Determination of the equilibrium constant for the triiodide ion formation using distribution coefficient and kinetics measurements
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Abstract:
The equilibrium constant for the triiodide formation was studied and determined using distribution coefficient and kinetics measurements. The equilibrium constant of iodine between water and carbon tetrachloride was previously determined at 25° and values of 681 is obtained, also in this study the equilibrium will be determined by reaction between 3-chloroperbenzoic acid and potassium iodide under pseudo-first order condition using large excess of iodide. The best fit values for equilibrium constant that obtained from kinetics data at 25° is 680, the result shows that this values are very close to that obtained from distribution coefficient measurement methods. This results show the usefulness of kinetics method for determining the equilibrium constant for this reaction.

1. Introduction
The equilibrium constant for reaction 1 has been determined previously using different technique and value of 698 has been reported. This value can be also obtained using kinetics data by utilizing the reaction of iodide with MCPBA (meta-chloroperbenzoic acid)

The oxidation of iodide by peracid is well known reaction and has been studied extensively at different condition. The present study investigates this reaction and utilising it to determine the equilibrium constant for the following equilibrium:

\[ \Gamma + I_2 \leftrightarrow \Gamma_3 \]  

There are different methods to measure the equilibrium constant. However, for the iodine triiodide system the distribution coefficient is the most widely used method. While the use of kinetics as method to determine the equilibrium constant is rare, therefore, this study will be focused on the determination of equilibrium constant using kinetics data. The reaction between metachloroperbenzoic acid (MCPBA) and iodide is very well known reaction which has been studied by Secco and Venturini. They found the reaction is independent of the salt effect and hydrogen ion concentration. However a solvent like 1,4-dioxin “hydrogen bond accepting solvent”, decreases the rate of the reaction because it stabilises the initial state with respect to the transition state, while hydrogen bond donor solvent increase the rate through

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thestabilisation of the transition state with respect to the initial state. The reaction is outlined in scheme 1. The nucleophilic iodide attacks the outer oxygen of the peracid to form HOI and the corresponding parent acid. HOI reacts with I\(^-\) to form iodine which equilibrates with iodide to form triiodide\(^5\).

\[
\text{RCO}_3\text{H} + \text{I}^- \rightarrow \text{HOI} + \text{RCO}_2^- \\
\text{HOI} + \text{I}^- \rightarrow \text{I}_2 + \text{HO}^- \\
\text{I}_2 + \text{I}^- \rightarrow \text{I}_3^- 
\]

Scheme 1

2. Experimental Section

2.1. Materials and methods

2.1.1. Materials

Metachloroperbenzoic acid (MCPBA) was purchased from Sigma Chemical Company with purity of 80%, the main impurity is the parent acid, metachlorobenzoic acid. Potassium iodide (Analar reagent, 99.5%), sulphuric acid with minimum assay of (95%), were obtained from Aldrich. Sodium thiosulphate (99%) was purchased from Fisher Chemical Company and was of the highest grade available. nitric acid which obtained from Aldrich

The reactants and reagents were prepared in distilled water.

2.2. Methods:

2.2.1. Solutions preparation

Solutions of metachloroperoxybenzoic acid were prepared normally by adding the required amount to distilled water and stirring for about an hour using a magnetic stirrer. These were filtered with a Duran Buchner funnel, 75 ml, with sintered disc 45 mm and pore diameter 16-40 micrometer. The concentration of MCPBA was determined iodometrically as described below. The required concentration for the working solution was obtained by further dilution in distilled water. The stock solutions of the MCPBA required regular standardisation due to their decomposition.

Potassium iodide, (4.15g) was dissolved and made up to 250 in a volumetric flask to obtain a stock solution of 0.1 M.

2.2.2. Metachloroperbenzoic acid determination

The concentration of peracid was determined by iodometric titration. Many methods used to determine organic peracids exist\(^6\).

The general method is as follows.

About 5 ml of 0.03 M potassium iodide and 10 ml of 2 M sulphuric acid were mixed in a 250 ml conical flask and 5.0 ml of the peracid was added by pipette and the mixture mixed thoroughly. The liberated iodine was titrated with the standard solution of sodium thiosulphate, 0.01 M, a small amount of iodine indicator was added toward the end of the titration. The end point is determined by the change of colour from pale blue to colourless.

\[
\text{RCO}_3\text{H} + 2 \text{I}^- + 2 \text{H}^+ \rightarrow \text{RCO}_2\text{H} + \text{H}_2\text{O} + \text{I}_2
\]
2 \text{S}_2\text{O}_3^{2-} + \text{I}_2 \rightarrow \text{S}_4\text{O}_6^{2-} + 2 \text{I}^{-}

It can be seen from the equations above that

\[ 2\text{I}^- \equiv 2\text{S}_2\text{O}_3^{2-} \equiv \text{RCO}_3\text{H} \]

Therefore the strength of metachloroperbenzoic acid can be calculated by the following equation.

\[
\text{[MCPBA]} = \frac{\text{V of Na}_2\text{S}_2\text{O}_3 \times 0.01 \text{ M}}{2 \times \text{volume of MCPBA}}
\]

\[
\text{[MCPBA]} = 0.01 \times \text{titre} / 10
\]

So the measured volume of Na\textsubscript{2}S\textsubscript{2}O\textsubscript{3} in cm\textsuperscript{3} is directly equal to the concentration of MCPBA in 10\textsuperscript{-3} mol dm\textsuperscript{-3}

\textbf{2.2.3. Stopped flow method}

A SX-17MV Stopped Flow Reaction Analyser from Applied Photophysics was used to measure

The rate of the reaction between iodide and meta-chloroperbenzoic acid, this reaction is known to be very fast so a stopped-flow is required.

Calibration of the stopped flow is carried out before every experiment using distilled water in both syringes. Following that, the syringes are filled with the relevant solutions. Air bubbles are removed before the runs by flushing backward and forward between the drive syringes and the reservoir syringes many times.

The kinetic run and the depression of the two reactants from syringes into the reactor chamber is done automatically, this forces the unreacted solution into the flow cell and also forces the reacted solution out of the cell. The concentration of triiodide formed was measured by mean of its absorption of ultra violet light.

\textbf{3. Results and Discussion}

\textbf{3.1. Analysing of the kinetic data}

The reaction was followed by monitoring the absorbance of the triiodide I\textsubscript{3}\textsuperscript{-} at 290 nm in nitric acid of 0.003 M. Pseudo first order rate constants were evaluated from the nonlinear plots of absorbance versus time using Equation 2 (shown below); the change in the absorbance is proportional to the amount of triiodide formed,

\[
(A_\infty - A_t) = (A_\infty - A_0) \exp(-k_{obs} \times t)
\]

Here, \(k_{obs}\) denotes the pseudo-first order rate constant, \(A_0\) is the initial absorbance, and \(A_\infty\) the final absorbance and \(t\) is the time. The path length of the spectrophotometer cell is 1 cm.

Grafit programme software\textsuperscript{7} was used to fit the absorbance difference versus iodide concentration to obtain the equilibrium constant. The kinetic data (absorbance difference versus iodide concentration) for the oxidation of iodide by 3-chloroperbenzoic acid obtained from the stopped flow machine was fitted using Grafit programme\textsuperscript{7} to Equation 12 using non-linear regression. While the Determination of equilibrium constant from distribution coefficient method are described elsewhere\textsuperscript{8} and will not be described in this study. The reaction between metachloroperbenzoic acid and iodide was carried out in the various amount of nitric acid, in order to achieve greater sensitivity the formation of I\textsubscript{3} was followed at 290 nm, where it has a larger
extinction coefficient. The data is tabulated in Table 1. Rate constant plotted against nitric acid concentration (Figure 1). The figure shows that the rate constant is independent of the concentrations of nitric acid thus; it will be used as reaction medium. The data obtained for the reaction between MCPBA $4.8 \times 10^{-6}$ M and various concentration of iodide in 0.003 M nitric acid at 25°C are in Table 2. The observed rate constant plotted against iodide concentration is show in Figure 2.

3.2. Determination of equilibrium constant from kinetics data

Figure 1 shows the plot of absorbance difference versus iodide concentration the data was treated using GraFit software programme and fitted to the equation 12. The equation used to fit the experimental data is derived as follow; the equilibrium for the formation of triiodide is represented by Equation [3]. The equilibrium constant defined in equation (4)

$$I + I_2 \rightleftharpoons I_3$$

$$K = \frac{[I_3]}{[I][I_2]}$$

$$E I_2 = 0$$

Where E denote the extinction coefficient of iodine

$$A = E I_3 [I_3]$$

The total concentration of iodide is given by equation (6) and that of iodine is defined by equation (7)

$$[I]_T = [I] + [I_3]$$

Assuming that $[I_3] \ll [I]$.

The total iodine liberated is equal to the oxidising agent Metachlororpebenzoic acid which is determined by the iodometric titration.

$$[I_2]_T = [I_2] + [I_3] = [\text{MCPBA}]$$

From equation 4,

$$K = \frac{[I_3]}{[I]_T[I_2]_T - [I_3]}$$

$$K [I]_T[I_2]_T - K [I]_T [I_3] = [I_3]$$

This is then rearranged to give the following form

$$[I_3^-] = \frac{K[I^-]_T [I_2]_T}{1 + K[I^-]_T}$$

From 5 and 10

$$A = \frac{[I_3^-][I^-]_T[I_2]_T}{(1 + K[I^-]_T)}$$

Which can be expressed as

$$A = \frac{a[I]_T}{(1+b[I]_T)}$$

$$b = K$$

$$a = E I_3 K [I_2]_T$$

The best fit value for the equilibrium constant obtained in this work at 25°C is 680 ± 15, which is determined by fitting the absorbance versus iodide concentrations
data to equation 12 using non-linear regression techniques.

This value is comparable to the value 698±10 reported by Donald and co-workers\(^1\), the small difference in these values can be due to the different in the conditions used.

Table 1 effect of nitric acid concentrations on the reaction rate of 0.0015 M iodide and 4.8×10\(^{-6}\) M of MCPBA at 25 °C

<table>
<thead>
<tr>
<th>HNO(_3)/ M</th>
<th>(k_{obs}) s(^{-1})</th>
<th>(A_\infty)</th>
<th>(A_0)</th>
<th>(A_\infty - A_0)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0003</td>
<td>8.23±0.9</td>
<td>0.0151</td>
<td></td>
<td>0.05</td>
</tr>
<tr>
<td>0.003</td>
<td>8.3±0.0</td>
<td>0.0242</td>
<td></td>
<td>0.06</td>
</tr>
<tr>
<td>0.001</td>
<td>8.37±0.0</td>
<td>0.0307</td>
<td></td>
<td>0.05</td>
</tr>
<tr>
<td>0.01</td>
<td>8.3±0.0</td>
<td>0.0332</td>
<td></td>
<td>0.05</td>
</tr>
<tr>
<td>0.03</td>
<td>8.32±0.3</td>
<td>0.0330</td>
<td></td>
<td>0.06</td>
</tr>
</tbody>
</table>

Table 2 the effect of iodide on the reaction rate in 0.003 M nitric acid and 4.8×10\(^{-6}\) MCPBA at 25 °C.

<table>
<thead>
<tr>
<th>[KI]/ M</th>
<th>(k_{obs}) s(^{-1})</th>
<th>(A_\infty)</th>
<th>(A_0)</th>
<th>(A_\infty - A_0)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0015</td>
<td>8.6±0.04</td>
<td>0.1479</td>
<td>0.069</td>
<td>0.0794</td>
</tr>
<tr>
<td>0.002</td>
<td>11.23±0.03</td>
<td>0.1709</td>
<td>0.082</td>
<td>0.0894</td>
</tr>
<tr>
<td>0.0025</td>
<td>14.1±0.05</td>
<td>0.1918</td>
<td>0.093</td>
<td>0.0991</td>
</tr>
<tr>
<td>0.003</td>
<td>16.94±0.07</td>
<td>0.2089</td>
<td>0.105</td>
<td>0.1040</td>
</tr>
<tr>
<td>0.005</td>
<td>27.58±0.1</td>
<td>0.2299</td>
<td>0.108</td>
<td>0.1220</td>
</tr>
<tr>
<td>0.01</td>
<td>52.06±0.28</td>
<td>0.2468</td>
<td>0.111</td>
<td>0.1340</td>
</tr>
<tr>
<td>0.015</td>
<td>71.92±0.7</td>
<td>0.2611</td>
<td>0.117</td>
<td>0.1440</td>
</tr>
</tbody>
</table>

Figure 1. Absorbance difference versus iodide concentration in the presence of 0.003 M nitric acid at 25 °C.

4. Conclusion

The observed rate constants show increase with increasing the iodide concentration, and for single run the absorbance is increased with time due to formation of the
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absorbing species triiodide. This study show that stopped flow method can be used to obtain the kinetics data for the reaction between MCPBA and iodide which can then be used also to determine the equilibrium constant for reaction 1 by fitting the kinetics data to the derived equation 12. The value obtained is very close to that determined previously.

However, the small different can be due to the solvent used which is nitric acid in this study.

Reference


