CHAPTER IV

DISCUSSION

The kinetics of oxidation of aliphatic carboxylic acid dihydrazides such as malonic acid dihydrazide and succinic acid dihydrazide are carried out in aqueous buffered medium (pH = 9.0) at $30^{\circ}C$. The oxidations of these dihydrazides are consecutive irreversible reactions. It is observed that the first steps of both these reactions are too fast to be measured and second steps are the slowest steps and hence are rate determining. Similar observations were reported by Radhakrishnamurthi[1] in the hydrolysis of diesters and Jagdale[2] et.al. in the hydrolysis of oxalic acid dihydrazide. Therefore the experimental rate constant values correspond to the oxidation of second hydrazide groups of these dihydrazides. The values of the rate constants for the oxidation of first hydrazide group and second hydrazide group are represented by k_1 and k_2 respectively. These k_1 and k_2 values are obtained by using a Swain's time ratio method.[3] The values of k_2 (i.e. oxidation of second hydrazide group) obtained by Swain's time ratio method are identical with the values of k obtained by first order rate equation for both dihydrazides.

So as to get the probable path way of these oxidation reactions it is necessary to find out different reaction parameters of these reactions. It is also necessary to get the idea regarding the order and molecularity of these reactions. Therefore these reactions are carried out at different concentrations of dihydrazides keeping all the reaction conditions constant e.g. pH, temperature, CAT , solvent etc.

The manner in which the rate of reaction varies with the concentration of reacting substances is indicated by the order of reaction. In the oxidation of dihydrazides by chloramine-T in aqueous buffered medium

(pH = 9.0) at $30^\circ C$, the order with respect to the malonic acid dihydrazide and succinic acid dihydrazide is found to be one. (Table 3.2, 3.4, Fig.3.1, 3.2). Similarly these reactions are carried out at different concentrations of chloramine-T keeping all other reaction conditions constant. In this case also reaction shows first order dependance on concentration of chloramine-T. (Table 3.6, 3.8 Fig. 3.9, 3.10). The same results are observed when logarithms of initial rates (log [-dco/dt]) were plotted against corresponding logarithms of initial concentrations of dihydrazide and chlora mine-T (Fig.3.4, 3.6, 3.12, 3.14). The slope represents the order. The values of [- dco/dt] are obtained from plots of (a-x) vs time 't' (Fig.3.3, 3.5, 3.11, 3.13). These orders obtained by above method are also supported by J.H.Vant Hoff's differential method

$$\text{Order(n)} = \frac{\log \left[\frac{-dco}{dt}\right]_2 - \log \left[\frac{dco}{dt}\right]_1}{\log [Co]_2 - \log [Co]_1} \quad \ldots (3.3)$$

Therefore these oxidation reaction are first order with respect to malonic acid dihydrazide, succinic acid dihydrazide and chloramine-T. As it is observed in the oxidation of benzoyl hydrazins,[5] salicylic acid hydrazide[6] and o-chlorobenzoic acid hydrazide[6] by chloramine-T.

Oxidation of first hydrazide group is a faster than the second one. Hence our information regarding this oxidation reaction is related with the oxidation of second hydrazide group. This step of reaction is irreversible so we can say that total reaction is consecutive irreversible.[7] The information of rate constants k, k_1 and k_2 is recorded in Table 2.1 to 2.8 (Chapter-II).

So as to get the information regarding the Arrhenius parameters these reactions are studied in the temperature range 25-45°C. It is observed that as the temperatures of the reactions are increased the rates of the reactions are also increased (Table 3.9, 3.10). This type of observation is matching with endothermic reaction where it is assumed that the reaction has to pass through the energy barrier[8] (activated complex or transition state). Energy of activation is calculated by equation 3.7. These values are also supported by a graphical method·(from the plots of log k Vs 10^3/T) (Fig. 3.19, 3.20). Values of frequency factor (A), entropy of activation (ΔS^{++}) and free energy of activation, (ΔG^{++}) are calculated by equation 3.6, 3.8, and 3.10 respectively. Data for various graphs are recorded in Table 3.9 and 3.10. The value of enthalpy (ΔH^{++}) is also supported by a graphical method (Fig.3.21, 3.22) and all these values of Arrhenius parameters are recorded in Table 3.11. The fairly high values of free energy of activation (ΔG^{++}) and enthalpy of activation (ΔH^{++}) indicates that transition state might be highly solvated[9] as the ΔH^{++} is the essential prerequsite for the reaction to take place and corresponds to the energy necessary to effect the stretching the bond or even breaking of bonds. And the large negative value for entropy of activation (ΔS^{++}) suggest the possibility of rigid transition state[10] and the ordered activated complex. Nearly similar values of free energy of activation in both the cases suggest the similarity in the mechanism of both these dihydrazides. This is also supported by the plots of k vs T (Fig. 3.27). The utility of ΔS^{++} has been well established by Frost and Pearson[4] in terms of frequency factor (A), for the reaction between like charges it is greater than 10^3 and for reaction between unlike charges it is less than 10^{13}.

Arrhenius parameters obtained in the oxidation of dihydrazides by chloramine-T are summarised in following table.

TABLE - 4.1

VALUES OF THE ACTIVATION PARAMETERS IN THE OXIDATION
OF DIHYDRAZIDES BY CHLORAMINE-T

Sr. No.	Parameters	Values for MAD	Values for SAD
1.	Energy of activation (Ea) K J mole^{-1}	58.81	59.132
2.	Enthalpy (H^{++}) K J mole^{-1}	57.38	56.98
3.	Frequency factor (A)S^{-1}	17.43×10^5	36.16×10^5
4.	Entropy (S^{++}) e.u.	-77.28	-76.09
5.	Free energy (G^{++}) K J mole^{-1}	156.4	155.6

Bronsted,[11] Bjerrum[12] and Christiansen[13] have applied the Debye-Huckel theory to study the influence of neutral salts on the rate of reaction in solution. These effects are of two kinds·In the first case the activities of reactant whether ions or polar molecules may be altered by the addition of electrolytes is referred 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 the decrease in the ionisation of the electrolyte because of the added salt·This is known as secondary salt effect.

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

1) The primary exponential salt effect   and

2) The primary linear salt effect.

The former for dilute solution is given by the Bronsted-Bjerrum equation.

$$\ln k = \ln k_o + 2\frac{Z_A Z_B \sqrt{\mu}}{1+\beta \text{ ai } \sqrt{\mu}} \qquad \ldots (4.1)$$

for very dilute solution 'μ' is very small and above equation reduces to :

$$\ln k = \ln k_o + 2 Z_A Z_B \propto \sqrt{\mu} \qquad \ldots (4.2)$$

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, 'ai' is the mean distance of the closest approach of ions, '$\propto$' and 'β' are the Debye-Huckel constants and k, k_o are the observed rate constant at ionic strength 'μ' and the rate constants at zero ionic strength.

In our study of oxidation of dihydrazides by chloramine-T we have studied the effect of addition of common salt, potassium chloride in case of oxidations of both these dihydrazides it is observed that addition of potassium chloride do not alter the rates of these oxidation reactions (Table 3.16, 3.17). The various runs carried out in presence of common salt (variation in the ionic strength) clearly shows that there is no influence of ionic strength on the oxidation reactions. This salt provides free chlorine in this reaction. Similar effects have been reported in the oxidation of amino acids[14] and iso-propyl alcohols[15] by chloramine-T.

So as to study the effect of pH on the oxidation of dihydrazides by chloramine-T we have carried out different runs in the pH range 7.55 to 10.54. We have studied this reaction in this small range of pH because

at higher concentrations of acids or bases at high temperature for pro-
longed time hydrolysis of dihydrazide is possible. We have also confirmed
that when this reaction is carried out in above pH range the rate of
hydrolysis is quite negligible. It is observed that as pH values of the
reaction media are increased the rates of reaction decreases (Fig. 3.25,
3.26). The plots of pH vs log k were found to be linear in both the cases.
This shows the similarity in the mechanisms of these two dihydrazides.

So as to differenciate whether these reactions are free radical or
ionic, these reactions are carried out in the presence of a free radical
scavenger, allyl acetate· It is observed that rates of these reactions are
not affected by added allyl acetate (Table 3.20, 3.21). These observations
are in favour of a charged species (might be involved in this reaction) but
free radicals are not participating in any step.

As this reaction is irreversible it is necessary to support this
statement by experiment. Therefore, we have carried out few runs in
presence of p-toluene sulphonamide which is proved to be one of the end
products. It is found that in case of oxidations of both these dihydrazides
by chloramine-T addition of p-toluene sulphonamide has no effect on the
rates of the reaction (Table 3.18, 3.19). No participation of p-toluene sulpho-
namide formed in these oxidation reactions gives support to the statement
that these reactions are irreversible.

The possibility of charged species in these reactions is supported
by the solvent effect. We have studied the effect of dielectric constant
on the oxidations of dihydrazides by chloramine-T. Different runs were
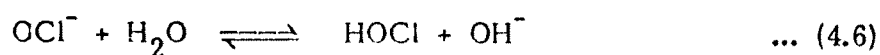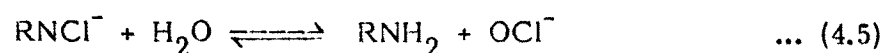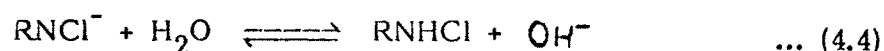carried out in different percent compositions of water/methanol mixtures

ranging from 95/5 (v/v) to 75/25 (v/v). It is found that the rate of reaction decreases with increase in percentage of methanol (Table 3.12, 3.13). The plots of log k vs. 1/D gives a straight line with negative slopes indicating reaction between negative ion and dipole or dipole dipole interaction.[16,17]

An end product analysis is very essential to visualise the mechanism of any reaction. In case of malonic and succinic_dihydrazides by chloramine-T following products are isolated (Detailed procedures are given in chapter-IIB). (1) Malonic acid dihydrazide gives malonic acid, p-toluene sulphonamide and nitrogen (2) Succinic acid dihydrazide gives succinic acid, p-toluene sulphonamide and nitrogen.

Chloramine-T is a fairly strong oxidising reagent. In order to see chloramine-T itself or its dissociated products are participating in a rate determining step it is necessary to see the equillibria of chloramine-T in alkaline medium at pH = 8 to 11. In aqueous solution chloramine-T ionises as

$$RNCl\ Na \rightleftharpoons RNCl^- + Na^+ \qquad ... (4.3)$$

Several workers[18-20] have suggested that reactivity of weakly alkaline CAT solution (pH = 8-11) is due to formation of the conjugate acid (RNHCl) from RNCl⁻

$$RNCl^- + H_2O \rightleftharpoons RNHCl + OH^- \qquad ... (4.4)$$

$$RNCl^- + H_2O \rightleftharpoons RNH_2 + OCl^- \qquad ... (4.5)$$

$$OCl^- + H_2O \rightleftharpoons HOCl + OH^- \qquad ... (4.6)$$

Therefore possible oxidising species in weakly alkaline solution (pH 8-11) are N-chloro-p-toluene sulphonamide (RNHCl), hypochlorite ion (OCl⁻),

hypochlorus acid (HOCl) and chloramine-T anion (RNCl⁻). As this reaction is carried out in aqueous medium RNCl⁻ is immediately converted to more reactive species RNHCl. Therefore RNCl⁻ is not a reacting species, p-Toluene sulphonamide is also not a reactive species because it has been proved by the experiment (Table 3.18, 3.19), hypochlorite ion (OCl⁻) is . . . very unstable and reacts with H_2O giving HOCl. Therefore this is also not reacting species in this reaction. The species HOCl is also not reactive because if it is reactive rates of reactions would be very high[21]. If HOCl would have been an active species the first order retardation of rate by the added p-toluene sulphonamide would be expected but no such effect has been noticed here. Possibility of halogen as reactive species is also ruled out by various experiments (Table 3.16, 3.17). Therefore, the only remaining species from the above equillibria that is R-NHCl in this reaction at this pH is the only reactive species.

CONCLUSIONS :

The various conclusions regarding the oxidations of dihydrazides by chloramine-T are summarised below.

(i) The order of this reaction is one in each i.e. dihydrazide and chloramine-T. Though in this reaction water is involved it is in much excess so its concentration is negligibly affected.

(ii) From Arrhenius parameters it is concluded that there is a presence of highly solvated transition state. Similarly these results are in favour of formation of rigid transition state and ordered activated complex. The similarity in the mechanism of both these cases is also supported by these results.

(iii) The study of variation in the ionic strength of the media has shown that there is no participation of free halogen in these reactions.

(iv) From the study of effect of pH it is concluded that there is similarity in the mechanism of both dihydrazides.

(v) The addition of allyl acetate i.e. free radical scavanger has given a support to the possibility that the charged species may be involved rather than free radicals in these reactions.

(vi) Addition of p-toluene sulphonamide had not altered the rate of oxidation of dihydrazides by chloramine-T which gives us a proof regarding irreversibility of reactioin. Similarly it is also proved that this reagent is not reacting species.

(viii) The results of the study of the solvent effect showed that this reaction is in between negative ion and dipole or dipole dipole interaction.
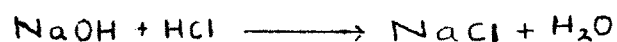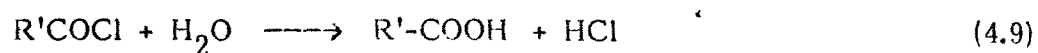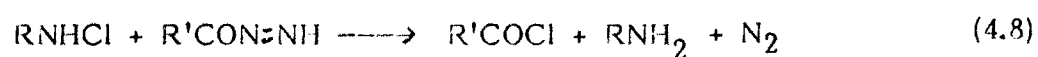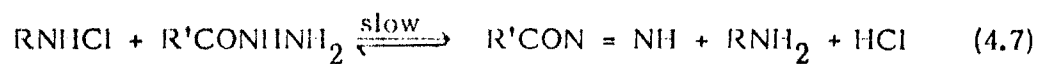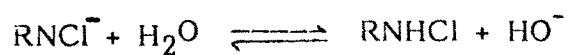
(viii) The results of the end product analysis show the formation of malonic acid, succinic acid, p-toluene sulphonamide and nitrogen.

By various experiments it is proved that R-NHCl is the reacting species in this oxidation reaction. Therefore, following types of reactions can be suggested to the oxidation of dihydrazides by chloramine-T.

Chloramine-T ionises as

$$RNClNa \rightleftharpoons RNCl^- + Na^+$$

Reactivity of weakly alkaline CAT solution (pH = 8 to 11) is due to formation of conjugate acid i.e. RNHCl (more reactive species[22]) from RNCl$^-$

$$RNCl^- + H_2O \rightleftharpoons RNHCl + HO^-$$

$$RNHCl + R'CONHNH_2 \xrightarrow{\text{slow}} R'CON = NH + RNH_2 + HCl \qquad (4.7)$$

$$RNHCl + R'CON{=}NH \longrightarrow R'COCl + RNH_2 + N_2 \qquad (4.8)$$

$$R'COCl + H_2O \longrightarrow R'{-}COOH + HCl \qquad (4.9)$$

$$NaOH + HCl \longrightarrow NaCl + H_2O$$

Therefore detailed path way for the oxidation of dihydrazides by chloramine-T can be presented as follows
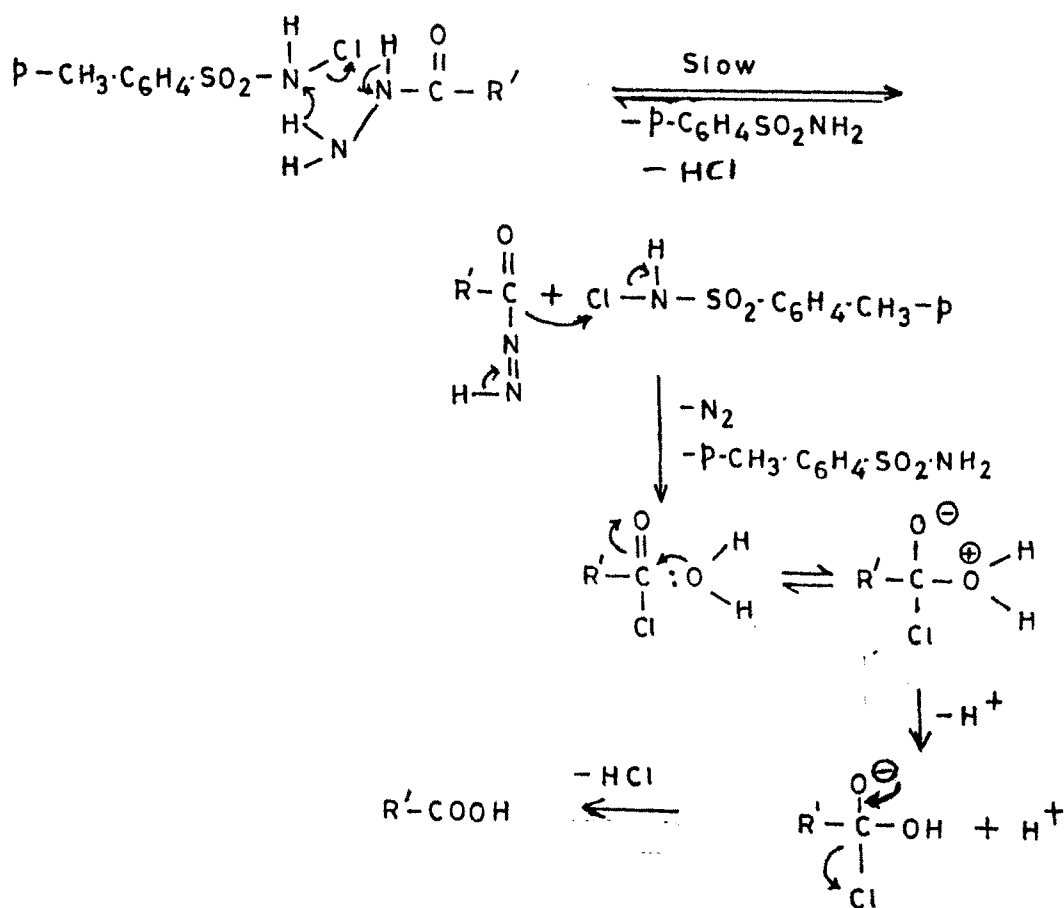
where, $R = p.CH_3 \cdot C_6H_4 \cdot SO_2 - \}$

$R' = HOOC - CH_2 - \}$

and $HOOC - CH_2 - CH_2 \}$

Conventional reaction scheme may be formulated as under and the deduced rate law is given below :

$$R' - \overset{O}{\underset{||}{C}} - NH - NH_2 + R\ NHCl \underset{\longleftarrow}{\xrightarrow{slow}} [\text{Activated complex}] \quad \ldots (4.10)$$

$$[\text{Activated complex}] \xrightarrow{fast} \text{Product} \quad \cdot \ (4.11)$$
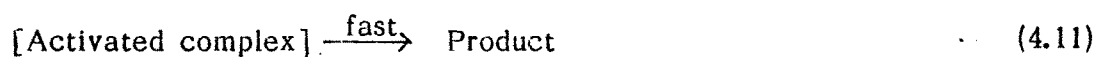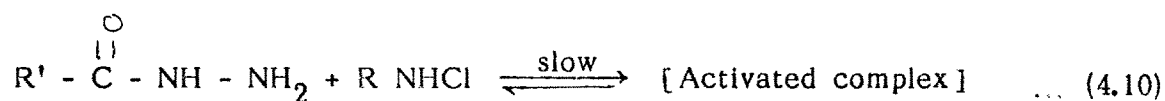
Rate $= k\ [\text{Activated Complex}]\ [H_2O]$

$$= k\ K\ [R'\text{-}CONHNH_2]\ [RNHCl][H_2O] \quad \cdots (4.12)$$

H_2O being in large excess, therefore,

overall kinetic order is two, one in each $[R'CONHNH_2]$ and $[RNHCl]$
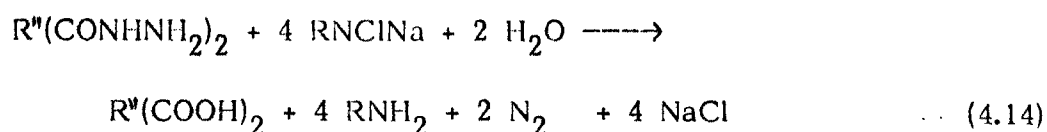
Thus the rate law is given as -

$$- \frac{d\ [R'CONHNH_2]}{dt} = k\ K[R'CONHNH_2]\ [RNHCl][H_2O] \quad \cdots (4.13)$$

in excess

$$\therefore\ k_{(obs)} = k\ K[R'CONHNH_2]\ [RNHCl]$$

STOICHIOMETRY :

Model stoichiometry for these oxidation reactions is given as follows.

$$R''(CONHNH_2)_2 + 4\ RNClNa + 2\ H_2O \longrightarrow$$

$$R''(COOH)_2 + 4\ RNH_2 + 2\ N_2 + 4\ NaCl \quad \cdots (4.14)$$

Where, $R'' = \{-CH_2-\}$ in case of malonic acid dihydrazide,

$R'' = \{-CH_2-CH_2-\}$ in case of succinic acid dihydrazide and

$R = p-CH_3.C_6H_4.SO_2^- \}$

These two dihydrazides we have selected so as to compare the difference between the rates of these reactions. The two hydrazide groups are separated by one $-CH_2-$ group in malonic acid dihydrazide and by two $- CH_2-$ groups in succinic acid dihydrazide. The rate of this oxidation reaction is found to be faster in case of succinic acid dihydrazide (Table-3.1 and 3.3, * marked k). This is because after the oxidation of first hydrazide group in both the cases $HOOC-CH_2-CO.NH.NH_2$ and $HOOC-CH_2-CH_2-CO.NHNH_2$ will be formed. In case of first species the electron with drawing $(-COOH)$ group will increase the electron deficiency of carbonyl carbon. Therefore this carbonyl carbon will become much electron deficient. In the first step of mechanism N-H bond is shifted towards the second nitrogen and N'-H bond is shifted towards RNHCl which requires electron release from carbonyl carbon and other part of a molecule. But here, this carbonyl carbon is itself too electron deficient hence the rate of reaction is slow. Whereas in case of second species $-COOH$ group is separated from carbonyl carbon by two $-CH_2-$ groups. Therefore, electron attracting power of $-COOH$ group does not affect the electron deficiency of carbonyl carbon, which is near to $-NH.NH_2$ group. So in this case the rate of reaction is faster one.

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