Kinetics of the Hydrolysis of Acetohydroxamic Acid in a Nitric Acid Solution

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Abstract: The acid-catalyzed hydrolysis of acetohydroxamic acid in a nitric acid solution has been studied spectrophotometrically. The hydrolysis provided carboxylic acid and hydroxylamine. First-order dependency on the hydronium ion concentration was observed in the acid-catalyzed reaction. The kinetics for the hydrolysis of the acetohydroxamic acid in a nitric acid solution fit the equation \(-d[AHA]/dt = k[AHA][H^+]\), with \(k = 0.0015 \text{ L/mol-min}\) at 25 ± 0.2 °C and \([\text{HNO}_3] \leq 4.0 \text{ M}\). The variation of the rate constant with respect to the temperature in terms of an Arrhenius-type relationship was examined. The activation energy, \(E_a\), was found to be 81.4 kJ/mol.

Keywords: hydrolysis, acetohydroxamic acid, kinetics, nitric acid

Introduction

Hydroxamic acids are weak proton donors that have numerous applications in analytical [1], biological [2], and medicinal fields, with uses such as drug delivery systems, enzyme inhibitors, siderophores, and iron transport and DNA cleavage agents [3-6]. Also, hydroxamic acids have been used as excellent spectrophotometric and gravimetric reagents, with current interest focused on their reduction/complexation chemistry with metals [7,8]. As O,O donor ligands, they have a strong affinity for ‘hard’ metal ions, such as Fe^{3+}, Al^{3+}, and Np^{4+} [9]. Hydroxamic acids can exist in two tautomeric forms (keto and enol). The keto-enol isomerism provides a number of sites for chelation. Spectral evidence indicates that the keto form is predominant in an acidic medium and the enol form in an alkaline medium [10]. Unsubstituted hydroxamic acids are organic ligands having the general formula RCONHOH; they act as good chelating agents for metal ions through the formation of five-membered chelate rings.

Recently, increasing interest in hydroxamic acids has been attributed, in part, to their application to nuclear fuel processing [11,12]. Hydroxamic acids with a low carbon backbone, such as FHA (formohydroxamic acid) and AHA (acetohydroxamic acid), have been shown to aid in the separation of tetravalent Np from hexavalent U through selective formation of a Np(IV) hydrophilic complex [13-15]. However, an additional property of these hydroxamic acids is that they can act as reducing agents for actinide ions [16]. Because hydroxamic acids are composed of only C, H, O, and N atoms, they can be decomposed to gases so that their incorporation in industrial processes will not lead to increases in the waste volume [17].

The hydrolysis mechanism, structure, acid-base equilibria, and overall stability of hydroxamic acids have important bearings of their general usefulness in many of these applications [18-20]. However, the hydrolysis of hydroxamic acids into parent carboxylic acids and hydroxylamines can result in several problems that must be faced to achieve desired objectives. Hence, their hydrolytic stabilities have been examined [21,22]. The kinetics of an acid-catalyzed hydrolysis of BHA in an aqueous solution was studied for the first time by Berndt and Fuller [23]. They reported that the rate increased linearly with an increasing acid concentration at a low acidity. At a higher concentration of acid, however, the rate rose to a maximum and then began decreasing. It seems reason-
able to suppose that in this region of acidity, complete conversion of the substrate into a conjugate acid occurs. Most of the studies that have been performed on the kinetics of hydrolysis deal primarily with unsubstituted hydroxamic acids. Only a few studies have been reported on the hydrolysis of hydroxamic acids under non-dilute acidic conditions. The hydrolysis of some aliphatic hydroxamic acids, such as methyl, isobutyl, and hexylhydroxamic acids has been studied spectrophotometrically in perchloric, hydrochloric, and sulfuric acids [24]; it would appear logical to compare their hydrolyses with the corresponding reaction amides. The dependency of the hydrolysis rate constants of some hydroxamic acids on the proton activity and dielectric constant of the medium has been studied by Mollin and Kucerova [25]. In a neutral region, this reaction is slower than that in an acidic medium by several orders of a magnitude. Hence, the non-catalyzed addition of water is kinetically insignificant [26,27]. AHA is unstable in acid solution and hydrolyzes to the parent acetic acid and hydroxylamine. In this study, the kinetics for the hydrolysis of AHA in nitric acid solution were determined.

**Experimental Section**

Acetohydroxamic acid (AHA), 98 % pure, was obtained from Aldrich Chemical Co. and dissolved in doubly distilled water to produce a 1.0 M stock solution. Reagent-grade nitric acid, 70 wt% from Aldrich Co., was diluted with distilled water to make a stock acid solution. All of the kinetic measurements were performed at a constant temperature, maintained within ± 0.2 °C.

Solutions for the rate measurements were prepared by adding a suitable sample of AHA stock solution to the appropriate temperature-equilibrated acidic solution; the initial AHA concentration was 0.1 M.

Hydroxamic acids tend to give very highly colored complexes; the absorbance of a complex with metal ions can be used to analyze either the metal ions or the hydroxamic acid. In this experiment, AHA was analyzed spectrophotometrically through measurement of the absorption of the Fe(III) - AHA complex at 503 nm. A 40-µL aliquot of the reaction solution was periodically removed and added to 4 mL of 1 M HNO3 - 0.1 M ferric nitrate solution; its absorbance was determined using a model 8453 Hewlett-Packard photo-diode array UV-VIS spectrophotometer. It was essential that the determination be made within a few minutes, because the Fe(III) - AHA complex began to hydrolyze after 5 ~ 10 min. Figure 1 shows the spectra for the Fe(III) - AHA complex at various AHA concentrations, and its standard curve. Beer's law was obeyed by the system.

**Results and Discussion**

**Kinetics for the Hydrolysis of AHA**

The acid-catalyzed hydrolysis of acetohydroxamic acid affords a carboxylic acid and hydroxylamine, according to equation (1).

$$CH_3CONHOH + H^+ + H_2O \rightarrow CH_3COOH + NH_2OH^+$$

(1)

The reaction that occurs as a result of hydrolysis is considered to follow pseudo-first-order kinetics with respect to the substrate, as follows:

$$-\frac{d[AHA]}{dt} = k[AHA][H^+]$$

$$= k'[AHA], \text{ where } k' = k[H^+]$$

(2)

Measurements of the acid hydrolyses of AHA were made at several different nitric acid concentrations. As seen in Figure 2, the dependency of log([AHA]/[AHA]o) on the time is a linear function of slope $k'$ at a constant acid concentration; this relationship which indicates that
the reaction is first-order with respect to AHA.

As shown in Figure 3, the change in \( k' \) versus the acid concentration yields a straight line of slope \( k \). The first-order rate constant \( k \) maintains a constant slope upon variation of the nitric acid concentration. On the other hand, the reaction rate increased linearly with increasing nitric acid concentration. The corresponding rate law is given by equation 3.

\[
k' = 0.0015[H^+] \tag{3}
\]

The hydrolysis of AHA has been reported by Taylor and May [12]; the kinetics were of first order, with a rate constant \( k = 0.00205 \text{ L/mol-min} \) at 25 °C. They reported that the hydrolysis of AHA was monitored using a colorimetric method based on the formation of a complex between Fe(III) and AHA at 499 nm. The authors did not, however, provide experimental data for their results. Our value of \( k \) is slightly different from theirs.

Equation 3 is written on the basis that the intercept in Figure 3 is zero, within experimental accuracy, and that the reaction is extremely slow in the absence of an added catalyst.

Hydroxamic acids are hydrolyzed through a mechanism in which the hydronium ion is transferred in the transition state; the reactions are specifically hydrogen ion-catalyzed [21]. In the simplest description, the first step is a pre-equilibrium protonation and the second step is a rate-determining attack of water on the protonated substrate.

The probable reaction path for hydrolysis of AHA starts with a rapid pre-equilibrium proton transfer (equation 4).

\[
\text{CH}_3\text{CONHOH} + H_3O^+ \xrightarrow{k_1} \text{CH}_3\text{COH}^+ \text{NHOH} + H_2O \tag{4}
\]

The carbon atom of the carbonyl group is then attacked by water (nucleophile), resulting in a tetrahedral intermediate being formed; the carbonyl group is again created by the loss of a leaving group (equation 5).

\[
\text{CH}_3\text{COH}^+ \text{NHOH} + H_2O \xrightarrow{k_1} \text{CH}_3\text{COOH} + NH_3OH^+ \tag{5}
\]

By analogy to the hydrolysis of other carboxyl derivatives [28,29], it is likely that tetrahedral intermediates exist in the present system. These intermediates (except for a few special cases) exist in only very small amounts in a solution; furthermore, protonated species, such as CH$_3$COH$^+$NHOH, will be present in only very small amounts in the acid range studied. Thus, the total stoichiometric amount of AHA will be essentially equal to that in the non-protonated form (see equation 6). The concentration of water has been treated as a constant; it includes the rate and equilibrium constants where appropriate. Equation 6 is of the form of equation 2.

\[
k' = k_1 K_1 \tag{6}
\]

The step shown in equation 7 is not included in the mechanism because no detectable reaction of AHA was observed at 45 °C in pure water for 24 h. Hence, we know that the non-catalyzed addition of water is kinetically insignificant.

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**Table 1.** Rate Constants of the Hydrolysis Reactions at Various Nitric Acid Concentrations and Temperatures

<table>
<thead>
<tr>
<th>[HNO$_3$] (M)</th>
<th>Temp. (°C)</th>
<th>( k' )</th>
<th>( k ) (mol/L·min)</th>
</tr>
</thead>
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<tr>
<td>1.0</td>
<td>25</td>
<td>0.00181</td>
<td>0.00181</td>
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<td></td>
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<td>0.03050</td>
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</table>
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Figure 3. Pseudo-first-order rate constants plotted as a function of the acid concentration at 25 °C.

\[ CH_3CONHOH + H_2O \rightarrow CH_3COOH + NH_2OH^+ \] (7)

Temperature Dependence

The influence of the temperature on the reaction rate in the range 25 ~ 45 °C has been studied. Variations of the rate constants \( k \) with the temperature at several nitric acid concentrations are given in Table 1. Arrhenius plots of \( k \) (Figure 4) gave an activation energy \( E_a^{(avg.)} \) of 81.4 kJ/mol. This value of \( E_a \) is in agreement with that reported by Taylor and May [12], who obtained a value of 79.9 ± 2.9 kJ/mol.

Conclusions

In this report, the kinetics of the acid-catalyzed hydrolysis of acetohydroxamic acid in nitric acid solution was studied spectrophotometrically. AHA hydrolyzes to provide acetic acid and hydroxylamine. For the hydrolysis of acetohydroxamic acid, the equation

\[ -\frac{d[AHA]}{dt} = k[AHA][H^+] \]

was attained, where \( k = 0.0015 \) (L/mol · min) at 25 °C and \([\text{HNO}_3] \leq 4.0 \) M. Also, an activation energy, \( E_a \), of 81.4 kJ/mol was obtained for the hydrolysis reaction.

Acknowledgments

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References