Checking the Kinetics of Acetic Acid Production by Measuring the Conductivity

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Abstract: The hydrolysis of acetic anhydride to acetic acid was studied by measuring the conductivity. The measurements were based on the conductivity of a weak electrolyte. The reaction kinetics when producing acetic acid (CH₃COOH) from acetic anhydride ((CH₃CO)₂O) and water (H₂O) was checked in a stirred batch reactor under different temperatures (T₁ = 20 °C, T₂ = 23 °C and T₃ = 26 °C): 

(CH₃CO)₂O + H₂O ⇌ 2 CH₃COOH

The course of the reaction was followed by measuring a weak electrolyte conductivity, in our case, acetic acid. The kinetic parameters of acetic acid production (activation energy, reaction rate constant, rate order) were determined. Experimental data agrees quite well with the data in the literature.

Keywords: hydrolysis of the acetic anhydride, production of the acetic acid, kinetics, reaction rate constant, activation energy, rate order, conductivity

Introduction

Quite a few studies have been reported in literature on the kinetics of acetic anhydride hydrolysis. Eldridge and Piret [1] obtained the pseudo-first-order reaction rate constant using a batch reactor. In order to determine the acetic anhydride concentration, samples from the reactor were withdrawn into tarred flasks containing 15 ~ 20 times the quantity of saturated aniline-water required to react with the sample. Since the anhydride rapidly acetylates the aniline, producing acetaldehyde and acetic acid, the samples were then titrated to determine the concentration of acetic acid. In another study, Shatyski and Hanesian [2] determined the kinetics of the above reaction by using temperature-time data obtained under adiabatic conditions in a batch reactor. The use of in-situ FTIR spectroscopy for following the hydrolysis of acetic anhydride reaction has been demonstrated [3]. The analysis of the batch reactor data showed that the hydrolysis of acetic anhydride is a pseudo-first order reaction. The rate constants were calculated from the batch data using both integral and differential methods of analysis.

In this paper the kinetics of the hydrolysis of acetic anhydride to acetic acid were studied by measuring the conductivity.

Conductivity

Further insight into the nature of molecular motion can be obtained by studying the motion of ions in solution, for ions can be dragged through the solvent by the application of a potential difference between two electrodes immersed in the sample.

The fundamental measurement used to study the motion of ions is that of the electrical resistance, R, of the solution [4]. The conductance, G, of a solution is the inverse of its resistance: R: G = 1/R. As resistance is expressed in ohms, Ω, the conductance of a sample is expressed as Ω⁻¹. The reciprocal ohm used to be called the mho, but its official designation is now the siemens, S, and 1S = 1 Ω⁻¹. The conductance of a sample decreases with its length l and increases with its cross-sectional area A. We therefore write:

\[ G = \frac{\kappa A}{l} \]  

where \( \kappa \) is the conductivity. With the conductance in
siemens and the dimensions in meters, it follows that the SI units of $\kappa$ are siemens per metre (S m$^{-1}$). The conductivity of a solution depends on the number of ions present, and it is normal to introduce the molar conductivity, $A_m$, which is defined as:

$$A_m = \frac{\kappa}{c} \quad (2)$$

where $c$ is the molar concentration of the added electrolyte. The SI unit of molar conductivity is siemens metre-squared per mole (S m$^2$ mol$^{-1}$).

The molar conductivity is found to vary according to the concentration. One reason for this variation is that the number of ions in the solution might not be proportional to the concentration of the electrolyte. For instance, the concentration of ions in a solution of a weak acid depends on the concentration of the acid in a complicated way, and doubling the concentration of the acid added does not double the number of ions. Secondly, because ions interact strongly with one another, the conductivity of a solution is not exactly proportional to the number of ions present. The concentration dependence of molar conductivities indicates that there are two classes of electrolyte. The characteristic of a strong electrolyte is that its molar conductivity depends only slightly on the molar concentration. The characteristic of a weak electrolyte is that its molar conductivity is normal at concentrations close to zero, but falls sharply to low values as the concentration increases.

**Weak Electrolytes**

Weak electrolytes are not fully ionised in solution [4]. They include weak Bronsted acids and bases, such as CH$_3$COOH and NH$_3$. The marked concentration dependence of their molar conductivities arises from the displacement of the equilibrium:

$$\text{HA}(aq) + \text{H}_2\text{O}(l) \leftrightarrow \text{H}_3\text{O}^+(aq) + \text{A}^-(aq)$$

$$K_c = \frac{a_{\text{H}_3\text{O}^+} \cdot a_{\text{A}^-}}{a_{\text{HA}}} \quad (3)$$

The acid is fully deprotonated at infinite dilution, and its molar conductivity is then $A_m^\circ$. Because only a fraction $\alpha$ is actually present as ions in the actual solution, the measured molar conductivity $A_m$ is given by:

$$\alpha = \frac{A_m}{A_m^\circ} \quad (4)$$

For the weak electrolyte the $\alpha$ is nearly 0 and for the strong electrolyte the $\alpha$ draws near to 1.

The concentration, $c$, is calculated from the eq. 3:

$$c = \frac{K_c \cdot (1 - \alpha)}{\alpha^2} \quad (5)$$

The degree of ionisation, $\alpha$, is calculated from the eq. 4 by considering eqs. 2 and 5:

$$\alpha = \frac{A_m^\circ \cdot K_c}{(\kappa + A_m^\circ \cdot K_c)} \quad (6)$$

**Reaction Rate**

For a constant-volume batch reactor [3], the rate of appearance of reactant A (acetic anhydride), $r_A$, is given by:

$$-r_A = \frac{dc_A}{dt} \quad (7)$$

where $r_A$ can be expressed as:

$$-r_A = k \cdot c_A^n \cdot c_B^m \quad (8)$$

where $k$ is the reaction rate constant, $n$ and $m$ are the reaction orders with respect to species A (acetic anhydride) and B (water), respectively. Since water is in excess, $c_B$ remains essentially unchanged during the course of the reaction:

$$-r_A = k' \cdot c_A^n \quad (9)$$

where $k'$ is a pseudo rate constant

$$k' = k \cdot c_{B0}^m \approx k \cdot c_{B0} \quad (10)$$

The concentration of B remains constant at volume ratio $V'(\text{Ac}:\text{H}_2\text{O}) = 1:10$ [5], but we use the volume ratio 1:25.
Checking the Kinetics of Acetic Acid Production by Measuring the Conductivity

Table 1. The Kinetics Parameters from the Literature

<table>
<thead>
<tr>
<th>Rate constant, $k$ (min$^{-1}$)</th>
<th>$T = 20, ^{\circ}\text{C}$</th>
<th>0.0924</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T = 25, ^{\circ}\text{C}$</td>
<td>0.1580</td>
<td></td>
</tr>
<tr>
<td>$T = 35, ^{\circ}\text{C}$</td>
<td>0.2752</td>
<td></td>
</tr>
<tr>
<td>Activation energy, $E_a$ (kJ/mol)</td>
<td>50.2</td>
<td></td>
</tr>
<tr>
<td>Order of reaction</td>
<td>Pseudo-first order</td>
<td></td>
</tr>
</tbody>
</table>

The specific reaction rate, $k$, is a function of reaction temperature and is given by the Arrhenius equation:

$$k = k_0 \cdot e^{-\frac{E_a}{R \cdot T}}$$

(11)

where $k_0$ is a pre-exponential factor, $E_a$ is the activation energy for the reaction, and $T$ is the absolute temperature.

The reaction order and rate constant can be determined by the integral method of analysis. In this method, the rate expression is guessed and the differential equation used to model the batch system is integrated. If the assumed order is correct, the appropriate plot (determined from the integration) of concentration-time data should be linear.

For the first-order case where $-r_A = kc_A$, integration of equation 7 yields:

$$k \cdot t = \ln \left( \frac{c_{A0}}{c_A} \right)$$

(12)

where $c_A$ is acetic anhydride concentration and $c_{A0}$ is initial acetic anhydride concentration.

The differential method can also be used to analyse the rate data. In this method, the reaction rate at each concentration is determined by differentiating concentration versus time data. By combining the mole balance (eq. 7) with the rate law (eq. 9), we obtain:

$$-\frac{dc_A}{dt} = k \cdot c_A^n$$

(13)

Taking the logarithm of both sides of eq. 13 gives:

$$\log\left( -\frac{dc_A}{dt} \right) = \log(k) + n \cdot \log(c_A)$$

(14)

The slope of a plot of $\log(-dc_A/dt)$ and $\log(c_A)$ is the reaction order.

**Kinetics Parameter**

The hydrolysis of acetic anhydride ($\text{(CH}_3\text{CO})_2\text{O}$) to acetic acid ($\text{CH}_3\text{COOH}$) takes place:

$$(\text{CH}_3\text{CO})_2\text{O} + \text{H}_2\text{O} \leftrightarrow 2 \text{CH}_3\text{COOH},$$

\[ \Delta H^{298} = -56 \text{ kJ/mol} \] (15)

The final reaction product is a harmless acetic acid solution in water with degree of conversion, $X_A = 98\%$.

The reaction is carried out in a batch reactor over three different temperatures ($T_1 = 20\, ^{\circ}\text{C}$, $T_2 = 23\, ^{\circ}\text{C}$ and $T_3 = 26\, ^{\circ}\text{C}$).

The kinetics parameters from the literature [3] are in Table 1:

The course of reaction was followed by measuring a weak electrolyte - acetic acid conductivity.

**Experiment**

A schematic diagram of the laboratory apparatus is shown in Figure 1. The reactor used in the experiment with the stirrer. Distilled water (1 L) is thermostated into a reactor at temperature 23 °C and 40 mL of acetic anhydride was added at the same temperature and is begins to measure the conductivity ($\kappa$) in dependence on time, $t$ (Table 2). The molar ratio between acetic anhydride (Ac) and water ($\text{H}_2\text{O}$) is $f(\text{Ac}:\text{H}_2\text{O}) = 1:131$.

The initial acetic anhydride concentration, $c_{A0}$, is 0.4075 mol/L. The molar conductivity at infinite dilution ($\Lambda_m^{\infty}$) of acetic acid is $39.05 \times 10^3$ S m$^2$ mol$^{-1}$ [4], the acidity constant, $K_a$, is $1.75 \times 10^{-5}$ at a temperature around 25 °C. It is assumed that the $\Lambda_m^{\infty}$ and $K_a$ are constant at a temperature of around 25 °C ($\pm 5\, ^{\circ}\text{C}$). Figure 2 illustrates the plot of $c_A$ as a function of time at temperature 23 °C.

After conductivity measurements can be calculated:

- degree of ionization, $\alpha$, from eq. 6
- concentration of acetic acid, $c$, from eq. 5 (Table 2).

The reacted acetic anhydride can be calculated (Table 2):
Table 2. The Experimental Data and Calculation at $T = 23 \, ^\circ C$

<table>
<thead>
<tr>
<th>$t$ (min)</th>
<th>$\kappa$ (µS/cm)</th>
<th>$c$ (mol/L)</th>
<th>$c_{A\text{ reacted}}$ (mol/L)</th>
<th>$c_{A}$ (mol/L)</th>
<th>$X_{A}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>0.0</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.4075</td>
<td>0.0000</td>
</tr>
<tr>
<td>1.15</td>
<td>431.7</td>
<td>0.07102</td>
<td>0.03551</td>
<td>0.37199</td>
<td>0.08714</td>
</tr>
<tr>
<td>2.62</td>
<td>692.0</td>
<td>0.18142</td>
<td>0.09071</td>
<td>0.31679</td>
<td>0.22260</td>
</tr>
<tr>
<td>4.05</td>
<td>873.6</td>
<td>0.28854</td>
<td>0.14427</td>
<td>0.26323</td>
<td>0.35404</td>
</tr>
<tr>
<td>6.07</td>
<td>1051.1</td>
<td>0.41716</td>
<td>0.20858</td>
<td>0.19892</td>
<td>0.51185</td>
</tr>
<tr>
<td>8.08</td>
<td>1163.2</td>
<td>0.51056</td>
<td>0.25528</td>
<td>0.15222</td>
<td>0.62646</td>
</tr>
<tr>
<td>10.08</td>
<td>1244.4</td>
<td>0.58411</td>
<td>0.29205</td>
<td>0.11545</td>
<td>0.71670</td>
</tr>
<tr>
<td>13.03</td>
<td>1323.0</td>
<td>0.66001</td>
<td>0.33001</td>
<td>0.07749</td>
<td>0.80983</td>
</tr>
<tr>
<td>14.8</td>
<td>1354.0</td>
<td>0.69122</td>
<td>0.34561</td>
<td>0.06189</td>
<td>0.84813</td>
</tr>
<tr>
<td>16.03</td>
<td>1370.0</td>
<td>0.70762</td>
<td>0.35381</td>
<td>0.05369</td>
<td>0.86824</td>
</tr>
<tr>
<td>18.02</td>
<td>1391.0</td>
<td>0.72942</td>
<td>0.36471</td>
<td>0.04279</td>
<td>0.89499</td>
</tr>
<tr>
<td>20.03</td>
<td>1406.0</td>
<td>0.74520</td>
<td>0.37260</td>
<td>0.03490</td>
<td>0.91435</td>
</tr>
<tr>
<td>22.87</td>
<td>1420.0</td>
<td>0.76008</td>
<td>0.38004</td>
<td>0.02746</td>
<td>0.93261</td>
</tr>
<tr>
<td>24.78</td>
<td>1427.0</td>
<td>0.76757</td>
<td>0.38379</td>
<td>0.02371</td>
<td>0.94180</td>
</tr>
<tr>
<td>28.25</td>
<td>1435.0</td>
<td>0.77618</td>
<td>0.38809</td>
<td>0.01941</td>
<td>0.95237</td>
</tr>
<tr>
<td>31.12</td>
<td>1438.0</td>
<td>0.77942</td>
<td>0.38971</td>
<td>0.01779</td>
<td>0.95635</td>
</tr>
<tr>
<td>34.75</td>
<td>1442.0</td>
<td>0.78375</td>
<td>0.39188</td>
<td>0.01562</td>
<td>0.96166</td>
</tr>
</tbody>
</table>

![Figure 2](image2.png)  
**Figure 2.** Concentration acetic anhydride, $c_{A}$, as a function of time at $23 \, ^\circ C$.

![Figure 3](image3.png)  
**Figure 3.** The plot of conversion degree $X_{A}$ as a function of time at $23 \, ^\circ C$.

The concentration of acetic anhydride can also be determined by the aniline-water method [5]. The quenching of reaction and the method of analysis depend on the rapid reaction of acetic anhydride with an excess of aniline (0.05 mol/L), to form acetanilide and acetic acid:

$$(\text{CH}_3\text{CO})_2\text{O} + \text{C}_6\text{H}_5\text{NH}_2 \rightarrow \text{CH}_3\text{COOH} + \text{C}_6\text{H}_5\text{NHCOCH}_3$$

Both quenched and unquenched samples are titrated to a phenolphthalein endpoint with 0.03 mol/L NaOH solution. The acetic acid produced by the hydrolysis and by the quenching reaction is determined since acetanilide is stable in the titration. In the unquenched samples hydrol-
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### Table 3. The Measured $c_A$ and Calculated $c_A$ at $T = 23 \, ^\circ\text{C}$

<table>
<thead>
<tr>
<th>$t/\text{min}$</th>
<th>Measured $c_A/(\text{mol/L})$</th>
<th>Calculated $c_A/(\text{mol/L})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.08</td>
<td>0.15222</td>
<td>0.15</td>
</tr>
<tr>
<td>16.03</td>
<td>0.05369</td>
<td>0.05</td>
</tr>
<tr>
<td>20.02</td>
<td>0.03490</td>
<td>0.03</td>
</tr>
</tbody>
</table>

### Figure 4. The pseudo-first order at temperature 27 $^\circ\text{C}$.

The measured $c_A$ after measuring the conductivity and calculated after titration with aniline $c_A$, can be compared (Table 3). The calculating of acetic anhydride concentration by the aniline-water method are not as repetitive as than measuring the conductivity.

The molar amount of acetic acid after the reaction 1 ($n_1$) is:

$$\text{(CH}_3\text{CO)}_2\text{O} + \text{H}_2\text{O} \leftrightarrow 2 \text{CH}_3\text{COOH}$$

$$2 \, n_1 = c (\text{NaOH}) \cdot V_1 (\text{NaOH})$$

The molar amount of acetic acid after the reaction 1 ($n_1$) and 2 ($n_2$) is:

$$\text{(CH}_3\text{CO)}_2\text{O} + \text{C}_6\text{H}_5\text{NH}_2 \rightarrow \text{CH}_3\text{COOH} + \text{C}_6\text{H}_5\text{NHCOCH}_3$$

$$\text{(CH}_3\text{CO)}_2\text{O} + \text{H}_2\text{O} \leftrightarrow 2 \text{CH}_3\text{COOH}$$

$$2n_1 + n_2 = c (\text{NaOH}) \cdot V_2 (\text{NaOH})$$

We have two equations with two variables:

$$2n_1 = c (\text{NaOH}) \cdot V_1 (\text{NaOH})$$

$$2n_1 + n_2 = c (\text{NaOH}) \cdot V_2 (\text{NaOH})$$

$$c (\text{NaOH}) \cdot V_1 (\text{NaOH}) + n_2 = c (\text{NaOH}) \cdot V_2 (\text{NaOH})$$

$$n_2 = c (\text{NaOH}) \cdot (V_2 (\text{NaOH}) - V_1 (\text{NaOH}))$$

$$n_2 = c (\text{NaOH}) \cdot \Delta V (\text{NaOH})$$

The molar amount of nonreacted acetic anhydride is:

$$n_A = c (\text{NaOH}) \cdot \Delta V (\text{NaOH}) \text{ in 10 mL sample}$$

$$c_A = \frac{n_A}{V_{\text{sample}}} = \frac{0.03 \text{ mol/L} \cdot \Delta V}{10 \text{ mL}}$$

### Table 4. The Reaction Rate Constant, $k$

<table>
<thead>
<tr>
<th>$T/\degree\text{C}$</th>
<th>$k/\text{min}^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>0.1060</td>
</tr>
<tr>
<td>23</td>
<td>0.1253</td>
</tr>
<tr>
<td>26</td>
<td>0.1602</td>
</tr>
</tbody>
</table>

### Figure 5. The plot of $\ln(c_{A0}/c_A)$ as a function of time at 20 $\degree\text{C}$.

The reaction was finished after about 30 min. The experiment at temperatures 23 $\degree\text{C}$ and 26 $\degree\text{C}$ is repeated using the same procedure.

The reaction rate constant agrees quite well with the data in the literature (Table 1 and 4).

The molar amount of acetic anhydride is rapid thus determining the acetic acid produced by complete hydrolysis. The anhydride present in the quenched samples is calculated from the difference in titration volumes for the two types of samples.

As eq (14) illustrates, a plot of $\log(-dc_A/dt)$ and $\log(c_A)$ should give a slope equal to the reaction order. Figure 4 represents a reaction at an order of one.

As Figure 5 illustrates, the plot of $\ln(c_{A0}/c_A)$ as a function of time is linear, which suggests that the rate law is first order with respect to acetic anhydride concentration under given reaction conditions for excess water. The slope represents the rate constant, $k$. The rate constant is found to be 0.1060 $\text{min}^{-1}$ at 20 $\degree\text{C}$. The data show the reaction is first order at all temperatures studied (Table 4).

The reaction was finished after about 30 min. The experiment at temperatures 23 $\degree\text{C}$ and 26 $\degree\text{C}$ is repeated using the same procedure.

The reaction rate constant agrees quite well with the data in the literature (Table 1 and 4).

Taking the logarithm of the Arrhenius equation (11):

$$\ln k = \ln k_0 - \frac{E_a}{R \cdot T}$$

a plot of $\ln(k)$ and $1/T$ should be a straight line and the slope is proportional to the activation energy. The activation energy is 50.1 kJ/mol (Figure 6). The average activation energy reported in the literature [3] is 50 241.6 J/mol, which differs by 0.28 % from the value reported in this experiment.

The slope of the graph is:

$$-\frac{E_a}{R} = 6026 \text{ K}$$
Figure 6. The plot of \( \ln k \) and \( 1/T \).

\[
E_a = 6026 \, \text{K} \cdot 8.314 \, \text{J/(molK)} = 50.1 \, \text{kJ/mol} \quad (22)
\]

Conclusions

We determined the kinetics of acetic anhydride to acetic acid by measuring the conductivity of a weak electrolyte - acetic acid in a batch reactor. The acetic acid concentration can be calculated on the theory basis of weak electrolytes ionisation. The analysis of the batch reactor data showed that the hydrolysis of acetic anhydride is a pseudo-first order reaction. The values determined in the experiment were compared to published literature values for the same reaction. The rate constant is found to be 0.106 min\(^{-1}\) at 20 °C and in the literature is reported as 0.0924 min\(^{-1}\) at the same temperature. The activation energy is 50.1 kJ/mol. The average activation energy reported in the literature is 50 241.6 J/mol, which differs by 0.28 % from the value reported in this experiment. The reaction rate constant agrees quite well with the data in the literature.

Nomenclature

\( c \) concentration, \( \text{mol/L} \)
\( E_a \) activation energy, \( \text{J/mol} \)
\( k \) reaction rate constant, \( \text{min}^{-1} \)
\( k_0 \) pre-exponential factor, \( \text{min}^{-1} \)
\( n, m \) rate order, / 
\( r \) rate of reaction, \( \text{mol/(L} \cdot \text{min)} \)
\( R \) gas law constant, \( \text{J/(mol} \cdot \text{K)} \)
\( T \) temperature, \( \text{K} \)
\( t \) time of reaction, \( \text{min} \)
\( X \) degree of conversion, / 
\( \alpha \) degree of ionization, / 
\( \kappa \) conductivity, \( \Omega^{-1} \text{m}^{-1} \)
\( \Lambda_m^\alpha \) molar conductivity at infinite dilution, \( \text{S} \text{m}^2 \text{mol}^{-1} \)
\( \Lambda_m \) molar conductivity, \( \text{S} \text{m}^2 \text{mol}^{-1} \)

References