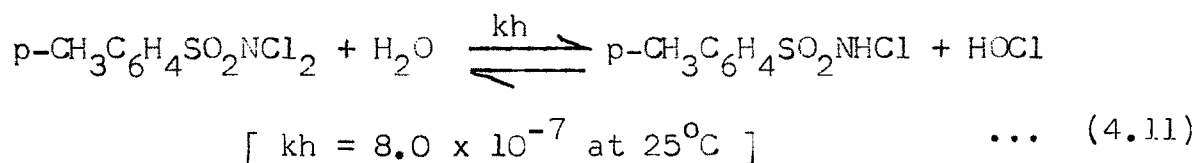
$$p-CH_3 - C_6H_4SO_2NClNa \rightleftharpoons Na^+ + p-CH_3C_6H_4SO_2N^-Cl$$

$$\quad \text{...} \quad (4.8)$$
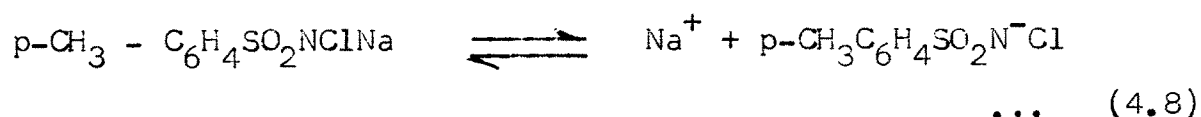
The anion then picks up proton from the acid medium to give free acid N-chloro-p-toluene sulphonamide[9]

$$p-CH_3-C_6H_4SO_2N^-Cl + H^+ \xrightarrow{ka} p-CH_3.C_6H_4SO_2NHCl$$

$$[ka = 2.82 \times 10^{-5}] \quad \text{...} \quad (4.9)$$
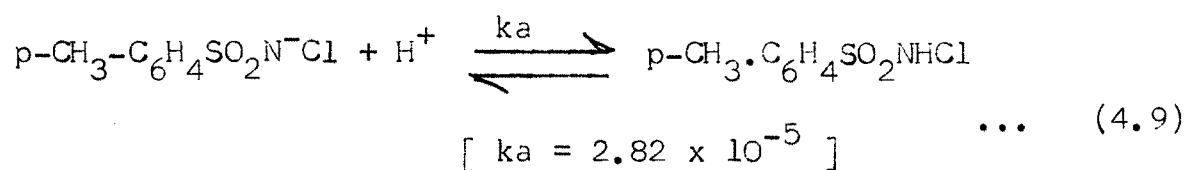
This free acid undergoes disproportion reaction giving rise to p-toluene-sulphonamide and Dichloramine-T [10]

$$2 \ p-CH_3C_6H_4SO_2NHCl \xrightarrow{kd} p-CH_3C_6H_4SO_2.NH_2 +$$

$$+ \ p-CH_3C_6H_4SO_2NCl_2 \quad \text{...} \quad (4.10)$$

$$[kd = 6.1 \times 10^{-2} \ \text{at} \ 25^oC]$$

The Dichloramine-T and the free acid N-chloro-p-Toluene sulphonamide hydrolyses to give hypochlorous acid[11]

$$p\text{-}CH_3C_6H_4SO_2NCl_2 + H_2O \underset{\longleftarrow}{\overset{kh}{\longrightarrow}} p\text{-}CH_3C_6H_4SO_2NHCl + HOCl$$

$$[\ kh = 8.0 \times 10^{-7} \text{ at } 25^{\circ}C \ ] \qquad \dots \quad (4.11)$$

$$p\text{-}CH_3C_6H_4SO_2NHCl + H_2O \underset{\longleftarrow}{\overset{k'h}{\longrightarrow}} p\text{-}CH_3C_6H_4SO_2NH_2 + HOCl$$

$$[k'h = 4.88 \times 10^{-8} \text{ at } 25^{\circ}C] \qquad \dots \quad (4.12)$$

Finally HOCl ionizes as follows

$$HOCl \underset{\longleftarrow}{\overset{Ka}{\longrightarrow}} H^+ + OCl^- \qquad \dots \qquad (4.13)$$

$$[\ ka = 3.3 \times 10^{-8} \text{ at } 25^{\circ}C \ ]$$
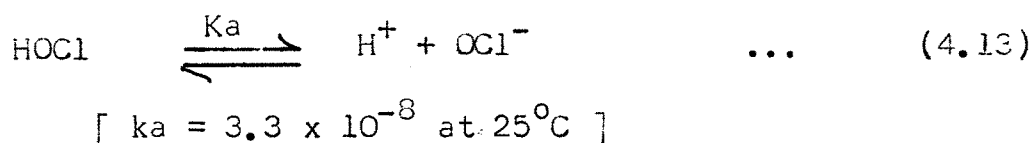
In aqueous solution chloramine-T hydrolyses as follows

$$p\text{-}CH_3C_6H_4SO_2NClNa + H_2O \underset{\longleftarrow}{\overset{}{\longrightarrow}} p\text{-}CH_3C_6H_4SO_2NHCl + NaOH$$

$$\dots \qquad (4.14)$$

$$p\text{-}CH_3C_6H_4SO_2NHCl + NaOH \underset{\longleftarrow}{\overset{}{\longrightarrow}} p\text{-}CH_3C_6H_4SO_2NH_2 + Na^+ + OCl^-$$

$$\dots \qquad (4.15)$$
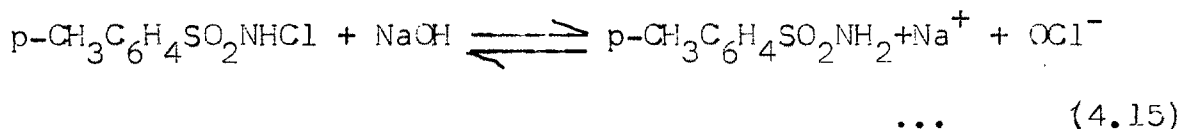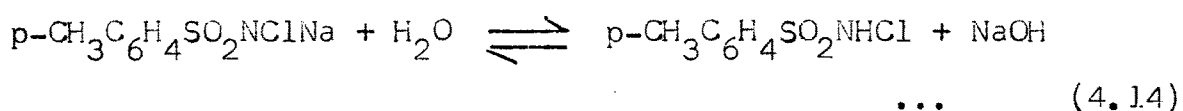
Therefore possible oxidizing species in alkaline chloramine-T solutions are N-chloro-p-toluene sulphanamide, hypochlorite ion and chloramine-T itself. As the rate of oxidation of hydrazide by chloramine-T is found to nearly constant at pH range from 8.85 to 9.95. This clearly indicates that reaction is independent of alkali concentration. Therefore,

the possibility of N-chloro-p-sulphonamide as oxidizing species has been ruled out. Similar type of alkali independantee of the rates has been observed by many authors[12,13,14]. Rx

Ramaih, Kodand and P.V.Krishnarao have observed that added p-toluene-sulphonamide has no effect on the rate of oxidation of aromatic acid hydrazides by chloramine-T. The hypochlorite ion may not be involved in the reaction otherwise reaction would have immesurably fast which is already investigated. The addition of sodium chloride does not enhance the rate of the reaction, so that intermediate formation of molecular chlorine is ruled out. Therefore we can assume that chloramine-T itself is the oxidizing species in the oxidation of the hydrazides. This type of observation was also made by Radhakrishnamurti[15], Krishnarao[14] and Mahadevappa[16] in the study of oxidation of benzoyl hydrazine, substituted benzoyl hydrazines amino acics and Anilines.
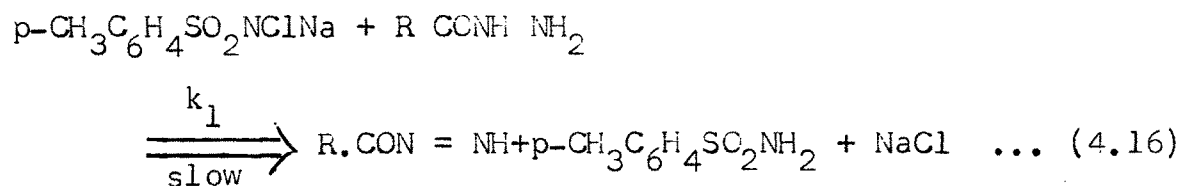
The product analysis shows the presence of p-toluene sulphonamide and oxidation product of hydrazide Bis-hydrazide ((R-CONH.NH.COR). The presence of p-toluene-sulphonamide was detected by paper chromatographic method. Similarly bis-hydrazide was detected by TLC method. Evolution of gas nitrogen is identified by usual method.

REACTION MECHANISM OF THE OXIDATION OF

HYDRAZIDES BY CHLORAMINE-T

On the bases of foregoing evidences the general
mechanism for the oxidation of hydrazides by chloramine-T
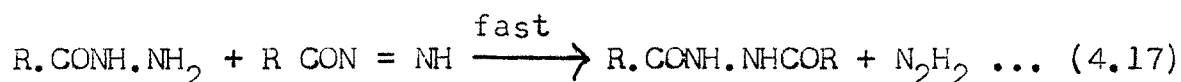may be formulated as shown in the following scheme :
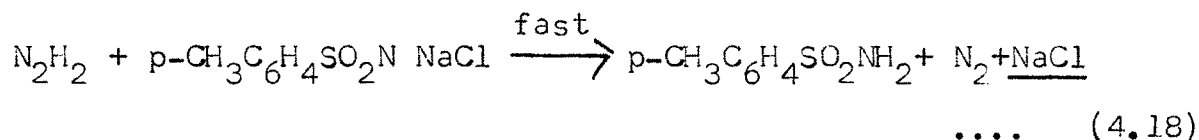
Scheme

Step I

$$p-CH_3C_6H_4SO_2NClNa + R\ CONH\ NH_2$$

$$\xrightarrow[\text{slow}]{k_1} R.CON = NH + p-CH_3C_6H_4SO_2NH_2 + NaCl \quad \ldots \ (4.16)$$

It is slowest and rate determining step.

Step II

$$R.CONH.NH_2 + R\ CON = NH \xrightarrow{\text{fast}} R.CONH.NHCOR + N_2H_2 \ \ldots \ (4.17)$$

Step III

$$N_2H_2 + p-CH_3C_6H_4SO_2N\ NaCl \xrightarrow{\text{fast}} p-CH_3C_6H_4SO_2NH_2 + N_2 + \underline{NaCl}$$

$$\ldots \ (4.18)$$

where   R = 3-5 Dinitrophenyl group or
              p-methoxy phenyl

This type of reaction scheme was also suggested by the
workers Ramaih A, Kodand and P.V.Krishnarao[14] in their work of

kinetic study of Benzoyl hydrazines by chloramine-T in alkaline medium. The mode of oxidation of hydrazides by chloramine-T is shown in above scheme. The chloramine-T molecule attacks on hydrazide molecule with giving acyldiimide intermediate in the slow and rate determining step. It further reacts with excess of hydrazide giving bis-hydrazide (R-CONH.NH COR) as the oxidation product in the fast step. This bis-hydrazide was also found to be the major oxidation product when selenium[17], lead tetra-acetate[18] and chlorine[19] are used as the oxidants.

The rate of oxidation of hydrazides by chloramine-T also depends upon the nature of groups present on the aromatic nucleus. From the comparison of results of oxidation of 3-5 dinitro benzoic acid hydrazide and p-methoxy benzoic acid hydrazide it is clear that rate of reaction is fast in case of 3-5 dinitrobenzhydrazide than p-methoxybenzhydrazide. The presence of nitro group may accelerates the reaction while methoxy group retards the reaction rate. Thus to conclude the discussion it can be said that the reaction is accelerated by presence of electron withdrawing groups and retarded by electron donating groups.

REFERENCES

1) Arrhenius,S.
   Z.Physik.Chem. 4, 226 (1889)

2) Evans,M.C. and Polynyi,M.
   Trans. Far.Soc. 31, 875 (1935) ibid 448 (1957)

3) Eyring,H.
   J.Chem.Phys. 3, 107 (1935)

4) Bronsted,J.N.
   Z. physik, chem. 102, 69 (1922)

5) Bjerrum,N.
   Z.physik. Chem. 108, 82 (1924)

6) Christeansan,J.A.
   Z.physik.Chem. 113, 35 (1924)

7) Frost A.A. and Pearson R.G.
   "Kinetics and mechanism"
   John Wiley & Sons Inc New York (1953)

8) Bishop,E. and Jennings,V.J.
   Talanta 1, 197 (1958)

9) Morris,J.C., Salazar,J.A. and Winemann,M.A.
   J.Am.Chem.Soc. 70, 2036 (1948)

10) Higuchi,T., Ideka,K. and Hussain,A.
    J.Am.Chem.Soc. (8), 546 (1967)

11) Soper,F.G.
    J.Chem.Soc.(B) 1899 (1924)

12) Adarshkumar, Bose,A.K., and Mushran,S.P.
    J.Ind.Chem.Soc. 53, 755 (1976)

13)   Adarshkumar, Bose,A.K., Sukhadev,P. and Mushran,S.P.
       Monatsh 106, 13 (1975)

14)   Ramaih,A., Kodand and P.V.Krishnarao
       Ind.J.Chem. 19(A), 1120 (1980)

15)   Radhakrishnamurti and Prasad Rao
       Ind.J.Chem. 148, 790 (1976)

16)   Mahadevappa,D.S., Rangappa,K.S., Gowda,N.M.M. and
       Gowda,B.T.
       Int.J.Chem.Kinet. 14, 1183 (1982)

17)   Back,J.G., Collins,S. and Kerr,R.G.
       J.Org.Chem. 46, 1956 (1981)

18)   Gladstone,W.A.F.
       J.Chem.Soc.(C) 1571 (1969)

19)   Imamoto,T.
       Bull.Chem.Soc.Japan 45, 2216 (1972)