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C H A P T E R - I I

[A] LITERATURE SURVEY

[B] CHLORAMINE-T
(A REAGENT)

[C] OBJECT AND SCOPE OF
THE WORK

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[A] LITERATURE SURVEY

Kinetics and Mechanism of Chloramine-T Reactions

The kinetics and mechanisms of reactions of chloramine-T have been investigated by many authors. Coull and co-workers[1] were the first to investigate the kinetics and mechanism of decomposition of Hydrogen Peroxide by Chloramine-T in presence of hydrochloric acid. Then Pryde and Soper[2] investigated the chlorination of p-cresol by chloramine-T. The kinetics of same reaction i.e. chlorination of p-cresol was investigated by Higuchi and Hussain.[3]

In recent years extensive study in kinetics and mechanism of oxidation of different types of compounds with chloramine-T have been reported. It is briefly reviewed here.

Oxidation of alcohols have been studied by Mushran et.al.[4] (n-butanol, iso-butanol and isopropanol) with chloramine-T in acidic medium. The mechanism proposed involves the hydrolysis of RNHCl giving rise to HOCl in slow step, which further reacts with substrate to form aldehyde. The rate law is given as

$$-\frac{d[CAT]}{dt} = K\,[CAT][H^+] \qquad \ldots \qquad (2.1)$$

where CAT means Chloramine-T

Further the reactions of secondary alcohols (propan-2-ol, butan-2-Ol, Pentan-2-ol, octan-2-ol and 1.3 dichloro propan-2-ol) with chloramine-T in aqueous acetic acid medium have been

studied by Natarajan and Thiagrajan[5] in presence of strong mineral acid in aqueous media. The rate law is suggested as follows:

$$\frac{-d[CAT]}{dt} = K[CAT][Alcohol] \quad \ldots \quad (2.2)$$

Oxidation of some other alcohols have been reported by Mahadevappa and Naidu[6]. They investigated the oxidation of allyl alcohol by chloramine-T at higher acid concentration. The rate law is given as

$$\frac{-d[CAT]}{dt} = K\,[CAT][H^+]^2 \quad \ldots \quad (2.3)$$

Kintics of oxidation of some aldoses with chloramine-T in highly alkaline medium have been investigated by Agrawal and Mushran.[7] The oxidation rates were found to follow the order.

xylose > arabinose > galactose > mannose

and rate determining step involves interaction of three charged ions OCl^-, OH^- and anion derived from aldoses. Identical mechanism was proposed by Mushran, Gupt and Sanehi[8] for oxidation of D-Ribose. Madnawet et al.[9] have studied the oxidation of fructose by chloramine-T in alkaline medium.

Oxidation of phenol and substituted phenols by chloramine-T in aqueous alkaline medium have been reported by Radhakrishnamurti.[10] The reaction is found to follow first order kinetics with respect to both substrate and chloramine-T concentration and has fractional order with respect to alkali concentration. The reactivity order shows that electron releasing groups accelarate the reaction.

Kinetics of oxidation of anisole and substituted anisoles by chloramine-T in aqueous acetic acid medium has been reported by Murti and Sasmal.[11]

Agrawal, Mushran and Sanehi[12] studied oxidation of formaldehyde and acetaldehyde with chloramine-T using osmium tetroxide as catalysis. The kinetics and mechanism of oxidation of ketones have been extensively studied by Mushran et al.[13] They have reported the oxidation of acetone and methyl ethyl ketone in alkaline medium in presence of osmium(VIII) catalyst. Same authors[14] have studied kinetics of ethylmethyl ketone and methyl isobutyl ketone by chloramine-T in alkaline medium. Formation of 1-2 diketones are reported. Sharma and coworkers[15] have reported the kinetics and mechanism of oxidation of methyl-isopropyl, methyl-n-propyl and ethyl-iso-propyl ketones by chloramine-T in alkaline medium.

Balasubramanian and Thiagarajan[16] have investigated the kinetics and mechanism of chlorination of ketones by chloramine-T in aqueous acidic medium in presence acetic acid and N-N' diethyl formamide. It has been observed that at high concentration of chloramine-T and in aqueous acetic acid in presence of sodium acetate, rate law is independent of [Ketone].

Naidu and Mahadevappa[17] have studied the oxidation of some aliphatic ketones by chloramine-T in hydrochloric acid medium. A rate expression of the form

$$-\frac{d\,[CAT]}{dt} = K\,[CAT][S][H^+] \qquad \ldots \qquad (2.4)$$

has been suggested. $[CAT] = [\text{Chloramine-T}]$

Oxidation of cyclohexanone and cyclo pentanone by chloramine-T in alkaline medium have been reported by Mushran and coworkers.[18-19] Singh et al.[20] have reported the oxidation of acetophene by chloramine-T in aqueous acetic acid medium. Murti and coworkers[21] have reported the kinetics of aliphatic, arylaliphatic and cyclic ketones by chloramine-T in aqueous ethanol medium under alkaline conditions. Solvent effect has been studied which had indicated involvement of neutral molecule in the rate determining step. The reaction products have been identified to be 1.2 diketones.

The kinetics and mechanism of amino acids by chloramine-T have been extensively investigated. Mushran and coworkers[22-24] have investigated the kinetics of oxidation of α-amino acids by chloramine-T in alkaline medium. The kinetic study of oxidation of glycine and valine by chloramine-T in hydrochloric acid medium has been reported by Gowda and Mahadevappa[25]. Naidu and coworkers[2] have reported the kinetics of oxidation of leucine, serine, glutamine, and glutamic acid by chloramine-T in perchloric acid medium. First order dependance of each chloramine-T and amino acids and inverse first order dependent with respect to $[H^+]$ ions have been reported. Chloride ion is found to catalyses the reaction.

Oxidation of ~~agrinine~~ arginine and histidine by chloramine-T in hydrochloric acid medium have been reported by Mahadevappa et al.[27-8] The reaction is simultaneously catalysed by H^+ and Cl^-. Addition of methanol decreases the rate. At HCl concentration 0.04 to 0.12 M the rate expression is suggested

as follows

$$-\frac{d[CAT]}{dt} = k_1[CAT][H^+][\text{amino acid}] + k_2[CAT][\text{amino acid}][Cl]^{0.6} \quad \ldots (2.5)$$

But at $[HCl] > 0.12$ the rate law becomes

$$\frac{-d[CAT]}{dt} = k\,[CAT][\text{amino acid}]^{0.6} \quad \ldots (2.6)$$

Kinetics of oxidation of orginine monohydrochloride by chloramine-T in alkaline medium have been investigated by Parihar and coworkers[29]. The kinetics were found to be first order in both chloramine-T and arginine. The rate was inversely dependant on NaOH concentration and the reaction had a negligible salt effect. The energy of activation was 18.5 K cal/mol and temperature coefficient was 2.7. Kinetics of oxidation of glutamic acid by chloramine-T in hydrochloric acid medium have been reported by Mahadevappa et al[30]. Kinetics of chloroaminometric oxidation of aspartic acid and glutamic acid in alkaline medium have been reported by Mushran et al[31].

Mahadevapp and coworkers[32] have investigated the kinetics and mechanism of arginine, histidine and theonine in alkaline medium at 35°C. The rates are first order in both [CAT] and [Amino acids] and inverse fractional order in $[OH^-]$ for arginine and histidine, and rate is independant of $[OH^-]$ for threonine. Salt had found to be no effect on reaction.

Kinetics of oxidation of l-histidine by chloramine-T in alkaline medium have been investigated by Gupta[33]. The rate of reaction was found to be decreases with increases in pH. Change

in ionic strength has no effect on rate of reaction. The suggested mechanism involves dipole-dipole interaction between histidine and chloramine-T.

Kinetics and mechanism of oxidation of glutamic acid by chloramine-T in alkaline medium with or without catalytic action of copper(II) ion have been reported by Varma and Yadav[34]. The order with respect to substrate and [CAT] is one each. Above 4.8×10^{-2} M NaOH concentration the reaction is found to be independant of $[OH^-]$. Copper (II) ion catalyses the reaction and catalytic action of copper(II) is ascribed to the complex formation with glutamic acid.

Kinetics of oxidation of 2-amino-isobutyric acid by chloramine-T in alkaline medium has been reported[35]. A mechanism involving an interaction between neutral molecule and charged ion or between two neutral molecules in rate determing step has been proposed.

Mushran and coworkers[36] have investigated the oxidation of α-hydroxy acids with chloramine-T in alkaline medium in presence of osmium(VIII) as catalyst.

Kinetic studies on oxidation of E.D.T.A. by chloramine-T in acid medium has been investigated by Sanehi et al.[37]. The protonated form of E.D.T.A. is assumed to react with RNHCl in slow step forming an intermediate which then interact with six molecules of RNHCl in fast step giving products.

Kinetics of oxidation of hydroxylamine hydrochloride by chloramine-T in hydrochloric acid and perchloric acid has been

investigated by Mahadevappa and coworkers[38]. The reaction shows the first order dependance on [CAT] and [substrate], but inverse first order dependance on $[H^+]$. Chloride ion catalyse the reaction. A mechanism involving interaction of unprotonated hydroxylamine and N-chloro-p-toluene sulphonamide giving an intermediate complex in slow step is suggested.

Krishnrao[39] has reported the oxidation of Benzoyl hydrazines by chloramine-T in alkaline medium. The order with respect to each [substrate] and [CAT] is found to be one. The rate is found to be independent of pH. The reaction is accelerated by electron withdrawing groups. The mechanism involves the attack of chloramine-T on benzoylhydrazine molecule in rate determing step.

Ramanujan and Trieff have reported the kinetics and mechanistic studies of chlorination of anilines[40]. A mechanism involving the formation of complex in a fast equilibrium step followed by a slow decomposition of complex yielding N-choro-anilines has been proposed.

Radhakrishnmurti[41] has also reported the mechanism of chlorination of anilines by chloramine-T in alkaline medium. It is believed that oxidizing species ~~is~~ are chloramine-T itself.

Antelo and coworkers[42] have studied the effect of pH in the reaction of diethanolamine with chloramine-T. The oxidation rate of diethanolamine with [CAT] have studied at pH range 8 to 13, it reaches maximum at pH 10.8 and then decreases to constant rate.

Kinetics of chlorination of toluene and some substituted toluenes by chloramine-T in aqueous acetic acid in presence of perchloric acid have been reported by Murti and coworkers[43]. Nuclear halogenation has observed with m-methyl toluene while nuclear and side chain halogenation for p-methyl toluene and o-methyl toluene, and side chain halogenation for toluene and m-chlorotoluene. Added acetate ion inhibits the reaction, and added p-toluene sulphonamide causes a pronounced retardation. A mechanism involving $ACO^{+}HCl$ as the important electrophile is discussed.

Chlorination of p-toluidines and p-nitroanilines has been reported by Murti et al[44]. The mechanism of chlorination is shown to be dipole-dipole type involving direct transfer of chloride from chloramine-T to the substrate.

Mahadevappa and coworkers have oxidised dimethyl sulphoxides[45,46] and diphenyl sulphoxide in perchloric acid, hydrochloric acid and sodium hydroxide media by chloriamine-T. The reaction mechanism in acid medium is assumed to involve an electrophilic attack by the free acid RNHCl at the sulphur site of dimethyl sulphonamide forming a reaction intermediate in slow step, which subsequently decomposes to dimethyl sulphone in fast step. In alkaline medium the catalyst osmium tetroxide is supposed to interact with RNHCl forming cyclic complex which in turn reacts with substrate in slow and rate determing step. The simplification of the rate equation at higher alkali concentration is attributed to a direct interaction between chloramine-T and the substrate.

Ganapathy and Jayagandhi[47] have reported kinetics of oxidation of methyl-phenyl sulphoxide, m- and p-substituted phenyl and alkyl sulphoxides in alkaline medium. The proposed mechanism of oxidation of methyl phenyl sulphoxide by chloramine-T in HCl medium involves a slow step in which hydrolysis of dichloramine-T occurs producing HOCl, which subsequently reacts with the substrate in fast step giving rise to products. The kinetics of oxidation of methyl phenyl sulphoxide by chloramine-T has studied in buffered ethanol water (1/1 v/v) of pH-7.0. The reaction was followed no simple order kinetics. A possible mechanism is suggested involving three rate controlling step i) The reaction between RNHCl ($R\text{-}CH_3C_6H_4SO_2$) and the sulphoxide ii) The disproportion of RNHCl iii) The reaction between $RNCl_2$ and the sulphoxide. A mixed order rate is derived.

Banerji[48] has investigated the kinetics of oxidation of substituted mandelic acids by chloramine-T in $HClO_4$ media. $[ClOH_2]^+$ is assumed to be the reactive species.

Singh and coworkers[49] have reported the kinetics of oxidation of α and β ketoglutaric acid by chloramine-T in acidic medium. A mechanism involves the interaction of enol form of the substrate with chloramine-T in the rate determining step.

Shrinivasan and coworkers[50] have reported the kinetics and mechanism of oxidation of (substituted phenyl thio) acetic acid by chloramine-T in alkaline medium, at pH 10.06. The oxidation rate decreased considerably with increasing pH. The oxidation proceeds via two paths the major one involving RNHCl as

the main oxidizing species and other involving ClO^- ions as oxidizing species.

Kinetics and mechanism of oxidation of lactic acid by chloramine-T catalysed by copper(II) ion have been reported by Gupta and coworkers[51]. Formation of complex between copper(II) and p-toluen sulphonamide has been suggested. Autoinhibition was observed after about 50 % reaction.

Kinetics and mechanism of oxidation of hypophosphorus acid with chloramine-T in acidic medium has been reported by Gupta et al[51].

Mahadevappa and coworkers[53] have reported the detailed investigation of the kinetics of oxidation of thiocynate ion by chloramine-T in alkaline medium. At low substrate concentration the rate law is shown to be

$$-\frac{d(CAT)}{dt} = K\frac{[CAT][NCS]}{[NaOH]^2} \quad \ldots \quad (2.7)$$

which simplifies to

$$-\frac{d(CAT)}{dt} = K\,[CAT][NaOH]^{-1} \quad \ldots \quad (2.8)$$

at higher concentration of [NCS] and solvent. Kinetic effect has been studied and a suitable mechanism has been reported.

Agrawal and Mushran[54] have investigated the kinetics of oxidation of hexacynoferrate(II) by chloramine-T in acidic medium. A mechanism involves the interaction of RNHCl with hexacynoferrate in slow rate determining step, forming a reactive intermediate which subsequently reacts with another molecule of

the substrate forming the product. The rate law of type

$$\frac{-d[Fe(CN)_6]^{-4}}{dt} = K\,[Fe(CN)_6]^{-4}\,[CAT][H^+] \quad \ldots \quad (2.9)$$

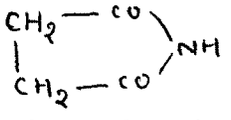
has been derived.

[B] CHLORAMINE-T (A REAGENT)

Chloramines are compounds in which one or more chlorine atoms are attached to nitrogen atom. Organic chloramines are N-chloro derivatives of following group of compounds

1) Sulphonamides $R\text{-}SO_2NH_2$

2) Heterocyclic chloramines with chlorine attached to nitrogen in the ring



3) Condensed amines from cynamide derivatives

$H_2N.C(NH)N{:}N\ C(NH)\ NH_2$

4) Anilides $C_6H_5NHCOCH_3$.

Generally organic chloramines are prepared by reaction of hypochlorous acid with above group of compounds. Commercial chloramines such as chloramine-T and chloramine-8 are used as antiseptic and disinfectant reagents in toothpastes, mouth washes, soaps and in the treatment of infected wounds.

Chlorine atom bonded to nitrogen in chloramines is positive with an oxidation state +1. So, all compounds

containing N-Cl group liberate iodine from acidified potassium iodide solution. The over all reaction for monochloramines can be written as

$$R.R'N\text{-}Cl + 2\ I^- + H^+ \longrightarrow R.R'NH + I_2 + Cl^- \quad \ldots \quad (2.10)$$

Fairly stable organic dichloramine-T (DCT) also react with acidified Potassium iodide solution with evolution of iodine.

$$RNCl_2 + 4\ I^- + 2\ H^+ \longrightarrow R.NH_2 + 2\ I_2 + 2\ Cl^- \quad \ldots \quad (2.11)$$

From the analytical point of view, the most important class of chloramines are perhaps the N-chloro derivatives of aromatic sulphanamides.

Chloramine-T [$p\text{-}CH_3\ C_6H_4SO_2NClNa.3H_2O$]

The sodium salt of N-chloro-p-toluene sulphonamide known as chloramine-T was first prepared by Chattway[55]. When toluene is allowed to react with chloro-sulphonic acid it gives ortho and para-toluene sulphonyl chloride. The para isomer on treatment with ammonia and then with aqueous sodium hypochlorite solution produces chloramine-T. It can be purified by recrystalization from hot water and dryed in air. Chloramine-T sample with maximum purity of 99.5 % can be obtained by successive recrystallization. The 0.5 % impurity is due to moisture. It is found to be difficult to prepare anhydrous salt and preserve this under laboratory conditions[56]. Hence this salt cannot be used as primary standard. Commercially available chloramine-T is about 98 % purity. By successive washing it with carbon

tetrachloride contamination of dichloramine can be removed.

Solubility of chloramine-T in water is 14 grams in 100 ml at 25° and 50 grams in 100 ml at 100°C. It is soluble in alcohol and acetone but it decomposes on standing. The available chlorine content in chloramine-T has been estimated to be 23 to 26 %.

There are conflicting reports on the stability of chloramine-T in solid state and in solution[56]. Dietzel and Toufel[57] have reported the decline in assay of 1.4 % in 12 months in brown coloured bottle and 5 % in clear glass bottle. Solution of chloramine-T exposed to direct sunlight is unstable, and it it is protected from day-light it is stable for nearly four weeks.

Chloramine-T is strong electrolyte and it dissociates in aqueous solution as

$$R\text{-}N\cdot Cl\ Na \rightleftharpoons R.NCl^- + Na^+ \quad \ldots \quad (2.12)$$

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

$$R\text{-}NCl^- + H^+ \rightleftharpoons R.NHCl \quad \ldots \quad (2.13)$$

The free acid has not been isolated but the evidence for existance has been reported[56]. The free acid then gives rise to p-toluene sulphonamide and dichloramine-T

$$2\ RNHCl \rightleftharpoons R.NH_2 + R.NCl_2 \quad \ldots \quad (2.14)$$

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

$$R.NCl_2 + H_2O \rightleftharpoons R.NHCl + HOCl \quad \ldots \quad (2.15)$$

$$R.NHCl + H_2O \rightleftharpoons R.NH_2 + HOCl \quad \ldots \quad (2.16)$$

Finally HOCl ionizes as

$$HOCl \rightleftharpoons H^+ + {}^-OCl \quad \ldots \quad (2.17)$$

[R = P^- $-CH_3$ - C_6H_4 SO_2]

It liberates iodine with acidified potassium iodide solution

$$R\text{-}NCl^-Na^+ + 2\ I^- + 2\ H^+ \longrightarrow R.NH_2 + I_2 + NaCl \quad (2.18)$$

Oxidizing properties of chloramine-T are well reviewed by many authors[58-61]. It is introduced as an analytical reagent by Null[62] and then large number workers are attracted towards the use of ~~xx~~ chloramine-T in analytical chemistry. The behaviour of chloramine-T as titrametric reagent and standardization methods have been critically examined by Bishop, Jennings[56] and Jennings[63].

Chloramine-T has been widely used as an oxidizing reagent in acid medium. Chloramine-T solution can be standardized by adding potassium iodide solution in presence of (2N)H_2SO_4 and titrating the liberated iodine against standard sodium thiosulphate solution. A large number of organic and inorganic reducing agents have been estimated using chloramine-T as an oxidant by volumetric, potentiometric and amperometric methods. The redox potential of 0.1 M chloramine-T solution saturated w with P-Toluene sulphonamide at different pH value have been

reported by Murthy and Rao[64]. The values are 1.139, 0.778 and 0.614 V at pH 0.65, 7.00 and 9.70 respectively.

[C] OBJECT AND SCOPE OF THE WORK

The chemistry of hydrazides is very important and interesting branch of organic chemistry due to physiological and other useful activities of hydrazides. Physiological effects of many hydrazides, perticularly various modified aromatic carboxylic acid hydrozides have been tested. Isonicotinic acid hydrazides were found to be a strong antituberculotic action.[65] Then many derivatives of this compound have been synthesised and tested for antibacterial properties[66-67]. In perticularly high activity of certain derivatives is assumed to be due to the diacyl hydrazine group as the biological active centre[68]. Carboxylic acid 1-2 diaryl hydrazides have been reported to possess anti-inflammatory properties[69]. Isoxazole carboxylic acid hydrazides[70] are active against leprosy and phenothiazine carboxylic acid hydrazide[71] has been reported to be anti-convulsive action. Dihydrazides have recently been introduced as anthelmintics[72]. Maleic acid hydrazide is used to regulate and inhibit the growth of the plants[73].

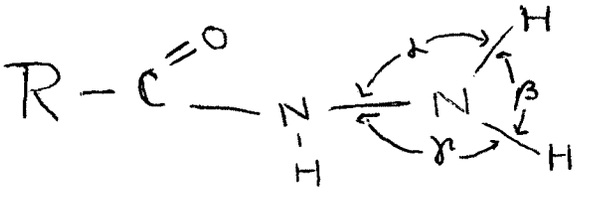
In view of their high reactivity, hydrazides are important starting materials and intermediates in the synthesis of certain amines, aldehydes and heterocyclic compounds, which otherwise would have been difficult to prepare. Hydrazides are used in

heat and corrosive stabilization of cellulose and cellulose derivatives[74], and as anti-oxidants for polyolefines and polyurethanes, which are otherwise oxidized in presence of copper. The incorporation of hydrazides[75] has improved the applicability of plastics and cable insulation. Small amount of hydrazides are useful in sensitizing electrophotographic layers made up of poly vinyl carbazole[76]. Dihadrazides can be used in cigaratte filters for the selective removal of aldehydes from tobacco smoke. Ion exchange resins for the separation of copper, nickel, cobalt, magnessium and transition metal ions have been prepared from co-polymer of 2-methyl-5-vinyl pyridine and hydrazides of 1-2-ethylene dicarboxylic acid[77].

Thus at a glance it is observed that the chemistry of hydrazides is not only expanding as a chemistry, but side by side it is also giving many compounds, application of which are very useful to human life.

The hydrazides are the derivatives of carboxylic acids and hydrazine. The preferred nomenclature is to describe any hydrazide as carboxylic acid hydrazide. This nomenclature is also used in chemical abstract. The nitrogen atoms of hydrazides are designated as 1 and 2, α and β or N and N', the first member is given to nitrogen present near the acyl group. The properties of hydrazides are important in their relevance to the chemistry of proteins, substances that are fundamental to all lives. Their characteristic properties being primarily due to polyamide structure. Hence the structure of hydrazides are

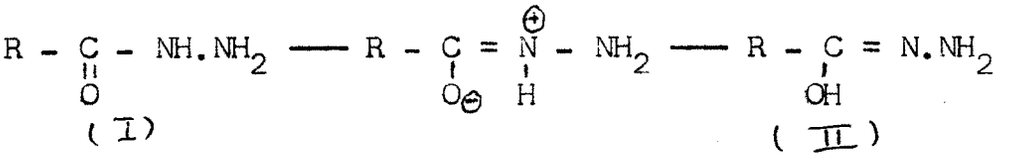
determined carefully using modern techniques of structure determination. The structure of isonicotinic acid hydrazide has been determined by x-ray crystallography[78]



$\alpha = 101^{\circ}$ $\beta = 98^{\circ}$ $\gamma = 109^{\circ}$

The N-N bond length is always lie between 1.39 and 1.42 A°. It is shorter than in hydrazine which is in between 1.46 and 1.47 A°. This is due to formal charge effect and to the fact that the electron attracting acyl group reduce the repulsion between the loan pair of electrons of nitrogen atoms. The C-N bond length is 1.33 A° which is same as in pyridine ring. This bond must have therefore roughly a 50 % double bond character. The two hydrogen atoms present almost exactly in the same plane.

The hydrazide group can change from its resonance stabilised amide form(I) to the toutomeric enol form(II) by the shift of a hydrogen from nitrogen to oxygen.



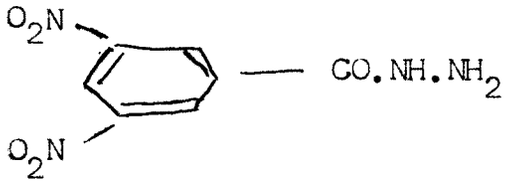
(I) (II)

Due to resonance stabilization of hydrozide group, its basicity is drastically reduced. In addition to this, the electron attracting phenyl group, so much lowers the basicity of hydrazides that the compounds assume an acidic character.

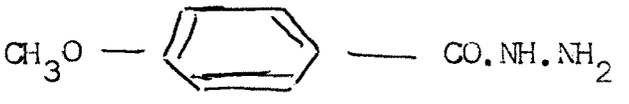
In the NMR spectra of hydrazides, the chemical shifts of the protons of hydrazides are similar to those of protons with a comparable chemical environment in other compounds such as amides. The IR spectra of crystalline hydrazides shows amide (N-N disuccinumide) band at 1625 - 1670 cm^{-1} due to the carbonyl group whose double bond character is reduced by the mesomeric effect of the amide system. A weak band at 1610 - 1620 cm^{-1} is attributed to - NH_2 deformation[79,80]. The spectra recorded for hydrazides in solution is different as regards the position and the number of absorption bands. U.V. absorption spectra of hydrazides has not been investigated extensively, but they are expected to resemble with those of amides.

Kinetics of oxidation of hydrazides by variety of oxidants have been studied by many authors[81] . As the aryl hydrazines (hydrazides) are of commandable pharmaceutical important compounds, so it is pertinent to understand the mechanism of their oxidation with view to specify their role in metabolic processes. Looking to previous survey and in light of above discussion it is clear that, it is necessary to make available some more information regarding mechanism of oxidation of hydrazides.

Observing these various important uses of hydrazides we have undertaken the study of kinetics of oxidation of hydrazides by chloramine-T in buffered solution. The different hydrazides selected for study are



3-5-Dinitrobenzoic acid hydrazide
[3-5 DNBH]



p-Methoxy benzoic acid hydrazide
[p-MBH]

These two compounds are selected in such a way that one contains two electron withdrawing groups and other an electron donating group.

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