Hydroxamic acids were discovered in 1869 by H. Losson who for the first time prepared oxalo-hydroxamic acid by reacting diethyl oxalate and hydroxylamine. It was Yalq who brought the hydroxamic acids into light through his review article giving exhaustive information regarding the methods of preparation and properties of these compounds. Since then, a large number of hydroxamic acids have been synthesised and their potentialities as organic analytical reagents investigated. Their increasing popularity as complexing agents is due to their capability of forming stable complexes, both coloured and colourless, with a large number of metal ions and therefore they have found applications in different fields of analytical chemistry.

Hydroxamic acids, represented by the general formula (I), are the N-acyl derivatives of hydroxylamine

\[
\begin{align*}
R & - N \quad OH \\
\text{I} & \quad | \\
R & - C = O \\
(1)
\end{align*}
\]
and are called primary \((R = H)\) or secondary \((N\)-substituted, 
\(R\)-alkyl or aryl group\). The primary hydroxamic acids are 
capable of undergoing keto and enol tautomerism [equation] 
\[
\text{H} - \text{N} - \text{OH} \quad \xrightarrow{\text{spectroscopic}} \quad \text{N} - \text{OH}
\]
\[
\mid \quad \quad \mid
\]
\[
\text{R}^1 - \text{C} = 0 \quad \xrightarrow{\text{spectroscopic}} \quad \text{R}^1 - \text{C} - \text{OH}
\]
\[
\text{(II)} \quad \text{(III)}
\]
62 evidence indicates that the keto-form (II) predominates.
These compounds are named by substituting 'O' for 'ic' of 
the corresponding carboxylic acid from which they are 
derived. Thus the hydroxamic acids derived from acetic 
and benzoic acids are named as acetoxydamic am benzohy-
droxyamic acid (BHA) respectively.

When the hydrogen attached to nitrogen atom of the 
primary hydroxamic acids is replaced by any other group 
they become \(N\)-substituted hydroxamic acids. Thus, in BHA(IV) 
when \(R\) is replaced by a phenyl group it becomes \(N\)-phenyl-
benzohydroxamic acid PBEA (V).

\[
\text{H} - \text{N} - \text{OH} \quad \circ \quad \text{N} - \text{OH}
\]
\[
\mid \quad \mid
\]
\[
\text{N} \quad \text{C} = 0 \quad \text{N} \quad \text{C} = 0
\]
\[
\text{(IV)} \quad \text{(V)}
\]

An alternative nomenclature of these compounds 
depending on the parent hydroxylamine as 'N-acyl-substituted
hydroxylamine is also prevalent; benzohydroxamic acid and N-phenylbenzohydroxamic acid being referred to as N-benzylhydroxylamine and N-benzyl-N-phenyl hydroxylamine respectively.

In 'Chemical Subject Index' of the 'Chemical Abstracts' beginning with volume 76 (1972) an alternative nomenclature is adopted considering hydroxamic acids as N-hydroxyl derivatives of amides. According to this classification BHA(IV) and PBHA(V) would be N-hydroxy-benzamide and N-hydroxy-N-phenyl-benzamide respectively. It appears that this nomenclature is limited to the 'Chemical Abstracts' only as it has not found use anywhere else in literature.

The hydroxamic acids, so far synthesised, are generally white or sometimes light yellow crystalline substances with definite melting points. They are quite stable at room temperature. Hydroxamic acids are weak acids though they are somewhat stronger acids than amides. They are able to co-ordinate to metal ions as bidentate ligands through the oxygen of carbonyl and hydroxyl groups.

The occurrence of hydroxamic acids in nature was first reported in 1960 (63, 64); most of these are N-substituted. Their presence in micro-organism is also reported. Hydroxamic acids show a wide range of biological activities which are mostly due to their chelating properties with
metal ions. Some of the hydroxamic acids and their derivatives are potential anti-malarials. As the hydroxamic acids show varied activities they are used in biological investigatios, medicine, soil science and industry.

Many times the synthesis and applications of hydroxamic acids involves the use of aqueous acidic, aqueous alkaline or mixed aqueous organic solvent medium at different temperatures and, therefore, there is always a possibility of their being hydrolysed to a smaller or greater extent depending upon the reaction conditions. A systematic study of the rate and mechanism of the hydrolysis of hydroxamic acids will prove useful in the judicious adjustment of the reaction conditions during their synthesis and applications.

In the present investigation the rate of hydrolysis of hydroxamic acids and their half life period under varied experimental conditions has been studied. On the basis of the experimental data a probable mechanism of the reaction has also been proposed.
REVIEW OF THE EARLIER WORK.

In this section the investigations done on the mode of hydrolysis of amides and hydroxamic acids by other workers in the past years are reviewed. Amides are structurally similar to hydroxamic acids and their hydrolysis is studied quite in detail in standard books and articles whereas a little work on the hydrolysis of hydroxamic acids is reported so far. Therefore a brief review of the kinetics and mechanism of the hydrolysis of amides is also given.

Hydrolysis of Amides.

Amides usually hydrolyse with N-acyl bond fission to regenerate the parent carboxylic acid and an amine (equation 1). The initial step requires nucleophilic addition to the carbonyl group and a leaving group. Amines (particularly amine anions) are poor leaving group so these reactions are often sluggish. Hydrolysis is much easier either under alkaline conditions, where the more powerful HO nucleophile is available, or under acidic conditions, where the protonation of the substrate assists both nucleophilic attack by H₂O and expulsion of the amine.

\[
\text{R CONHR} + \text{H}_2\text{O} \xrightarrow{\text{H}^+\text{ or }\text{OH}^-} \text{R COOH} + \text{R}_2\text{NH}
\]
Substantial evidence, including the existence of rate maxima in concentrated acids related to complete substrate protonation, an inversion of solvent deuterium and $^{18}$O isotope effects and a study of other parameters show that the attack by $\text{H}_2\text{O}$ on the conjugate acid of the amide is rate-limiting \textsuperscript{71,87}. The dispute is whether this slow step involves the formation of a tetrahedral intermediate from the O-conjugate acid, or direct (SN2) displacement on the N-conjugate acid, or possibly a combination of both. The alternative pathways are shown in the following scheme.

Alternative mechanism for the acid-catalysed hydrolysis of amides.

Although the mechanism may be contentious, there is no doubt that hydrolysis rates for most amides pass through a maximum, dependent on both solvent acid and amide structure, but usually \( C_\text{a} 2-5\% \text{H}_2\text{SO}_4 \). This corresponds to 100\% protonation
of the amide and the subsequently decreasing rate relates to the reduction in water activity. Many attempts have been made to specify the role of water in these reactions by correlating rates with acidity function ($H_\alpha$ and $H_\omega$) and related data. These analyses suggest a highly solvated transition state.

Systematic studies of alkylamides, benzanilides, and anilides show that acid-catalysed amide hydrolyses are much more sensitive to steric than electronic substituent effects. This fits with either pathway in the scheme. Because of steric effects, primary amides are generally more reactive than secondary and tertiary compounds. Data for alkylamides completed by Boiten and his colleagues show that rate correlates well with a modified Taft equation containing terms for steric and hyperconjugative but not polar interaction. Similar findings apply to substituted benzamides, where only small rate perturbations are found for m- and p-substituents, but ortho-substituted group exert large steric retardations. For acetonilides, electron-withdrawing p-substituents only mildly accelerate hydrolysis in 70% (w/w) $H_2SO_4$ ($\rho=1.0$), but much larger accelerations pertain at higher acidities owing to changed mechanism.

Under special circumstances, acid-catalysed hydrolysis may proceed by different mechanisms to the bimolecular
N-acyl bend fission discussed above. Another mechanism involving N-alkyl bend fission has been observed for secondary amides bearing N-t-alkyl groups in $\text{H}_2\text{SO}_4$.

**Hydrolysis of hydroxamic acids.**

It has been noted that so far only few workers have studied the kinetics of the hydrolysis of hydroxamic acids. This field remained untouched until 1966 when Berndt and Fuller first published their work on the hydrolysis of benzohydroxamic acid. A survey of literature reveals that most of the work in this field concerns with the primary hydroxamic acids which are analogues of benzohydroxamic acid. Only few from the series of N-substituted hydroxamic acid have been investigated. The hydroxamic acids so far studied are given in Table I.

Berndt and Fuller and other workers (105,106, 108,114,115) have observed that the base catalysed hydrolysis of benzohydroxamic acids and its analogues is pseudo first order and the rate increases with the increase of the concentration of the alkali. Ahmad et al reported that salt effect does not operate in the hydrolysis and the reaction is not subject to general base catalysis. The formation of tetra-hedral intermediate in the alkaline hydrolysis of benzohydroxamic acid is presumed.
The acid catalysed hydrolysis is studied in dilute and moderately concentrated acid medium. It is observed that the rate of hydrolysis is a function of proton activity. A rate maxima is reported in moderately concentrated acidic medium the behaviour is similar to amide. The range of acid concentration for rate maxima depends on the relative basicity of the substrate. The more basic substrate has low acidic range, as compared to relatively low basic substrate, for rate maxima.

The catalytic effect of the mineral acids is found to be
in the order $\text{H}_2\text{SO}_4 \rightarrow \text{HCl} > \text{HClO}_4$, which indicates a nucleophilic attack of water on the carbonyl carbon and thus suggesting a bimolecular mechanism. In the presence of salts the reaction exhibits a positive ionic strength effect.

It is observed for the acid catalysed hydrolysis of hydroxamic acids, that, a greater hydrolytic rate constant results in deuterium oxide than in protium oxide. The higher rate in heavy water suggests that a rapid transfer of protons to the substrate occurs in the reaction and the pre-equilibrium step is not the rate determining step. The suggested reaction takes place according to equation:

$$
\begin{align*}
\text{R} - \text{N} - \text{OH} + \text{H}_3\text{O}^+ & \rightarrow \text{R} - \text{N} - \text{OH}^+ \\
\text{R} - \text{C} = \text{O} + \text{H}_2\text{O} & \rightarrow \text{R} - \text{C} = \text{O}^+ \text{H}^+ + \text{H}_2\text{O} \\
\end{align*}
$$

The conjugate acid is represented as oxygen protonated form like the protonation in amide, in which the oxygen protonated form is dominant. The rate of hydrolysis of hydroxamic acids is reported to increase with the increase of dielectric constant in the mixed solvent. Logarithm of the rate constant ($\log K$) is linearly related to $(D-I)/(2D+1)$, but it is not true if wider range of dielectric constant is used.
Effect of substituents on the rate limiting step and the relative reactivities were reported by Tilleit and others \textsuperscript{102,103,104} for BHA. The observed substituent effect supports bimolecular mechanism ($A_2$); electron withdrawing substituents accelerate the hydrolysis and electron donating substituents retard it supporting the $A_2$ mechanism. The values for substituent constant $p$ found donot much differ from that of the amides. The effect of substituents influence both the proton equilibrium and rate limiting reaction step.

It is observed that the meta and para substituents however strongly polar have little effect on the reaction rate \textsuperscript{110}. This also leads to the conclusion that the hydrolysis is bimolecular because of a bimolecular mechanism requires that substituents should exert only weak polar effects but that when suitably situated they should exert strong steric effect \textsuperscript{70}.

As o-substituted BHA hydrolys\textsuperscript{es} in moderately 107 acidic solution it shows that the polar effect of substituent is greater than the steric effect for chloro and brome while reverse is true for the methoxy and ethoxy substituent relative to methyl. This result is in contrast to the acid catalysed hydrolysis of amides.
The distribution between organic solvents and aqueous acid is reported for N-phenyl-benzohydroxamic acid and some of its analogues. It is observed that the distribution constant between organic phase and aqueous acid solution is affected significantly by the acid concentration. The work was initiated by and was extended by Feuche. It is reported that the increase in aqueous solubility in acidic medium is due to increase in pretonation of the hydroxamic acid. Feuche and Tillett reported pretonation constants. The pretonation behaviour is used for establishing mechanism of the hydrolysis of hydroxamic acids.

After the initial preton transfer pre-equilibrium in the decomposition of

\[
\begin{align*}
\text{I} & \quad \text{II} \\
R-C-NHOH + H_3O^+ & \rightleftharpoons R-C-NHOH + H_2O
\end{align*}
\]

the conjugate acid species would occur in principle by either unimolecular \((A_1)\) or bimolecular \((A_2)\) mechanism. Information about the mechanism of the rate limiting step can be obtained from the dependence on acidity of the rate of hydrolysis.

The catalytic action of the acids on the hydrolysis rate is in the order \(H_2SO_4 > HCl > HClO_4\), typical
of bimolecular reaction. The observed value of Bunnett's W and Bunnett and Olsen fall in the range where water acts as nucleophile and proton transfer agent in the rate limiting step. Furthermore, the values of activation parameters are also consistent with the proposed bimolecular mechanism.

According to Mollin and Kuzeeva the dependence of $K_0$ in the proton activity does not confirm the idea of one acid-catalysed reaction step as it is given in literature. The found dependence agrees better with the mechanism of the acid catalysed hydrolysis of amides. On the basis of the pK values obtained it can be stated that in acidic medium pyridine carboxyhydroxamic acids are protonated at the ring nitrogen atom according to eq. A.

$$\text{HO-NH-CO-C}_6\text{H}_4\text{N}^+ + H^+ \rightleftharpoons K_1 \text{HO - NH-CO-C}_6\text{H}_4\text{H}^+ \text{H}^- \quad (A)$$

The subsequent reactions take place at the functional group and are common for all the substances investigated.

In accord with current conception the first reaction step of the mechanism of hydroxamic acids hydrolysis consists in addition of water to the carbonyl carbon atom. In neutral region this reaction is slower than in acid medium by several orders of magnitude hence the non-catalysed addition of water is kinetically insignificant in the medium studied and was not involved
in further considerations. The acid catalysed addition of water results in formation of the cation $C_1$. The found activation entropy values prefer the idea of bimolecular character of the rate limiting step. Therefore, it can be supposed that the addition of water is slow.

The formed cation $C_1$ is not stable and splits off the proton to give the free base of the tetrahedral intermediate $C_2$. Suppose this intermediate to be unstable, too, being able to split off water not only by acid catalysis but also through hydrogen bonds. Finally, with respect to the acid medium in which the reaction takes place, the tetrahedral intermediate $C_2$ can be protonated and the cation $C_3$ thus formed can split into hydroxylamine proton and carboxylic acid

![Reaction path suggested by Mane and Jugdale](https://example.com/image1.png)

\[ R - C - \text{NH}_2 \text{OH} \rightleftharpoons R - C - \text{NH}_2 \text{OH} + H_2O \longrightarrow RCOOH + NH_3^+ \text{OH} \]

\[ NH_2OH + H^+ \]
<table>
<thead>
<tr>
<th>S. No.</th>
<th>R</th>
<th>T (°C)</th>
<th>Catalyst</th>
<th>Remark</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
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<td>1</td>
<td>CH₃</td>
<td>90.5°</td>
<td>-</td>
<td>Hydrolysis is studied as reverse of the formation of HA cat. by N₂ CH₃COOH between pH 0.73-10.80</td>
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<tr>
<td></td>
<td></td>
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<td>Acid</td>
<td>Aq. p. toluene sulphamic acid</td>
<td>162</td>
</tr>
<tr>
<td></td>
<td></td>
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<td>HClO₄·H₂SO₄·HCl</td>
<td>112</td>
</tr>
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<td></td>
<td>40.0°</td>
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<td>NaOH</td>
<td>114</td>
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<tr>
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<td>50.5°</td>
<td>Acid</td>
<td>Aqueous p-toluene sulphonic acid</td>
<td>105</td>
</tr>
<tr>
<td>3</td>
<td>(CH₃)₂CH</td>
<td>50.5°</td>
<td>Acid</td>
<td>Aqueous p-toluene sulphamic acid</td>
<td>105</td>
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<td>40.0°</td>
<td>Acid</td>
<td>HClO₄·H₂SO₄·HCl</td>
<td>112,113</td>
</tr>
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<td>NaOH</td>
<td>114</td>
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<td>HClO₄·H₂SO₄·HCl</td>
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<td>114</td>
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<td>Acid</td>
<td>Aq. p. toluene sulphonic acid</td>
<td>105</td>
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<td>S.No.</td>
<td>X</td>
<td>T°</td>
<td>Catalyst</td>
<td>Remark</td>
<td>Ref.</td>
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<tr>
<td>------</td>
<td>-----</td>
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<td>-------------------------------</td>
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<td></td>
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<td>N CH</td>
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<td>Alk</td>
<td>N CH</td>
<td>106</td>
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<tr>
<td></td>
<td></td>
<td>80°</td>
<td>acid</td>
<td>HClO₄</td>
<td></td>
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<td>Acid</td>
<td>HClO₄, Ha taken in</td>
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<tr>
<td></td>
<td></td>
<td>50°</td>
<td>2M HCl</td>
<td>50% (by wt) ethanol</td>
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<tr>
<td>2</td>
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<td>HCl</td>
<td>[0.605] HCl Prusnity effect</td>
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<td></td>
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<td></td>
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<tr>
<td></td>
<td>O=Cl</td>
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<td>O=Br</td>
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<tr>
<td>3</td>
<td>m-Me</td>
<td>111,80°</td>
<td>N CH</td>
<td>1 M</td>
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<td>m-Cl</td>
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<td>HClO₄</td>
<td>5% &amp; 10.1% HClO₄</td>
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<td>80°</td>
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<td>80°</td>
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<tr>
<td></td>
<td></td>
<td>50°</td>
<td></td>
<td></td>
<td>106</td>
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<tr>
<td></td>
<td>m-No₂</td>
<td>50°</td>
<td>2M HCl</td>
<td></td>
<td>110</td>
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<tr>
<td></td>
<td>m-Br</td>
<td>80°</td>
<td>HClO₄</td>
<td></td>
<td>106</td>
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<td></td>
<td></td>
<td>50°</td>
<td>2M HCl</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>m-No₂</td>
<td>50°</td>
<td>2M HCl</td>
<td></td>
<td>110</td>
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<td>Remark</td>
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<tr>
<td>4</td>
<td>p-MeO</td>
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<td>HClO₄, HCl, H₂SO₄</td>
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<td>p-Br</td>
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<td></td>
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<td></td>
<td>50°</td>
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<tr>
<td>5</td>
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<td>111°</td>
<td>N O</td>
<td></td>
<td>105, 106</td>
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<td>80°</td>
<td>N O</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>80°</td>
<td>HClO₄</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>C₆H₄COOH</td>
<td></td>
<td></td>
<td>Intramolecular catalysis 2 carboxylic benzoH₂A</td>
<td>104</td>
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</table>
### HETEROCYCLIC HYDROXAMIC ACIDS

\[
\begin{align*}
H &= N - \text{CH} \\
R &= \text{C} = 0
\end{align*}
\]

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<th>Catalyst</th>
<th>Remark</th>
<th>Ref.</th>
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<td>1</td>
<td>Picolino</td>
<td>90.1</td>
<td>HClO(_4)</td>
<td>50% ethanol solution(by wt)</td>
<td>109</td>
</tr>
<tr>
<td>2</td>
<td>Nicotino</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Iso nicotino</td>
<td></td>
<td></td>
<td></td>
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</table>

**Series II. N-Substituted hydroxamic acids**

\[
\begin{align*}
R &= N - \text{CH} \\
R &= \text{C} = 0
\end{align*}
\]

<table>
<thead>
<tr>
<th>S.No.</th>
<th>R</th>
<th>R'</th>
<th>T°c</th>
<th>Catalyst</th>
<th>Remark</th>
<th>Ref.</th>
</tr>
</thead>
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<td>1</td>
<td>(\text{C}_6\text{H}_5)</td>
<td>(\text{CH}_3(\text{CH}_2))</td>
<td>40,50°</td>
<td>0.1-0.8 MHCl</td>
<td>1-5 M HCl</td>
<td>110</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>40°</td>
<td></td>
<td>1-5 M HCl</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>(\text{C}_6\text{H}_5)</td>
<td></td>
<td>90.1°</td>
<td>HClO(_4)</td>
<td>50%(by wt) 109 ethanol solution</td>
<td></td>
</tr>
<tr>
<td>3</td>
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<td>(\text{C}_6\text{H}_4)</td>
<td>90°</td>
<td>0.76 MHCl</td>
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In the present investigation the kinetics of the acid catalysed hydrolysis of some N-substituted hydroxamic acids is carried out. On the basis of the conclusions derived by the application of the principles of chemical kinetics a probable mechanism of the reaction is proposed.

The main object of the present investigation is to study the kinetics of acid catalysed hydrolysis of N-phenyl-2-furo hydroxamic acid (I) (P-FHA).

It is carried out by following the mechanistic criteria based on the studies of the effect of different variables like concentration of the catalyst, temperature, salt effect and solvent effect on the reaction rate. A detailed study of this work is presented in CHAPTER II.

The hydrolysis of P-FHA has been studied in moderately concentrated hydrochloric, sulphuric and perchloric acids. Since the compound is appreciably stable in solutions containing less than 1M concentration of acids, hydrolysis is carried out in one to eight molar.
hydrochloric and sulphuric acid at 50° and 60° and 1 to 8 M perchloric acid at 60°. The rate constant and the effect of catalyst concentration were determined. The experimental data are analysed by correlating the rate with Hammett acidity function, $H^+$, and discussed in the light of Zucker-Hammett treatment, Bunnett's treatment and Olsen's parameter treatment.

The hydrolysis is carried out at four different temperatures from 40 to 70° at ten degree interval in 4 molar hydrochloric acid and the Arrhenius parameters are calculated.

Salt effect on the rate of hydrolysis has been studied at 5M ionic strength using hydrochloric acid and sodium chloride and also perchloric acid and sodium perchlorate. Effects of organic solvents on the rate of hydrolysis are also studied.

The products of hydrolysis of PFHA have been isolated, identified and the mode of bond fission is established.

The protonation behaviour of PFHA is studied by distribution method. The distribution ratios of PFHA between chloroform and hydrochloric acid of different concentrations have been determined and the value of protonation constant calculated.
In CHAPTER III, the results obtained for the acid catalysed hydrolysis of PFHA are summed up and a mechanism based on the above result is suggested.

In CHAPTER IV hydrolysis of l-Benzyl benzohydroxamic acid (BBHA) and its para substituted analogues in hydrochloric acid is studied in the light of Hammett equation. From the point of view of comparison of rate of hydrolysis a few different hydroxamic acids have been studied. The hydroxamic acids, whose rate of hydrolyses have been studied are Benzylbenzo hydroxamic acids, Benzyl 2-furo hydroxamic acid, Benzyl phenylaceto hydroxamic acid, phenyl-benzo hydroxamic acid, phenyl-monochloro aceto hydroxamic acid and p-ch-phenyl aceto hydroxamic acid.

CHAPTER V includes a colorimetric method for the estimation of N-phenyl-2-furohydroxamic acid. This method is developed to determine the progress of the hydrolysis conveniently and reliably, utilising the property of PFHA to form a chloroform extractable violet complex with vanadium(V). Beer's law and the effect of various substances have also been studied.
The experimental data were analysed by the well-known statistical methods. The standard deviation, \( \sigma \), was calculated from the expression,

\[
\sigma = \sqrt{\frac{\sum (x_i - \bar{x})^2}{n-1}}
\]

The method of least squares analysis was adopted wherever necessary. The fit of linear relation was judged by calculating the correlation coefficient, \( r \), from the expression

\[
r = \sqrt{\frac{\sum (x_i - \bar{x}) (y_i - \bar{y})^2}{\sum (x_i - \bar{x})^2}}
\]

where \( \bar{x} = \frac{1}{n} \sum x_i \) and \( \bar{y} = \frac{1}{n} \sum y_i \).

The coefficient of variation, C.V., was calculated from the following formula

\[
C.V. = \frac{100 \sigma}{\bar{x}}
\]
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