Chapter 5

Protonation Behaviour Of N-Arylsubstituted Hydroxamic Acids
PROTONATION BEHAVIOUR OF N-ARYLSUBSTITUTED HYDROXAMIC ACIDS

N-Arylsubstituted hydroxamic acids behave as weak organic bases in presence of strong acidic solutions.

This chapter presents the results of the determination of various protonation parameters in hydrochloric and perchloric acid solutions. The parameters include, the dissociation constants ($pK_{BH^+}$), of conjugate acid of these reagents, the slope values ($m$, $\phi$ and $m^*$), and the values of correlation coefficients ($r$), derived by following the Hammett Acidity Function Method, Brunett-Olsen Method and Excess Acidity Method. The effect of acidity, on partition data of these reagents between an organic solvent and aqueous acid solutions and on percentage of protonation of hydroxamic acids is studied. Effect of various substituents on protonation behaviour of hydroxamic acids is also discussed.
PROTONATION BEHAVIOUR OF N-ARYLSUBSTITUTED HYDROXAMIC ACIDS

The relative basicities of organic bases have long been of interest both as a source of information about electronic structures and reactivities, and as a means of estimating the amount of various protonated forms of a base in solutions of different acid concentration. The most common measure of basicity has traditionally been the $pK_{B^+}$ of the conjugate acid of the base.

Numerous methods have been devised for the measurement of $pK_{B^+}$ (104–123). One requirement for all the methods is that, measurements are made under conditions where significant amounts of the unprotonated and protonated forms of the base are present simultaneously in solution. Many interesting bases, however, are very weak, and in order to achieve this requirement, they must be studied in concentrated acid and then calculating their $pK_{B^+}$, by one of the procedure based on the use of Acidity Function.

Review of literature (107, 124) shows a number of methods have been adopted to study the trend of protonation of different compounds including weak bases. Potentiometric methods are included among the most useful for the determination of the protonation constants of a monoprotic acid–base systems. Potentiometric methods are considered to be more precise, but they cannot be applied to systems in which protonation constant is either particularly high or low, spectrophotometric method has the advantage to being suitable in extreme cases.

The problem of estimating $pK_{B^+}$ of N-arylsubstituted hydroxamic acids is still an open question. These metal extractants serve as weak organic bases and have been the subject of a large number of physico-chemical investigations because of their wide applications in several fields as shown in CHAPTER I. With this view in mind, we report here some considerations about the protonation behaviour of these reagents. Since as metal extractants, most of the studies were carried out in presence of hydrochloric acid, and in the framework of our researches (125–129) in the field of protonation studies on weak organic bases, we have measured the $pK_{B^+}$ values of these reagents in hydrochloric acid and perchloric acid solutions.
EXPERIMENTAL

APPARATUS

As described in earlier CHAPTERS.

A pentium 166 MMX computer was used for slope determination and calculations.

CHEMICALS

These have also been described in CHAPTERS III and IV.

Analytical grade hydrochloric and perchloric acids were used for determining distribution ratios. These were standardised with sodium hydroxide solution (which was standardised against potassium hydrogen phthalate), phenolphthalein was used as indicator. Acidic mixtures were prepared by dilution of concentrated acid with glass distilled water.

MEASUREMENT OF DISTRIBUTION RATIOS (D) AS A FUNCTION OF ACID CONCENTRATIONS

Hydroxamic acids are hydrolysed in presence of acid. The rate constants are dependent on the acid concentration. Besides, the values of rate constants for the hydrolysis reactions of different hydroxamic acids vary under wide limits. Thus, for determining distribution ratios of these reagents as a function of acid concentrations, time of shaking should be made as small as possible. Vigorous shaking for short periods gave fairly reproducible results. For this, a quick technique was adopted [125]. It was observed that with sufficient shaking, equilibrium could be achieved within five minutes. Thus the hydrolysis of hydroxamic acids is negligible during the time required for measuring D.
A solution of hydroxamic acid in carbontetrachloride or benzene was (20–25 mg) shaken for five minutes with acid solutions of increasing acidity, 1–10M. The volumes of the two phases to be taken were dependent on the magnitude of D. After separation, the phases were analysed colorimetrically.

All the experiments were done thrice.

ANALYSIS OF PHASES

The determination of hydroxamic acid by its absorbance in the UV gave unsatisfactory results, because of the variation of its spectral characteristics with change in the solvent and with the acidity of the aqueous phase. The reagent concentrations were therefore determined spectrophotometrically by solvent extraction method as described in CHAPTER III. Although, this method is more time consuming, it gives reproducible and accurate results. It is an ideal method for the study of sparingly soluble substances or those substances, whose constants are particularly low or high. Solvent extraction method has the advantage, that the occurrence of the side reactions does not necessarily invalidate the measurement.

RESULTS AND DISCUSSION

The acid–base properties of a substance are important parameters, especially for investigation of acid–base catalysed reactions. Evaluation of the relative basicities of weak organic bases has attracted much interest both as a source of information about electronic structures and as a means of interpreting the reactivities of acid, catalysed reactions. Understanding of the acid–base interaction facilitates to suggest optimum conditions for separating similar compounds by extraction with acid.

DISTRIBUTION RATIOS (D) AS A FUNCTION OF ACID CONCENTRATIONS

In the present investigation distribution ratios (D), were measured between an organic solvent and a series of increasingly hydrochloric and perchloric acid solutions. The organic
solvent chosen for this kind of study is carbontetrachloride except in case of 3,5-dinitro derivatives where benzene was taken, due to solubility factor. Carbontetrachloride was found to be the most suitable solvent for physico-chemical studies, because of its favourable physical properties, such as non-polar inert solvent, adequate difference in density from water, low dielectric constant and vapour pressure, zero dipole moment and very low mutual solubility with water (130). The results are presented in Tables 1 and 2 and the plots of D vs hydrochloric and perchloric acid molarities are given in the Figures 21 to 30. As the acid concentration increases, the values of distribution ratio decreases.

DETERMINATION OF ACIDITY CONSTANTS ($\text{pK}_{\text{BH}^+}$) OF PROTONATED HYDROXAMIC ACIDS

A knowledge of acidity constants of weakly basic substances is of central importance to the study of mechanisms of reactions which take place in acidic media. Such reaction are also important in organic chemistry and biochemistry. Acidity constants of organic bases are obtained from an analysis of the variation of some physical properties of the substrate with changing acid concentration. The three properties most commonly used are the UV-visible spectrum (107-109) and $^1\text{H}$ and $^{13}\text{C}$ n.m.r. spectra (110-112, 118-120). The change observed with increasing acidity is from spectrum characteristics of the free base to that of the protonated form. In the present investigation, as the free base and its protonated species do not differ appreciably in their UV properties, hence we apply the solvent extraction technique, using visible spectrosopy. Indeed, the solvent extraction method used should be capable of yielding more reliable $\text{pK}_{\text{BH}^+}$ values.

In acidic solutions –

$$\text{B} + \text{H}^+ \rightleftharpoons \text{BH}^+ \quad [1]$$

where B is the base and BH$^+$ is the protonated species or a conjugate acid of base B. For this equation, the ionisation ratio, I, is calculated using the formula –

$$I = \frac{C_{\text{BH}^+}}{C_{\text{b}}} \quad [2]$$
<table>
<thead>
<tr>
<th>No.</th>
<th>Hydroxamic Acid</th>
<th>Organic Solvent</th>
<th>Carbotetracloroide</th>
<th>Benzene</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>N-Phenylbenzoic</td>
<td>1.10</td>
<td>30.21</td>
<td>10.00</td>
</tr>
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<td>2</td>
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<td>10.00</td>
<td>28.11</td>
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<tr>
<td>3</td>
<td>N-Phenyl-3,5-dinitrobenzoic</td>
<td>8.95</td>
<td>11.10</td>
<td>25.11</td>
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<tr>
<td>4</td>
<td>N-o-Tolylbenzoic</td>
<td>7.95</td>
<td>12.10</td>
<td>22.21</td>
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<tr>
<td>5</td>
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<td>6.95</td>
<td>13.10</td>
<td>21.21</td>
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<tr>
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<td>14.10</td>
<td>19.21</td>
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<tr>
<td>7</td>
<td>N-p-Chlorophenyl-4-bromobenzoic</td>
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<td>17.21</td>
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<tr>
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<td>3.95</td>
<td>16.10</td>
<td>15.21</td>
</tr>
<tr>
<td>9</td>
<td>N-p-Chlorophenyl-4-methylbenzoic</td>
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<td>13.21</td>
</tr>
<tr>
<td>10</td>
<td>N-p-Chlorophenylbenzoic</td>
<td>1.00</td>
<td>18.10</td>
<td>11.21</td>
</tr>
</tbody>
</table>
### TABLE 2

**Distribution Ratios of N-Arylsubstituted Hydroxamic Acids between Organic Solvent and Aqueous Hydrochloric Acid Solutions.**

<table>
<thead>
<tr>
<th>Hydrochloric Acid</th>
<th>0.1 M</th>
<th>0.2 M</th>
<th>0.3 M</th>
<th>0.4 M</th>
<th>0.5 M</th>
<th>0.6 M</th>
<th>0.7 M</th>
<th>0.8 M</th>
<th>0.9 M</th>
<th>1.0 M</th>
</tr>
</thead>
<tbody>
<tr>
<td>N-Phenylbenzo-</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N-Phenyl-2-nitrobenzo-</td>
<td>20.12</td>
<td>17.31</td>
<td>15.50</td>
<td>13.70</td>
<td>12.00</td>
<td>10.31</td>
<td>8.62</td>
<td>7.03</td>
<td>5.43</td>
<td>3.83</td>
</tr>
<tr>
<td>N-Phenyl-3,5-dinitrobenzo-</td>
<td>53.50</td>
<td>51.30</td>
<td>49.10</td>
<td>46.90</td>
<td>44.70</td>
<td>42.50</td>
<td>40.30</td>
<td>38.10</td>
<td>35.90</td>
<td>33.70</td>
</tr>
<tr>
<td>N-o-Tolylbenzo-</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N-o-Tolyl-4-bromobenzene-</td>
<td>59.36</td>
<td>57.16</td>
<td>55.06</td>
<td>52.86</td>
<td>50.66</td>
<td>48.46</td>
<td>46.26</td>
<td>44.06</td>
<td>41.86</td>
<td>39.66</td>
</tr>
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<td>N-m-Chlorophenylbenzo-</td>
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<td>67.01</td>
<td>64.81</td>
<td>62.61</td>
<td>60.41</td>
<td>58.21</td>
<td>56.01</td>
<td>53.81</td>
<td>51.61</td>
<td>49.41</td>
</tr>
<tr>
<td>N-m-Chlorophenyl-2-methoxybenzene-</td>
<td>60.21</td>
<td>58.01</td>
<td>55.81</td>
<td>53.61</td>
<td>51.41</td>
<td>49.21</td>
<td>47.01</td>
<td>44.81</td>
<td>42.61</td>
<td>40.41</td>
</tr>
<tr>
<td>N-p-Chlorophenyl-4-bromobenzene-</td>
<td>65.11</td>
<td>62.91</td>
<td>60.71</td>
<td>58.51</td>
<td>56.31</td>
<td>54.11</td>
<td>51.91</td>
<td>49.71</td>
<td>47.51</td>
<td>45.31</td>
</tr>
<tr>
<td>N-p-Tolyl-4-bromobenzene-</td>
<td>33.71</td>
<td>31.51</td>
<td>29.31</td>
<td>27.11</td>
<td>24.91</td>
<td>22.71</td>
<td>20.51</td>
<td>18.31</td>
<td>16.11</td>
<td>13.91</td>
</tr>
<tr>
<td>N-p-Tolyl-3,5-dinitrobenzo-</td>
<td>123.01</td>
<td>118.81</td>
<td>114.61</td>
<td>110.41</td>
<td>106.21</td>
<td>102.01</td>
<td>97.81</td>
<td>93.61</td>
<td>89.41</td>
<td>85.21</td>
</tr>
</tbody>
</table>

**Organic Solvent** - CARBON TETRACHLORIDE, BENZENE.
where $C_B$ and $C_{BH^+}$ are the molar concentration of base and conjugate acid, respectively.

The protonation studies of N-arylsulfonated hydroxamic acids are done following three classical procedures –

1. Hammett Acidity Function Method (HAFM).

It is important to discuss the methodology, used to calculate $pK_{BH^+}$ by these three procedures.

**HAMMETT ACIDITY FUNCTION METHOD (HAFM)**

The first method is the traditional Hammett Acidity Function Method (66), suitably modified by using acidity function appropriate to the class of bases under consideration. The acidity function $H_o$ was originally proposed by Hammett and Deyrup (66) to describe the ionisation behaviour of weak organic bases in concentrated acid solutions. It is generally applicable to uncharged bases, ionising by simple proton addition as in equation [1].

To determine $pK_{BH^+}$ values for equation [1], three requirements must be made –

(i) Availability of suitable acidity function.
(ii) It must be possible to measure some physical properties that accurately determines the ionisation ratio $I = C_{BH^+}/C_B$.
(iii) Methods must be available to analyse a plot of a function of $C_{BH^+}/C_B$ against the acidity of the solution.

Study of protonation of weak bases in strong aqueous acid media, led to the definition of some acidity function scale valid for each acidic medium (131). Dissociation constant, $pK_{BH^+}$,
for weak base, B can be defined as the acid dissociation constant of the protonated base BH⁺ and for equation [1] –

\[ K_{BH^+} = \frac{a_B a_{H^+}}{a_{BH^+}} = \left( \frac{C_B}{C_{BH^+}} \right) C_{H^+} \left( \frac{f_{BH^+}}{f_{H^+}} \right) \]  \[ [3] \]

where,

- \( a \) = Activity
- \( C \) = Molarity
- \( f \) = Molar activity coefficient.

On taking logarithms, the equation becomes –

\[ pK_{BH^+} = \log \left( \frac{C_{BH^+}}{C_B} \right) - \log C_{H^+} - \log \left( \frac{f_{BH^+}}{f_{H^+}} \right) \]  \[ [4] \]

This equation is thermodynamically exact. The ratio \( f_{BH^+}/f_{H^+} \) is symbolised as \( h_0 \) and serves as a unique definition of the acidity of the medium, and –

\[ H_0 = -\log h_0 \]  \[ [5] \]

In water equation [4] reduces to –

\[ pK_{BH^+} = \log I + pH \]  \[ [6] \]

where \( I = C_{BH^+}/C_B \)

If this equation is extended into non-ideal, strongly acidic media, the activity coefficient term in equation [4], must be accounted for, in some way. This was first attempted by
Hammett and Dayrup(66). They postulated, there exists an Acidity Function, $H_0$, defined so as to be an extension of the pH scale.

$$pK_{BH^+} - \log I = H_0 = -\log C_{H^+} - \log \left( f_{B_{aq}} f_{H^+} / f_{BH^+} \right)$$  \hspace{1cm} [7]

Here $H_0$ represent the quantitative measure of acidity of solutions. For the measurement of $I$, the requirement for all the methods is that, measurements are made under conditions, where significant amount of the free base and protonated form are present simultaneously in solutions. In the present investigation, protonation equilibria by UV method cannot be studied because of insufficient differences between the spectra of the substrate and its conjugate acid. Tillett et al had also experienced the same observation(132). At the same time, hydroxamic acids investigated here are very weak bases. In such systems, conditions may not exist under which it is both fully protonated and stable. Thus, we determine the protonation equilibria following the solvent extraction technique(125), using visible spectroscopy. This method can be used, when the absorbance of $B$ and $BH^+$ cannot be determined directly(125). For such systems, the most widely quoted reference source for $pK_{BH^+}$ has been 1963 review by Arnett(133). According to him the weak bases are protonated into their conjugate acids in presence of strong acidic solutions, and the distribution ratio, $D$, of a base between the organic solvent and aqueous acidic solutions is a function of the respective concentrations. Thus, $I$ is measured by the equation that describes the variation of distribution ratio, $D$, with changing acidity, as follows –

Thus for equation [1] \hspace{1cm} I = \frac{K_D - D}{D} \hspace{1cm} [8]

and \hspace{1cm} D = \frac{[B]_{org}}{[B]_{aq} + [BH^+]} \hspace{1cm} [9]

In strong solutions –

$$D = \frac{[B]_{org}}{[B]_{aq} + [BH^+]_{aq}} \hspace{1cm} [10]$$

Applying the law of mass action in the reverse equation.
\[ K_{BH^+} = \frac{a_{H^+} + a_g}{a_{BH^+}} \quad [11] \]

or

\[ K_{BH^+} = a_{H^+} \frac{f_g}{f_{BH^+}} \frac{[B]}{[BH^+]} \quad [12] \]

since

\[ h_0 = a_{H^+} f_{in} / H_{in} \quad [13] \]

\[ K_{BH^+} = \frac{h_0 [B]}{[BH^+] \quad [14] \]

Equations [10] and [14] give –

\[ D = \frac{[B]_{org}}{[B]_{eq} + \frac{h_0 [B]_{eq}}{K_{BH^+}}} \quad [15] \]

or

\[ D = \frac{[B]_{org}}{[B]_{eq} + \frac{1 + h_0}{K_{BH^+}}} \quad [16] \]

as

\[ K_D = \frac{[B]_{org}}{[B]_{eq}} \quad [17] \]

Therefore,

\[ D = \frac{K_D}{1 + \frac{h_0}{K_{BH^+}}} \quad [18] \]

or,

\[ K_D = D \frac{Dh_0}{K_{BH^+}} \quad [19] \]

or,

\[ \frac{K_D - D}{D} = \frac{h_0}{K_{BH^+}} \quad [20] \]
\[ pK_{BH^+} = H_a + \log \frac{K_0 - D}{D} \]  

or

\[ pK_{BH^+} = \frac{K_0 - D}{K_{BH^+}} \]

\[ \frac{K_0 - D}{D} = I, \] the ionisation ratio. Where \( K_0 \) is the thermodynamic distribution constant of hydroxamic acid between the organic layer and aqueous acid in the region where appreciable protonation is occurring, and is estimated by the equation –

\[ D = \frac{K_0 - D_{H^+}}{K_{BH^+}} \]

and \( K_{BH^+} \) can be written as \( K_a \)

\[ pK_{BH^+} = -\log K_a \]

or, from the intercept of a plot \( D \) vs \( D_{H^+} \) or by calculating from least square method. All the three methods used here, gave the closely matched results. In the present investigation the \( K_0 \) values obtained by least square method are used to calculate the ionisation ratio, I. The data on \( K_0 \) are presented in Tables 4, 6 and 8.

The solvent extraction method used here (as described in CHAPTER III) determined the total concentration of both the molecular and protonated species.

One of the principal uses of Acidity Function is to provide a means of extrapolating measurements made in concentrated acid to dilute solutions. Such extrapolations have usually been performed with the assumption that \( \log I \) is proportional to an appropriate Acidity Function, \( H_x \).
\[
\log I = -H_x + pK_{BH^+} \tag{25}
\]

When a correct Acidity Function is not available, the further assumption that different Acidity Functions are linearly related to one another\(^{(134)}\) and therefore to \(H_0\) –

\[
H_x = mH_0 \tag{26}
\]

At present, there is available a large number of Acidity Functions\(^{(135-137)}\) but unfortunately it is not always possible to find one well suited to the base under study. The slope, \(m\), enables us to verify if the \(H_x\) has been correctly chosen. If \(m\) is close to unity then the function \(H_x\) is correct, since Hammett's postulation is satisfied\(^{(134)}\) and the deviation from this value is taken as being non-ideal behaviour.

Figures 1A (ii) to 10A (ii) are the plots of \(\log I\) against \(H_0\) and the plots of \(\log I\) against \(H_A\) are shown in Figures 1A (i) to 10A (i).

**BUNNETT-OLSEN METHOD (BOM)**

An alternative method of determining \(pK_{BH^+}\) is to use the linear free energy approach of Bunnett and Olsen\(^{(67)}\) following the equation –

\[
\log I + H_0 = \phi (H_0 + \log C_{H^+}) + pK_{BH^+} \tag{27}
\]

provided the plot of the left hand side of equation \([27]\) against \((H_0 + \log C_{H^+})\) is linear. The slope \(\phi\) is a measure of the susceptibility of the equilibrium to changing acid concentration and \((1 - \phi)\) is the slope of free energy relationship. In equation\(^{(27)}\). The slopes for the Bunnett–Olsen plots are presented in Figures 1B to 10B. The correlation coefficients for the BOM plots are satisfactory and the \(\phi\) values are in the expected range.
EXCESS ACIDITY METHOD (EAM)

Excess Acidity(68, 69) or X–function or Mc Function(138) are used in a method for the evaluation of acidity constants of weak bases from ionisation ratio measurements in strong acid solutions, by the extrapolation to the aqueous standard state. This extrapolative method was an earlier approach proposed by Marziano and Passerini(70). EAM method has been shown both accurate and general(68, 139–140). R. A. Cox(141) assumed that for carbonyl compounds, use of spectrophotometric methods like UV and n.m.r., the situation is more complex, since the spectra of free base or protonated species or of both are usually subject to substantial medium effects(134, 142–144). In view of this Cox and his coworkers developed a method for obtaining acidity constants, inspite of possible medium effects, based on the excess medium acidity, X, which represents the excess acidity. This term was first used by Perrin(145) as "it is the difference between the observed acidity and that which the system would have, if it were ideal",(68, 69). X scale is derived from the indicator ratio data for many bases.

For a proton transfer to a base B as in equation [1], the general thermodynamic equation [28] can be written from the definition of $pK_{BH^+}$,

$$\log \left( \frac{C_{BH^+}}{C_B} \right) - \log C_H^+ = \log \left( \frac{f_{BH^+}}{f_B} \right) + pK_{BH^+}$$ \hspace{1cm} [28]

where $C$ is the molar concentration, $f$ is the molar activity coefficient, and $pK_{BH^+}$ is the acid ionisation constant of $BH^+$. The assumption is then made that the activity coefficient term in equation [28] is a linear function of a similar term for a standard base, $B^*$, slope $m^*$, which is the previously derived $X$–function, gives equation [29].

$$\log \left( \frac{f_{BH^+}}{f_{B^*}} \right) = m^* \log \left( \frac{f_{BH^+}}{f_{BH^+}} \right) = m^* X$$ \hspace{1cm} [29]

for equation [1], it involves proton concentration $C_H^+$ and the concept of Excess medium acidity rather than classical Hammett type acidity function and is summarised as equation [30].
\[ \log I = pK_{BH^+} + \log C_{H^+} + m^* X \]

Values of \( X \) as a function of weight percent composition are available for the aqueous perchloric and hydrochloric acid systems (68, 146–149) and are given in Table 3 along with the corresponding \( H_0 \) and \( H_A \) values. The slope parameter \( m^* \) expresses the sensitivity of the substrate to the changing acidity or in other words, we can say that \( m^* \) describes the protonation behaviour of \( B \), relative to the hypothetical standard base \( B \), used in defining \( X \) with values in hydrochloric and perchloric acid–water systems. Slopes, \( m^* \) are the plots of \( \log I \) vs \( X \) and are presented in Figures 1C to 10C. \( m^* \) corresponds to \((1 - \phi)\), but this correspondence seems to be less operative in perchloric acid solutions.

**PROTONATION BEHAVIOUR OF N-ARYLSUBSTITUTED HYDROXAMIC ACIDS IN PERCHLORIC ACID**

Protonation analysis of N-arylsubstituted hydroxamic acids was done in perchloric acid following the HAFM, BOM and EAM methods for the equations [25], [27] and [30], respectively. Perchloric acid is a monobasic acid and is much more completely dissociated in concentrated solutions, rendering it an attractive medium for mechanistic studies.

For HAFM, to avoid the necessity of developing a separate scale, we analyse the data in terms of the \( H_0 \) acidity scale. As hydroxamic acids are structurally related to amides, the analysis is also done by applying the amide acidity function, \( H_A \). The need for individual acidity function can be overcome by BOM and EAM methods. BOM method has been found to be less reliable when used with acidity functions other than \( H_0 \) (150). Thus, in the present investigation the protonation data are analysed using \( H_0 \) acidity function for BOM. EAM method does not involve an acidity function but uses overlapping indicators.

For N-arylsubstituted hydroxamic acids, the slopes (\( m, \phi \) and \( m^* \)), correlation coefficients (\( r \)), standard deviation (\( \sigma \)) and derived protonation constant values (\( pK_{BH^+} \)) by HAFM, BOM and EAM methods are listed in Table 4.
### Table 3

Values of $H_A$, $H_0$, and $X$ as a function of acid concentrations.

<table>
<thead>
<tr>
<th>S. No</th>
<th>Acid</th>
<th>$H_A$</th>
<th>$H_0$</th>
<th>$X$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.50</td>
<td>0.20</td>
<td>0.50</td>
<td>0.120</td>
</tr>
<tr>
<td>2</td>
<td>0.78</td>
<td>0.69</td>
<td>0.479</td>
<td>0.49</td>
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<td>3</td>
<td>1.05</td>
<td>0.563</td>
<td>0.86</td>
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<td>0.87</td>
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<td>25</td>
<td>7.00</td>
<td>0.02</td>
<td>0.56</td>
<td>0.10</td>
</tr>
</tbody>
</table>

*Perchloric Acid, Hydrochloric Acid*
SLOPES FOR N-PHENYL-BENZOHYDROXAMIC ACID IN HClO₄

**Figure 1A**
- Plot of log I vs. X for HAFM
  - Slope = 0.88

**Figure 1B**
- Plot of (log I + pH) vs. (H⁺ + log C₄⁺) for BOM
  - Slope = 0.56

**Figure 1C**
- Plot of log I vs. X for EAM
  - Slope = 0.62

**Figure 1D**
- Plot of log I vs. X for HAFM
  - Slope = 0.49
Slopes for N-Phenyl-2-Nitrobenzohydroxamic Acid in HClO

Fig. 2A. Plot of log I vs -H$_0$ for HAFM

Slope = 0.38

Fig. 2B. Plot of log (I + H$_0$) vs (H$_0$ + log C$_F$) for BOM

Slope = 0.52

Fig. 2A (ii). Plot of log I vs -H$_0$ for HAFM

Slope = 0.53

Fig. 2A (i). Plot of log I vs -H$_0$ for HAFM

Slope = 0.58

Fig. 2C. Plot of log I vs X for EAM

Slope = 0.89

Slopes for N-Phenyl-2-Nitrobenzohydroxamic Acid in HClO
SLOPES FOR N-PHENYL-3,5-DINITROBENZOHYDROXAMIC ACID IN HClO

FIG. 3A (i). PLOT OF LOG I vs -H₀ FOR HAFM

SLOPE = 0.42

FIG. 3A (ii). PLOT OF LOG I vs -H₀ FOR HAFM

SLOPE = 0.48

FIG. 3B. PLOT OF LOG I vs (H₀ + log CH⁺) FOR BOM

SLOPE = 0.64

FIG. 3A (iii). PLOT OF LOG I vs (H₀ + log CH⁺) FOR BOM

SLOPE = 0.42

FIG. 3C. PLOT OF LOG I vs X FOR EAM

SLOPES FOR N-PHENYL-3,5-DINITROBENZOHYDROXAMIC ACID IN HClO.
FIG. 4A. PLOT OF LOG I vs HA FOR EAM

SLOPE = 0.92

FIG. 4B. PLOT OF (LOG I + HO) vs (H0 + LOG CH+) FOR BOM

SLOPE = 0.56

FIG. 4A (II). PLOT OF LOG I vs -H0 FOR HAFM

SLOPE = 0.54

FIG. 4A (I). PLOT OF LOG I vs -HA FOR HAFM

SLOPE = 0.56
SLOPES FOR N-o-TOLYL-4-METHYLBENZOHYDROXAMIC ACID IN HClO.

**Fig. 5A(i).** Plot of \( \log I \) vs. \(-H^0_0\) for HAFM.

\( H^0 + \log C_{H^+} \)

Slope = 0.51

**Fig. 5A(ii).** Plot of \( \log I \) vs. \(-H^0_0\) for HAFM.

Slope = 0.54

**Fig. 5A(iii).** Plot of \( \log I \) vs. \(X\) for EAM.

Slope = 0.61
Slopes for N-M-Chlorophenylbenzoxadroxamic acid in HClO₄.

**Figure 6a (i).** Plot of log I vs $-H_0$ for HAFM

**Figure 6a (ii).** Plot of log I vs $H_0 - H_+^0$ for HAFM

**Figure 6b.** Plot of log I vs $H_+^0$ + log $C^+$ for BOM

**Figure 6c.** Plot of log I vs X for EAM

Slopes: 0.57, 0.42, 0.58, 0.25

SLOPE = 0.57

SLOPE = 0.42

SLOPE = 0.58

SLOPE = 0.25
SLOPES FOR N-m-CHLOROPHENYL-2-METHOXYBENZOXYDROXAMIC ACID IN HClO.

FIG. 7A. PLOT OF LOG I vs HAFM FOR EAM

FIG. 7B. PLOT OF (LOG I + H0) vs (H0 + LOG CH+) FOR BOM

FIG. 7C. PLOT OF LOG I vs X FOR EAM

SLOPES = 0.59

SLOPES = 0.50

SLOPES = 0.56
SLOPES FOR N-p-CHLOROPHENYL-4-BROMOBENZOHYDROXAMIC ACID IN HClO

FIG. 8A (i). PLOT OF LOG I vs -H0 FOR HAFM

SLOPE = 0.59

FIG. 8A (iii). PLOT OF LOG I vs -H0 FOR HAFM

SLOPE = 0.59

FIG. 8B. PLOT OF (LOG I + H0) vs (H0 + LOG C'H1)

SLOPE = 0.54

FIG. 8C. PLOT OF LOG I + H0 vs H0 FOR HAFM

SLOPE = 0.59

FIG. 8D. PLOT OF LOG I vs X FOR HAFM

SLOPE = 0.59

FIG. 8E. PLOT OF LOG I vs -H0 FOR HAFM

SLOPE = 0.59

SLOPES FOR N-p-CHLOROPHENYL-4-BROMOBENZOHYDROXAMIC ACID IN HClO.
SLOPES FOR N-p-TOLYL-4-BROMOBENZOHYDROXAMIC ACID IN HClO₄

FIG. 9A. PLOT OF (LOG I + Hₐ) vs (Hₐ + LOG Cₐ) FOR BOM

SLOPE = 0.64

FIG. 9B. PLOT OF (LOG I + Hₐ) vs (Hₐ + LOG Cₐ) FOR HAFM

SLOPE = 0.40

FIG. 9C. PLOT OF LOG I vs X FOR EAM

SLOPE = 0.64

FIG. 9D. PLOT OF LOG I vs X FOR HAFM

SLOPE = 1.06
FIG. 10A. PLOT OF LOG I vs -HA FOR HAFM  
FIG. 10B. PLOT OF LOG I vs (H^+ + LOG CH^+) FOR BOM  
FIG. 10C. PLOT OF LOG I vs X FOR EAM  

SLOPES FOR N-P-TOLYL-3,5-DINITROBENZOHYDROXAMIC ACID IN HCI0.
FIG. 7A. PLOT OF LOG I vs X FOR EAM

SLOPE = 0.59

FIG. 7B. PLOT OF (LOG I + H0) vs (H0 + LOG C+H) FOR BOM

SLOPE = 0.50

FIG. 7C. PLOT OF LOG I vs X FOR HAFM

SLOPE = 0.56

SLOPES FOR N-M-CHLOROPHENYL-2-METHOXYBENZOXHYDROXAMIC ACID IN HClO.

SLOPES FOR N-CHLOROPHENYL-2-METHOXYBENZOXYBENZAMIDE ACID IN HClO.
Fig. 8A (i). Plot of Log I vs -H₀ for HAFM.

Fig. 8A (ii). Plot of Log I vs -H₀ for HAFM.

Fig. 8B. Plot of (Log I + H₀) vs (H₀ + log CH₂) for BOM.

Fig. 8C. Plot of Log I vs X for HAFM.

Slopes for N-p-Chlorophenyl-4-Bromobenzohydroxamic Acid in HClO₄.
SLOPES FOR N-P-CHLOROPHENYL-4-BROMOBENZOXYDROXAMIC ACID IN HClO4

FIG. 8A (I). PLOT OF LOG I vs. -H0 FOR HAFM

FIG. 8A (II). PLOT OF LOG I vs. -H0 FOR HAFM

FIG. 8A (III). PLOT OF LOG I vs. -H0 FOR HAFM

FIG. 8B. PLOT OF (LOG I + H0) vs. (H0 + LOG CH3+ ) FOR BOM

FIG. 8C. PLOT OF LOG I vs. X FOR EAM

SLOPE = 0.54

SLOPE = 0.59

SLOPE = 0.53

SLOPE = 0.59
SLOPES FOR N-p-TOLYL-4-BROMOBENZOHYDROXAMIC ACID IN HClO4

Figure 9A. Plot of log I vs log CH+ for HAFM

Figure 9B. Plot of (log I + Ho) vs (Ho + log CH+) for BOM

Figure 9C. Plot of log I vs H0 for HAFM

FIG. 9A (I). PLOT OF LOG I vs -HA FOR HAFM

FIG. 9A (II). PLOT OF LOG I vs -HA FOR HAFM

FIG. 9A (III). PLOT OF LOG I vs -HA FOR HAFM

SLOPES FOR N-p-TOLYL-4-BROMOBENZOHYDROXAMIC ACID IN HClO4.
SLOPES FOR N-p-TOLYL-3,5-DINITROBENZOHYDROXAMIC ACID IN HCI

FIG. 10A (I). PLOT OF LOG I vs -H^+ FOR HAFM

FIG. 10A (II). PLOT OF LOG I vs -H^+ FOR HAFM

FIG. 10A (III). PLOT OF LOG I vs -H^+ FOR HAFM

SLOPES FOR N-p-TOLYL-3,5-DINITROBENZOHYDROXAMIC ACID IN HCI.
<table>
<thead>
<tr>
<th>S.No</th>
<th>HYDROXAMIC ACIDS</th>
<th>pKBH⁺</th>
<th>1/m</th>
<th>I₁</th>
<th>p~H⁺</th>
<th>1/m</th>
<th>I₂</th>
<th>p~H⁻</th>
<th>1/m</th>
<th>I₁</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>N-Phenyl-2-nitrobenzohydroxamic acid</td>
<td>2.92</td>
<td>0.53</td>
<td>0.935</td>
<td>0.31</td>
<td>1.80</td>
<td>0.58</td>
<td>0.992</td>
<td>0.13</td>
<td>-1.97</td>
</tr>
<tr>
<td>2</td>
<td>N-Phenyl-3,5-dinitrobenzohydroxamic acid</td>
<td>20.24</td>
<td>0.42</td>
<td>0.919</td>
<td>0.27</td>
<td>-1.41</td>
<td>0.64</td>
<td>0.964</td>
<td>0.25</td>
<td>-2.09</td>
</tr>
<tr>
<td>3</td>
<td>N-o-Tolylbenzohydroxamic acid</td>
<td>15.21</td>
<td>0.56</td>
<td>0.940</td>
<td>0.31</td>
<td>-1.44</td>
<td>0.56</td>
<td>0.966</td>
<td>0.10</td>
<td>-2.17</td>
</tr>
<tr>
<td>4</td>
<td>N-m-Chlorophenylbenzohydroxamic acid</td>
<td>18.13</td>
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<td>0.992</td>
<td>0.11</td>
<td>-1.59</td>
<td>0.42</td>
<td>0.974</td>
<td>0.17</td>
<td>-2.30</td>
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<td>N-p-Chlorophenyl-4-bromobenzohydroxamic acid</td>
<td>52.88</td>
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<td>0.986</td>
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<td>-1.64</td>
<td>0.54</td>
<td>0.984</td>
<td>0.14</td>
<td>-2.14</td>
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<td>6</td>
<td>N-p-Tolyl-4-methylbenzohydroxamic acid</td>
<td>15.84</td>
<td>0.50</td>
<td>0.994</td>
<td>0.13</td>
<td>-1.04</td>
<td>0.56</td>
<td>0.989</td>
<td>0.09</td>
<td>-1.58</td>
</tr>
<tr>
<td>7</td>
<td>N-o-Tolyl-2-methoxybenzohydroxamic acid</td>
<td>15.84</td>
<td>0.50</td>
<td>0.994</td>
<td>0.13</td>
<td>-1.04</td>
<td>0.56</td>
<td>0.989</td>
<td>0.09</td>
<td>-1.58</td>
</tr>
<tr>
<td>8</td>
<td>N-Phenylbenzohydroxamic acid</td>
<td>16.06</td>
<td>0.62</td>
<td>0.992</td>
<td>0.09</td>
<td>-1.49</td>
<td>0.49</td>
<td>0.980</td>
<td>0.10</td>
<td>-2.07</td>
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<td>9</td>
<td>N-o-Tolyl-3,5-dinitrobenzohydroxamic acid</td>
<td>18.13</td>
<td>0.58</td>
<td>0.992</td>
<td>0.11</td>
<td>-1.59</td>
<td>0.42</td>
<td>0.966</td>
<td>0.20</td>
<td>-2.30</td>
</tr>
<tr>
<td>10</td>
<td>N-p-Tolyl-3,5-dinitrobenzohydroxamic acid</td>
<td>15.84</td>
<td>0.50</td>
<td>0.994</td>
<td>0.13</td>
<td>-1.04</td>
<td>0.56</td>
<td>0.989</td>
<td>0.09</td>
<td>-1.58</td>
</tr>
</tbody>
</table>

TABLE 4
PROTONATION PARAMETERS OF N-ARYL SUBSTITUTED HYDROXAMIC ACIDS IN PERCHLORIC ACID BY H⁺
The slopes \( m, \) are the plots of \( \log I \) vs \( \frac{H_0}{H} \). \( \phi \) are the plots of \( (H_0 + \log C_{H^+}) \) vs \( (\log I + H) \) and \( m' \) are the plots of \( \log I \) vs \( X \) for HAFM, BOM and EAM methods, respectively. In these equations slope is a measure of the protonation behaviour of substrate \( B \) in equation [1], relative to Hammett base (primary aromatic amines), used for the determination of \( H_0 \). In other words slope expresses the sensitivity of the substrate to the changing acidity. The excess acidity slopes like Bunnett-Oelsen values are the slopes of LFER plots, and thus have mechanistic values.

If slope = 1, then \( B \) is a Hammett base. For \( N \)-arylhydroxamic acids the slopes are considerably lower than those of around 1.0. Typical protonation slope values for the carbonyl groups are around 0.6 (68). The slope values for structurally related compounds, the amids, have been observed in the range 0.51 to 0.57 (67) and for sulfoxides this range is 0.4 to 0.6 (133). Values of similar magnitude have been obtained for \( N \)-arylhydroxamic acids. It ranges from 0.42 to 0.64 in HAFM, from 0.40 to 0.64 in BOM and from 0.46 to 0.62 in EAM methods. From these data it is inferred that hydroxamic acids do not behave like Hammett Bases. In such case, the \( pK_{BH^+} \) values are not thermodynamic quantities but represent the \( pK_{BH^+} \) values corresponds numerically to the \( H_0 \) values of the acid, in which the base is half protonated. This statement seems to be correct in case of \( N \)-arylsubstituted hydroxamic acids. In the present investigations if we plot a graph between percentage protonation and \( H_0 \) values, the derived \( pK_{BH^+} \) values match exactly to \( H_0 \) values at fifty percent protonation as observed in Table 5.

Hydroxamic acids are structurally realted to amides thus, amide acidity function \( H_A \) describes the protonation behaviour of these weak bases, and it is of interest to analyse the ionization data in terms of amide acidity function(134) for HAFM. As observed in Table 6, and Figures 1A (i) to 10A (i) the slopes of the plots of \( \log I \) against \( H_A \) are close to unity, and lie in the range 0.84 to 1.11. In this case, values of \( pK_{BH^+} \) should represent thermodynamic values, based on equation [25].

**EFFECT OF SUBSTITUENTS ON PROTONATION BEHAVIOUR OF N-ARYL SUBSTITUTED HYDROXAMIC ACIDS IN PERCHLORIC ACID**

\( N \)-arylsubstituted hydroxamic acids are weak bases and protonated in
<table>
<thead>
<tr>
<th>S. No.</th>
<th>Hydroxamic Acid</th>
<th>Acidity, M</th>
<th>pkH⁺, M</th>
<th>Derived pkH⁺, Values</th>
<th>Perchloric Acid</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>N-p-Tolyl-3,5-dinitrobenzo-</td>
<td>7.57</td>
<td>2.81</td>
<td>2.81</td>
<td></td>
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<tr>
<td>2</td>
<td>N-p-Tolyl-4-bromobenzo-</td>
<td>7.76</td>
<td>2.51</td>
<td>2.51</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>N-p-Chloroanisyl-4-bromobenzo-</td>
<td>7.20</td>
<td>2.90</td>
<td>2.90</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>N-o-Tolylbenzo-</td>
<td>6.82</td>
<td>2.46</td>
<td>2.46</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>N-m-Chloroanisylbenzo-</td>
<td>6.39</td>
<td>2.41</td>
<td>2.41</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>N-m-Chloroanisyl-2-methoxybenzo-</td>
<td>6.22</td>
<td>2.38</td>
<td>2.38</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>N-p-Tolyl-4-bromobenzo-</td>
<td>7.57</td>
<td>2.81</td>
<td>2.81</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>N-p-Tolyl-3,5-dinitrobenzo-</td>
<td>7.57</td>
<td>2.81</td>
<td>2.81</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>N-p-Tolyl-3,5-dinitrobenzo-</td>
<td>7.57</td>
<td>2.81</td>
<td>2.81</td>
<td></td>
</tr>
</tbody>
</table>

**Protonation values of H⁺ and pkH⁺ of N-arylsubstituted hydroxamic acids at fifty percent**
### Table 6

**Protonation Parameters of N-Arylsubstituted Hydroxamic Acids in Perchloric Acid**

By HAFM (Applying Amide Acidity Function, H⁺)

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Hydroxamic Acid</th>
<th>Ka</th>
<th>β</th>
<th>pKᵢ</th>
<th>m</th>
<th>r</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>N-p-Tolyl-3,5-dinitrobenzo-</td>
<td>9.18</td>
<td>0.59</td>
<td>1.64</td>
<td>2.1</td>
<td>0.1</td>
</tr>
<tr>
<td>2.</td>
<td>N-p-Tolyl-4-nitrobenzo-</td>
<td>0.21</td>
<td>0.06</td>
<td>-1.62</td>
<td>0.6</td>
<td>-2.5</td>
</tr>
<tr>
<td>3.</td>
<td>N-p-Chlorophenyl-2-methoxybenzo-</td>
<td>0.08</td>
<td>0.58</td>
<td>2.34</td>
<td>0.5</td>
<td>0.7</td>
</tr>
<tr>
<td>4.</td>
<td>N-o-Tolylbenzo-</td>
<td>0.08</td>
<td>0.58</td>
<td>2.34</td>
<td>0.5</td>
<td>0.7</td>
</tr>
<tr>
<td>5.</td>
<td>N-o-Cl-3,5-dinitrobenzo-</td>
<td>0.08</td>
<td>0.58</td>
<td>2.34</td>
<td>0.5</td>
<td>0.7</td>
</tr>
<tr>
<td>6.</td>
<td>N-o-Cl-4-nitrobenzo-</td>
<td>0.08</td>
<td>0.58</td>
<td>2.34</td>
<td>0.5</td>
<td>0.7</td>
</tr>
<tr>
<td>7.</td>
<td>N-o-Cl-2-nitrobenzo-</td>
<td>0.08</td>
<td>0.58</td>
<td>2.34</td>
<td>0.5</td>
<td>0.7</td>
</tr>
<tr>
<td>8.</td>
<td>N-o-Cl-4-bromobenzo-</td>
<td>0.08</td>
<td>0.58</td>
<td>2.34</td>
<td>0.5</td>
<td>0.7</td>
</tr>
<tr>
<td>9.</td>
<td>N-o-Cl-3,5-dinitrobenzo-</td>
<td>0.08</td>
<td>0.58</td>
<td>2.34</td>
<td>0.5</td>
<td>0.7</td>
</tr>
<tr>
<td>10.</td>
<td>N-o-Cl-4-bromobenzo-</td>
<td>0.08</td>
<td>0.58</td>
<td>2.34</td>
<td>0.5</td>
<td>0.7</td>
</tr>
<tr>
<td></td>
<td><strong>Total</strong></td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>
concentrated acidic solutions, therefore, $pK_{BH^+}$ values reported here are determined in 4–10M acidic solutions. Insufficient protonation at lower acidity hinders the determination of protonation constants at this stage. The average $pK_{BH^+}$ values in perchloric acid are reported in Table 4 and the acidity function $pK_{BH^+}$ values derived from $H_1$ are compared, here. The effect of substituents on acidity constants derived from HAFM, BOM or EAM is the same.

In case of N-arylsubstituted hydroxamic acids, the results obtained show a dependence of measured basicity on the substituent. The substitutions at various positions of the N-phenyl or C-phenyl rings produces both base-strengthening and base-weakening effects.

**EFFECT OF ALKYL AND ALKOXY GROUPS**

Introduction of electron donating substituent decreases the acidity of conjugate acid of hydroxamic acids. Thus, alkylation would produce a stronger base. At the same time, the presence of electron releasing group stabilises the protonated base and decreases the interaction with the solvent.

From the data presented in Table 4, the following logic is inferred –

The $pK_{BH^+}$ value of N-phenylbenzo hydroxamic acid, PBHA is $-2.74$. Introduction of a methyl group in ortho-position of N-phenyl-ring in PBHA, makes the N-o-tolybenzohydroxamic acid, o-TBHA, 0.21 $pK_{BH^+}$ unit more basic than PBHA ($pK_{BH^+}$ of o-TBHA is $-2.53$). Whereas, introduction of one more methyl group at para-position of o-TBHA, further increases the basicity by 0.12 $pK_{BH^+}$ unit as the $pK_{BH^+}$ of N-o-tolyl-4-methylbenzo hydroxamic acid is $-2.41$. Thus, the ortho-substituent has greater effect on basicity than, when it is present in para-position.

The alkoxy group produces the same effect as the alkyl group. It has unshared electron pairs, thus it is an electron donating group and exerts base-strengthening mesomeric effect on basicity of the product. It is find in the Table 4, that, N-m-chlorophenyl-2-
methoxybenzo hydroxamic acid \( pK_{BH^+} = -2.37 \), is a stronger base as compared to N-m-chlorophenylibenzo hydroxamic acid \( pK_{BH^+} = -2.46 \).

**EFFECT OF HALO-GROUPS**

The effect of introducing electron withdrawing halogens are, to decrease the basicity, due to \(-I\) effect.

The data in the table shows that, N-p-chlorophenylibenzo hydroxamic acid is a weaker base than its parent compound, N-p-chlorophenylibenzo hydroxamic acid. The values of \( pK_{BH^+} \) are -2.90 and -2.29(127), respectively. Thus introduction of one more halogen in the former make it more weaker.

In another case, N-p-tolyl-4-bromobenzo hydroxamic acid is also a weaker base \( pK_{BH^+} = -2.51 \), when compared with N-p-tolylbenzo hydroxamic acid, p-TBHA \( pK_{BH^+} = -2.30 \) in ref., 125).

**EFFECT OF OXYGEN CONTAINING GROUPS**

Nitro groups are oxygen containing groups and thus having electron withdrawing property. Substituents containing these groups are less basic then the unsubstituted product. These groups are expected to interact strongly and specifically with the solvent through the formation of strong O–H–O type hydrogen bonds. With increasing acidity, the water content decreases and so solvation decreases, and influence of substituent on the reaction centre should go up. The data presented in Table 4, reveals that the substituents containing these groups are less basic than their parent products.

Thus, the conjugate acids of, N-phenyl-2-nitrobenzohydroxamic acid \( pK_{BH^+} = -2.92 \) is 0.18 \( pK_{BH^+} \) unit and N-phenyl-3,5-dinitrobenzohydroxamic acid \( pK_{BH^+} = -3.19 \) is 0.45 \( pK_{BH^+} \) unit less basic than their parent product, PBHA \( pK_{BH^+} = -2.74 \). At
the same time introduction of two nitro-groups is more effective.

In case of N-p-tolyl-3,5-dinitrobenzohydroxamic acid, which contain both electron-donating and electron-withdrawing groups has the $pK_{BH^+}$ value of 2.81, comparatively less than that of $pK_{BH^+}$ value, 2.30(125) of p-TBHA. Presence of two base-weakening groups influenced markedly in presence of alkyl group.

It is also concluded that, conjugate acids of nitro-substituted hydroxamic acids are strong acids (weaker base), as compared to halo derivatives and the parent products. Although, halogens are also electron-withdrawing, would be expected to produce weaker and less specific solute–solvent interaction.

**PROTONATION BEHAVIOUR OF N-ARYLSUBSTITUTED HYDROXAMIC ACIDS IN HYDROCHLORIC ACID**

All the N-arylsubstituted hydroxamic acids are versatile metal extractants. Hydrochloric acid is generally involved in these extraction processes. Therefore, protonation behaviour of these metal extractants is also investigated in hydrochloric acid, following the same procedures and equations as in perchloric acid.

The data on distribution ratios and percentage of protonated hydroxamic acids, as a function of hydrochloric acid concentrations are presented in Tables 2 and 7. Figures 21 to 30 show that the trend of protonation is in accordance with distribution data. As the acidity increases, the percentage of protonated species increases, thus the distribution ratio decreases, as the protonated hydroxamic acids are hydrophilic in nature.

Table 8 is the summary table presenting the data on protonation parameters, viz, $pK_{BH^+}$, $m$, $\psi$, $m^+$, $r$ and $\sigma$ for N-arylsubstituted hydroxamic acids in hydrochloric acid, following the HAFM, BOM and EAM methods. Values of the ionisation ratios($I$) measured at various hydrochloric acid concentrations are used to determine $pK_{BH^+}$ values of conjugate acids according to equations [25], [27] and [30].
TABLE 7

PERCENTAGE PROTONATION OF N-ARYLSUBSTITUTED HYDROXAMIC ACIDS AS A FUNCTION OF HYDROCHLORIC ACID CONCENTRATION

<table>
<thead>
<tr>
<th>No</th>
<th>Hydrochloric Acid Concentration (M)</th>
<th>Hydroxamic Acid</th>
<th>Percentage Protonation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.1</td>
<td>N-P-Tolyl-3'-dimethylbenzeno</td>
<td>1.30</td>
</tr>
<tr>
<td>2</td>
<td>0.1</td>
<td>N-P-Tolyl-4'-bromobenzo</td>
<td>1.71</td>
</tr>
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<td>3</td>
<td>0.1</td>
<td>N-P-Chlorophenyl-4'-bromobenzo</td>
<td>1.16</td>
</tr>
<tr>
<td>4</td>
<td>0.1</td>
<td>N-P-Chlorophenyl-4'-bromobenzo</td>
<td>1.16</td>
</tr>
<tr>
<td>5</td>
<td>0.1</td>
<td>N-P-Chlorophenyl-4'-bromobenzo</td>
<td>1.16</td>
</tr>
<tr>
<td>6</td>
<td>0.1</td>
<td>N-P-Chlorophenyl-4'-bromobenzo</td>
<td>1.16</td>
</tr>
<tr>
<td>7</td>
<td>0.1</td>
<td>N-P-Chlorophenyl-4'-bromobenzo</td>
<td>1.16</td>
</tr>
<tr>
<td>8</td>
<td>0.1</td>
<td>N-P-Chlorophenyl-4'-bromobenzo</td>
<td>1.16</td>
</tr>
<tr>
<td>9</td>
<td>0.1</td>
<td>N-P-Chlorophenyl-4'-bromobenzo</td>
<td>1.16</td>
</tr>
<tr>
<td>10</td>
<td>0.1</td>
<td>N-P-Chlorophenyl-4'-bromobenzo</td>
<td>1.16</td>
</tr>
</tbody>
</table>

Note: The percentage protonation values are given for each hydroxamic acid at various concentrations of hydrochloric acid.
<table>
<thead>
<tr>
<th>No</th>
<th>HYDROXAMIC ACIDS</th>
<th>pKBH+</th>
<th>KOH (m)</th>
<th>BOH (m)</th>
<th>HAHP (m)</th>
<th>Kp</th>
<th>pKH+</th>
<th>pK0H</th>
<th>m</th>
<th>[H+]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>N-p-Tolyl-3',5'-dimethoxybenzo-</td>
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<tr>
<td></td>
<td></td>
<td>104A</td>
<td>0.00</td>
<td>0.26</td>
<td>0.47</td>
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<tr>
<td>2</td>
<td>N-3,4-Dihydroxybenzoyl-</td>
<td></td>
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<td>217</td>
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<tr>
<td>3</td>
<td>N-4-Chlorophenyl-4-bromobenzo-</td>
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<td>56A</td>
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<td>4</td>
<td>N-p-Tolyl-2-methoxybenzo-</td>
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<td>62A</td>
<td>0.52</td>
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<tr>
<td>5</td>
<td>N-3-Chlorophenyl-3,5-dinitrobenzo-</td>
<td>6.74</td>
<td>0.32</td>
<td>0.99</td>
<td>0.32</td>
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<tr>
<td>6</td>
<td>N-p-Tolyl-3-methylbenzo-</td>
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<tr>
<td>7</td>
<td>N-3-Chlorophenyl-2-methoxybenzo-</td>
<td>6.74</td>
<td>0.32</td>
<td>0.98</td>
<td>0.32</td>
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<td>8</td>
<td>N-3-Chlorophenyl-2-methoxybenzo-</td>
<td>6.74</td>
<td>0.32</td>
<td>0.98</td>
<td>0.32</td>
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<tr>
<td>9</td>
<td>N-p-Tolyl-4-bromobenzo-</td>
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<td></td>
<td></td>
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<tr>
<td>10</td>
<td>N-p-Tolyl-3,5-dinitrobenzo-</td>
<td></td>
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<tr>
<td>11</td>
<td>N-p-Tolyl-4-bromobenzo-</td>
<td></td>
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</tbody>
</table>

Protonation Parameters of N-Arylsubstituted Hydroxamic Acids in Hydrochloric Acid.

Table 8
Hydroxamic acids are considerably weaker bases than amines and cannot be measurably ionised in dilute acidic solutions. The interpretation of protonation behaviour in hydrochloric acid is more complex and difficult to make any quantitative comparison, since there has been little protonation work carried out in this acid.

In Figures 11 to 20, the slopes of N-arylsubstituted hydroxamic acids for HAFM, BOM and EAM methods, in hydrochloric acid are presented. In Table 8 slope values are quoted in two decimal places. The data analysed by HAFM utilising H⁺ produced slopes which are close to unity. The values are mostly in the 0.92 to 1.09 range. The results on ψ and m* values for BOM and EAM are ill defined. These are not in agreement with perchloric acid data and not in the expected range, as for carbonyl groups. Although their protonation data in perchloric acid justifies that hydroxamic acids are not Hammett bases.

Examination of the values in Tables 4, 6 and 8, obtained in different acid systems shows that the \( pK_{BH^+} \) values determined in hydrochloric acid are less negative than those in perchloric acid.

**EFFECT OF SUBSTITUENTS ON PROTONATION BEHAVIOUR OF N-ARYLSUBSTITUTED HYDROXAMIC ACIDS IN HYDROCHLORIC ACID**

From the data presented in Table 8, it is concluded that in hydrochloric acid substituents exert the same effect on basicity of hydroxamic acids as in perchloric acid. Alkyl and alkoxy derivatives are stronger bases than their parent compounds. All the oxygen containing groups exhibit base-weakening effects, as observed in nitro-derivatives. Substitution of two nitro groups further decreases the basicity. Comparatively, the electron withdrawing halo-groups produces weaker effect on basicity.

**COMPARISION OF HAFM, BOM AND EAM METHODS**

The HAFM, BOM and EAM methods have been compared in order to rationalize the differences observed between \( pK_{BH^+} \) values estimated by each classical method.
SLOPES FOR N-PHENYLBENZOXYDROXAMIC ACID IN HCl

**FIG. 11A. PLOT OF LOG I vs -HA FOR HAFM**

**FIG. 11B. PLOT OF (LOG I + H0) vs (H0 + LOG C(r)) FOR BOM**

**FIG. 11C. PLOT OF LOG I vs X FOR EAM**
SLOPES FOR N-PHENYL-2-NITROBENZOHYDROXAMIC ACID IN HCl

FIG. 12A. PLOT OF LOG I vs -HAFM

FIG. 12B. PLOT OF LOG I vs H0 + LOG C00 FOR BOM

FIG. 12C. PLOT OF LOG I vs X FOR EAM

SLOPES FOR N-PHENYL-2-NITROBENZOHYDROXAMIC ACID IN HCl
SLOPES FOR N-O-TOLYL BENZOHYDROXAMIC ACID IN HCl

FIG. 14A. PLOT OF LOG I vs -HA FOR HAFM

FIG. 14B. PLOT OF (LOG I + H0) vs (H0, LOG C+) FOR BOM

FIG. 14C. PLOT OF LOG I vs X FOR EAM

SLOPE: 0.34

SLOPE: 1.34

SLOPE: 0.92

LOG I

LOG I + H0

X

LOG I

SLOPE: 0.34
FIG. 15A. PLOT OF LOG I vs X FOR EAM

FIG. 15B. PLOT OF LOG I vs H^+ FOR HAFM

SLOPES FOR N-O-TOLYL-4-METHYLBENZOXAZOLOXYDROXAMIC ACID IN HCl

SLOPE = 1.30

SLOPE = 0.20

SLOPE = 0.92

SLOPE = 0.5
SLOPES FOR N-m-CHLOROPHENYL-BENZOXYDROXAMIC ACID IN HCl

FIG. 16A. PLOT OF LOG I vs X FOR EAM

FIG. 16C. PLOT OF LOG I vs X FOR EAM

SLOPE = 0.30

FIG. 16B. PLOT OF LOG I vs H+ FOR HAFM

SLOPE = 1.23

FIG. 16A. PLOT OF LOG I vs -H+ FOR HAFM

SLOPE = 1.01

SLOPES FOR N-m-CHLOROPHENYL-BENZOXYDROXAMIC ACID IN HCl
FIG. 17A. Plot of Log I vs -H₂ for HAFM

SLOPE = 1.38

FIG. 17B. Plot of Log (H⁺ + log C₁⁺) vs H⁺

SLOPE = 0.20

FIG. 17C. Plot of Log I vs X for EAFM

SLOPE = 1.07

SLOPES FOR N-M-CHLOROPHENYL-2-METHOXYBENZOHYDROXAMIC ACID IN HCl
SLOPES FOR N-P-CHLOROPHENYL-4-BROMOBENZOHYDROXAMIC ACID IN HCl

FIG. 18A. PLOT OF LOG I vs X FOR EAM

FIG. 18B. PLOT OF LOG (I + H0) vs (H0 + LOG Cm) FOR BOM

FIG. 18C. PLOT OF LOG I vs X FOR HAM

SLOPE = 0.25

SLOPE = 0.30

SLOPE = 0.92

SLOPE = 1.30
FIG. 19A. PLOT OF $\log I$ vs $-\text{HA}$ FOR EAM

FIG. 19B. PLOT OF $\log (I + H_0)$ vs $(H_0 + \log C_w)$ FOR BOM

FIG. 19C. PLOT OF $\log I$ vs $X$ FOR EAM

Slopes for N-p-tolyl-4-bromobenzohydrazonic acid in HCl

SLOPE $= 1.21$

SLOPE $= 0.39$

SLOPE $= 1.09$
Fig. 20A. Plot of log I vs -Ha for HAFM

Fig. 20B. Plot of log (log I + Hb) vs (Hb + log Cb) for BOM

Fig. 20C. Plot of log I vs X for EAM
BOM and EAM methods have to be considered essentially as equivalent methods (151). Consequently X corresponds approximately to \((-H_0 + \log C_{H+})\). The major difference between BOM and EAM methods is the use of Acidity Function in the latter. If we consider a complete range of acidity for hydrochloric and perchloric acid, the function X, and \((-H_0 + \log C_{H+})\) are linearly correlated to each other, the slope and the intercept values of these correlations being almost one and zero, respectively. The use of excess acidity function based on nitroanilines allows one to give a physical meaning to the slope parameter \(m^*\) (152).

An examination of data presented in Tables 4 and 8 reveals that in both the acids, the three different approaches give different \(pK_{BH+}\) values. At the same time, nature of the acid is also responsible for difference in \(pK_{BH+}\) values. In hydrochloric acid the values of \(pK_{BH+}\) determined by EAM are least negative and those obtained by BOM are the most negative among the three methods. In perchloric acid the trend is somewhat different. Bunnell-Olsen \(pK_{BH+}\) are still the most negative ones but the acidity function \(pK_{BH+}\) are least negative values.

Thus, for the weaker bases, the N-arylsubstituted hydroxamic acids, HAFM, BOM and EAM methods give quite different \(pK_{BH+}\) values. Furthermore, it is interesting to notice that \(pK_{BH+}\) values of similar compounds, the weak amides, also furnished different values by HAFM and EAM methods (153). Differences in \(pK_{BH+}\) values have been found for other weak bases also (154).

Although the practical and theoretical advantage of EAM method should render this method most suitable in less concentrated acid solutions. But in the case of very weak bases for which more concentrated acid solutions are necessary, the validity of the results obtained by EAM method is questionable. Probably, as suggested by Johnson and Stratton (155), the X scale in the higher region of the acidity must be perfected again in order to contribute the desirable Universal Function. Sometimes both BOM and HAFM methods are more satisfactory. Even BOM method has been found to be less reliable when used with acidity functions other than \(H_0\) (156). In those cases in which disagreement between the three methods is observed, the question arises as to which method gives the more accurate estimate of the real thermodynamic quantity. However, it has been observed that particularly in case of weak organic bases HAFM method works better than BOM and
EAM methods. At the same time, EAM method is capable of providing mechanistic information which the other methods cannot.

**PERCENTAGE PROTONATED OF HYDROXAMIC ACIDS**  
**AS A FUNCTION OF ACID CONCENTRATIONS**

Measurement of percentage of protonated hydroxamic acids at various acidity in hydrochloric and perchloric acids, were calculated following the equation –

\[
\% \text{ Protonated} = \frac{h_a}{h_0/h_a + K_a} \times 100 \quad [31]
\]

Where \( h_0 = -\log h_0 \) and \( K_a = -\log pK_{BH^+} \)

These data are presented in Tables 7 and 9. In perchloric acid the percentage of protonation estimated, following the \( h_0 \) function. In hydrochloric acid, the data are analysed using \( h_a \) function. Going from 1 to 10M acid concentrations, the percentage of protonated species increases at different rates depending upon the structure of hydroxamic acid in both the acids. The extent of protonation of these reagents at increasing perchloric and hydrochloric acid concentrations is presented in Figures 21 to 30, and the trend is in accordance with distribution data.

**SITE OF PROTONATION**

The site of protonation is of equal importance to the study of hydroxamic acids protonation equilibria. Evidences exist in favour of Oxygen protonation(I) and Nitrogen protonation(II).
## Percentage Protonation of N-Arylsubstituted Hydroxamic Acids as a Function of perchloric Acid Concentration

### Table 9

<table>
<thead>
<tr>
<th>Hydroxamic Acid</th>
<th>1.0</th>
<th>0.16</th>
<th>0.48</th>
<th>1.44</th>
<th>2.56</th>
<th>3.68</th>
<th>4.80</th>
<th>5.92</th>
<th>7.04</th>
<th>8.16</th>
<th>9.28</th>
<th>10.40</th>
</tr>
</thead>
<tbody>
<tr>
<td>N-p-Tolyl-3,5-dichlorobenzo-</td>
<td>1.0</td>
<td>0.16</td>
<td>0.48</td>
<td>1.44</td>
<td>2.56</td>
<td>3.68</td>
<td>4.80</td>
<td>5.92</td>
<td>7.04</td>
<td>8.16</td>
<td>9.28</td>
<td>10.40</td>
</tr>
<tr>
<td>N-p-Tolyl-4-bromobenzo-</td>
<td>0.9</td>
<td>0.32</td>
<td>0.65</td>
<td>1.44</td>
<td>2.22</td>
<td>0.96</td>
<td>0.22</td>
<td>0.00</td>
<td>0.13</td>
<td>0.39</td>
<td>0.99</td>
<td>2.01</td>
</tr>
<tr>
<td>N-p-Chloro-phenyl-4-bromobenzo-</td>
<td>0.8</td>
<td>0.45</td>
<td>1.30</td>
<td>1.00</td>
<td>0.33</td>
<td>0.14</td>
<td>0.09</td>
<td>0.03</td>
<td>0.17</td>
<td>0.31</td>
<td>0.40</td>
<td>0.13</td>
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<tr>
<td>N-p-Chloro-phenyl-2-methoxybenzo-</td>
<td>0.7</td>
<td>0.04</td>
<td>0.03</td>
<td>0.02</td>
<td>0.01</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
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<td>0.00</td>
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<tr>
<td>N-m-Chlorophenyl-2-methoxybenzo-</td>
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<td>N-m-Chlorophenyl-4-methylbenzo-</td>
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<td>N-o-Tolyl-4-nitrobenzo-</td>
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<tr>
<td>N-o-Tolyl-3,5-dinitrobenzo-</td>
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<td>0.00</td>
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<tr>
<td>N-p-Tolyl-3,5-dinitrobenzo-</td>
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<td>N-p-Tolyl-4-bromobenzo-</td>
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**Note:** Hydroxamic acid concentration is given in molar concentration.
FIG. 21. DISTRIBUTION RATIOS AND PERCENTAGE PROTONATION OF N-PHENYL BENZOHYDROXAMIC ACID AS A FUNCTION OF HYDROCHLORIC (---) AND PERCHLORIC (•••) ACID CONCENTRATIONS.
FIG. 22. DISTRIBUTION RATIOS AND PERCENTAGE PROTONATION OF N-PHENYL-2-NITROBENZOHYDROXAMIC ACID AS A FUNCTION OF HYDROCHLORIC (***) AND PERCHLORIC (•–•) ACID CONCENTRATIONS.
FIG. 23. DISTRIBUTION RATIOS AND PERCENTAGE PROTONATION OF N-PHENYL-3,5-DINITROBENZOHYDROXAMIC ACID AS A FUNCTION OF HYDROCHLORIC (•••••) AND PERCHLORIC (–•–••) ACID CONCENTRATIONS.
FIG. 24. DISTRIBUTION RATIOS AND PERCENTAGE PROTONATION OF N-o-TOLYLBENZOHYDROXAMIC ACID AS A FUNCTION OF HYDROCHLORIC ( ⬤ ⬤ ⬤ ) AND PERCHLORIC ( ⬤ ⬤ ⬤ ) ACID CONCENTRATIONS.
FIG. 25. DISTRIBUTION RATIOS AND PERCENTAGE PROTONATION OF N-o-TOLYL-4-METHYLBENZOHYDROXAMIC ACID AS A FUNCTION OF HYDROCHLORIC (●●●●) AND PERCHLORIC (●●●) ACID CONCENTRATIONS.
FIG. 26. DISTRIBUTION RATIOS AND PERCENTAGE PROTONATION OF N-m-CHLOROPHENYL BENZOHYDROXAMIC ACID AS A FUNCTION OF HYDROCHLORIC (•••••) AND PERCHLORIC (●●●) ACID CONCENTRATIONS.
FIG. 27. DISTRIBUTION RATIOS AND PERCENTAGE PROTONATION OF N-\textit{m}-CHLOROPHENYL-2-METHOXYBENZOHYDROXAMIC ACID AS A FUNCTION OF HYDROCHLORIC (\textbullet\textbullet\textbullet\textbullet) AND PERCHLORIC (\textbullet\textbullet\textbullet) ACID CONCENTRATIONS.
FIG. 28. DISTRIBUTION RATIOS AND PERCENTAGE PROTONATION OF N-p-CHLOROPHENYL-4-BROMOBENZOXYDROXAMIC ACID AS A FUNCTION OF HYDROCHLORIC (••••) AND PERCHLORIC (●●●●) ACID CONCENTRATIONS.
FIG. 29. DISTRIBUTION RATIOS AND PERCENTAGE PROTONATION OF N-\textit{p}-TOLYL-4-BROMOBENZOHYDROXAMIC ACID AS A FUNCTION OF HYDROCHLORIC (\bullet••) AND PERCHLORIC (\bullet–\bullet–) ACID CONCENTRATIONS.
FIG. 30. DISTRIBUTION RATIOS AND PERCENTAGE PROTONATION OF N-p-TOLYL-3,5-DINITROBENZOHYDROXAMIC ACID AS A FUNCTION OF HYDROCHLORIC (•••••) AND PERCHLORIC (○○○○○) ACID CONCENTRATIONS.
Site of protonation favoured which structure, is still a point of discussion. Of the two possibilities for a protonated species I and II, the favoured site of protonation is the carbonyl-oxygen, presumably due to its better charge delocalisation available, into the ring and the oxygen. Lobo (157) has examined the n.m.r. spectra of N-methylbenzohydroxamic acid and concluded that hydroxamic acids protonated chiefly on oxygen. Further, the carbonyl oxygen protonation has the characteristics m* values in the range 0.6–0.7 (68, 158).

The infrared absorption peaks of these reagents are assigned in accordance with the earlier works as described in CHAPTER II. It was observed that both $\nu_{\text{O-H}}$ and $\nu_{\text{C=O}}$ appear at lower wave numbers than expected, and the position of these bands remain unaffected by dilution. It is thus inferred that intramolecular hydrogen bonding exists in the molecule and hence the conjugated acid can be written in the N-protonated form –

This will be in equilibrium with an O-protonated form at lower acidity. Besides, the acidity at which the solvent extraction is performed, does not greatly influence the complex formation. This also suggests that protonation may be possible at the nitrogen site, rather than at the oxygen site. Moreover, chelation occurs through both oxygen atoms –
which also indicate the possibility of the N-protonation in hydroxamic acids.

A very little information is available in the literature (122, 133, 157) regarding the site of protonation, concerned with the hydroxamic acids. According to Tillet and Lobo (132, 157) both hydroxamic acids and amides show similar protonation behaviour as they are structurally related compounds, and favoured protonation at carbonyl oxygen, in presence of strong acidic solutions, whereas at lower acidity both O-protonated and N-protonated forms are present. Still, N-protonation is not completely impossible in amides, since tert-amides show an acid catalysed isomerism, which can occur only by N-protonation. besides, amides with electron donating substituents exchange by N-protonation (159).

To investigate the site of protonation, further and detail studies are needed, applying the modern technique of n.m.r. spectroscopy.