Bis(2-ethylhexyl) phthalate合成의 速度論(II)
——黃酸觸媒 反應——

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Kinetics of Bis(2-ethylhexyl) phthalate Synthesis (II)
Sulfuric Acid-Catalytic Reaction

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요 약

Mono(2-ethylhexyl) phthalate와 2-ethyl hexanol의 反應에 의한 bis(2-ethylhexyl) phthalate 合成에서
黃酸을 觸媒로 使用할 경우의 反應速度를 測定하여 反應機構을 究明하였다.

黃酸觸媒使用로의 反應주요는 mono(2-ethylhexyl) phthalate와 관하여 1次이고 2-ethyl hexanol
에 관하여도 1次이며 따라서 全次数는 2次이었다.

이 反應의 活性化能은 13 kcal/mole이었다.

黃酸觸媒의 濃度 및 反應温度에 따라는 反應速度定數는 下式으로 表示할 수 있었다.
\[ k = (3 \times 10^7 + 1.5 \times 10^9 C_C) e^{-13000/RT} \]

또한 反應의 反應機構에 대한 考察을 行하였다.

Abstract

Chemical kinetic study for the esterification of mono(2-ethylhexyl) phthalate with 2-ethyl hexanol was
carried out to find the reaction mechanism when sulfuric acid was used as the catalyst.

Experimental results gave a rate equation which was first order for both mono(2-ethylhexyl) phthalate
and 2-ethyl hexanol. Activation energy value of 13 kcal per mole was obtained by the plot of temperature
dependence of the rate equation.

The rate constant was expressed as a function of catalyst concentration and reaction temperature by the
following equation.
\[ k = (3 \times 10^7 + 1.5 \times 10^9 C_C) e^{-13000/RT} \]

Some discussion of the catalytic reaction mechanism was also given.
緒論

前報1)에서는 무식물판의 mono(2-ethylhexyl) phthalate와 2-ethyl hexanol로부터 bis(2-ethylhexyl) phthalate를 합성한 때의 반응속도에 관하여 보고하였다.

前報에서 이미 말한 바와 같이 무식물판과 2-ethyl hexanol 사이의 반응에 관한 연구는 많으나 이를 연구에 있어서 특히 반응속도의 인 것은 거의 찾아 볼 수 없었다. 것이 찾아 볼 수 있었던 반응속도 연구로서는 무식물판과 2-ethyl hexanol이 아닌 다른 알코올을 취약한 것이었다. 즉 Berman 등은 황산 무식물판에서 n-부탄올과 무식물판의 반응에서 n-부탄올을 보조로 사용한 경우 반응속도는 monobutyl phthalate의 농도에 관하여 2차이 있다고 하였고 van der Zeeuw2)는 역시 황산 무식물판에서 n-부탄올로부터 n-decanol까지의 몇몇 알코올과 무식물판의 monooester 사이의 반응에서 알코올을 보조로 사용한 경우 반응속도는 monooester 농도에 관하여 1차이 있다고 하였다.

본 연구에서는 무식물판과 2-ethyl hexanol에 무식물판이 존재가나의 반응을 실험하기 위하여 반응속도를 측정하여 반응속도를 결정하고 반응속도를 결정하기 위하여 렌치 실험의 상황에 의한 다가를 얻고 이들에 따르는 무식물판의 반응에서의 속도의 정상은 비교적 풍부하다.

実験

1. 試薬：黄酸은 日本和光製造 学問用 1級으로 일정한 839 97%의 것이며 기타 試薬는 前報1)에서와 같다.

2. 黄酸 무식물판에 의한 bis(2-ethylhexyl) phthalate의 合成：前報1)에서와 같이 무식물판과 2-ethyl hexanol은 反応시켜 mono(2-ethylhexyl) phthalate(以下monooester라 함)를 합성하여 이를 측정한 후 monooester의 一定量과 2-ethyl hexanol 및 黄酸의 所定量을 6 mm×150 mm의 유리관으로 만든 암경에 담고 一定temperature로 保満하여 있는 一定圧力 엄밀에서 加熱 反応시켜 一定時間에 이관함에 따라 이 암경을 개내어 중분히 반응을 중단시킨 후 암경을 개여 반応物 約 15 g을 提取하여 약 20 ml에 均一하게 溶解시키고 phenolphthalein指示薬에 의하여 1/10 N苛性ソーダ 水溶液으로 滴定하여 酸価를 溶定하고 이

酸価로부터 bis(2-ethylhexyl) phthalate(이하 disester라 함)의 生産量을 計算하였다. 實験温度範囲는 120～180℃이며, monooester와 2-ethyl hexanol의 水比는 1:4:1:9의 範囲이며, 黄酸 무식물판의 濃度範囲는 0.1～1%이다.

3. 達成酸価의 補正：反応物中에 존재하는 monooester의達成酸価을 補正3)하여야 한다. 反応物中에 있는 黄酸 무식물판은 溶存하는 2-ethyl hexanol과 反応하여 2-ethylhexyl monosulfate를 생성하고平衡에 到達함으로써 R-2-ethylhexyl monosulfate의 補正一定だ하다.

\[
\begin{align*}
\text{CH}_3(\text{CH}_2)_2\text{CHCH}_2\text{OH} + \text{H}_2\text{SO}_4 & \rightleftharpoons \text{C}_6\text{H}_5 \\
\text{CH}_3(\text{CH}_2)_2\text{CHCH}_2\text{OSO}_3^- + \text{H}_2\text{O}^- & \\
\text{C}_6\text{H}_5 & 
\end{align*}
\]

(1)

(1) 式과 같이 反応系中에서의 2-ethyl hexanol와 黄酸의 反応を考慮하여補正할 酸価의 値を 알기 위하여 下記와 같이 行行った。即 本報의 反応速度実験과 同じ方法으로 行行った一定量의 2-ethyl hexanol와 一定量の 黄酸 無色液中で 一定温度 質験範囲 120～180℃で 反応させ 1/10 N苛性ソーダ水溶液で 溶定하여 이로부터 2-ethylhexyl sulfuric acid의 無色液が 있을 に於ける 溶定値を於て Eqを以下の 式により 求めている。

\[
\text{Eq} = (49.04)(100)/100 - \frac{P_1}{2}
\]

(2)

Table 1에 2-ethyl hexanol과 黄酸の 反応の結果를 表示하였다. 2-ethyl hexanol과 黄酸の 反応は 각 實験温度に於て 관계없이 약 2분 후에는 平衡에 도달하였으며 補正한 酸価의 値を于て求め는 平均 86이었다.

結果 및 考察

Table 2에 monooester와 2-ethyl hexanol이 黄酸無色液에의 反応を 表示하였다.

이 결과들을 여러可能한 反応機構에 대한 反応速度와의 比較検討により 黄酸無色液에의 monooester와 2-ethyl hexanol의 反応機構 및 反応速度는 다음과 같이 생각할 수 있었다。

\[
\begin{align*}
\text{COO} & \rightleftharpoons \text{COO}^- \\
\text{C} & \rightleftharpoons \text{C}^+ \\
\text{OH} & \rightleftharpoons \text{OH}^{-} 
\end{align*}
\]

(3)
### Table 1. Reaction of 2-ethyl hexanol and sulfuric acid (0.378 % H₂SO₄)

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>Time [min]</th>
<th>Sample [g]</th>
<th>Equivalent of 1 N NaOH [ml]</th>
<th>Original H₂SO₄ [m-mole]</th>
<th>Remaining H₂SO₄ [m-mole]</th>
<th>Combined H₂SO₄ [%]</th>
<th>Combined H₂SO₄ [m-equiv]</th>
<th>Apparent milliequivalent</th>
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### Table 2. Reaction rate equation data

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<th>Catalyst correction [%]</th>
<th>Time [min]</th>
<th>Free acidity [%]</th>
<th>Actual monoester [%]</th>
<th>Monoester converted [mole·l⁻¹]</th>
<th>( \frac{1}{C_m - C_A} \ln \frac{C_A(C_m - C_B)}{C_m(C_m - C_B)} ) [l·mole⁻¹]</th>
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<td>Time (min)</td>
<td>Free acidity (%)</td>
<td>Actual monoester (%)</td>
<td>Monoester converted (mole⁻¹)</td>
<td>( \frac{1}{C_{\text{MO}} - C_{\text{MO}}/C_{\text{MO}}} ) (l mole⁻¹)</td>
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<td>Monoester converted (mole·L⁻¹)</td>
<td>( \frac{1}{C_{M0} - C_B} )</td>
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\( C_C = 4.59 \times 10^{-2} \) (= 0.500 %), 120 °C, \( C_{AB}/C_{M0} = 9 \), \( C_{MB} = 0.604 \)

(278/86) × 0.500

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<th>Free acidity (%)</th>
<th>Actual monoester (%)</th>
<th>Monoester converted (mole·L⁻¹)</th>
<th>( \frac{1}{C_{M0} - C_B} )</th>
<th>( \frac{\ln \frac{C_{M0} - C_B}{C_{M0} - C_B}}{C_{M0} - C_B} )</th>
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\( C_C = 4.73 \times 10^{-2} \) (= 0.516 %), 120 °C, \( C_{AB}/C_{M0} = 4 \), \( C_{MB} = 1.13 \)

(278/86) × 0.516

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<th>Time (min)</th>
<th>Free acidity (%)</th>
<th>Actual monoester (%)</th>
<th>Monoester converted (mole·L⁻¹)</th>
<th>( \frac{1}{C_{M0} - C_B} )</th>
<th>( \frac{\ln \frac{C_{M0} - C_B}{C_{M0} - C_B}}{C_{M0} - C_B} )</th>
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\( C_C = 9.34 \times 10^{-2} \) (= 1.02 %), 120 °C, \( C_{AB}/C_{M0} = 4 \), \( C_{MB} = 1.13 \)

(278/86) × 1.02

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<th>Time (min)</th>
<th>Free acidity (%)</th>
<th>Actual monoester (%)</th>
<th>Monoester converted (mole·L⁻¹)</th>
<th>( \frac{1}{C_{M0} - C_B} )</th>
<th>( \frac{\ln \frac{C_{M0} - C_B}{C_{M0} - C_B}}{C_{M0} - C_B} )</th>
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\( C_C = 0.768 \times 10^{-2} \) (= 0.0867 %), 140 °C, \( C_{AB}/C_{M0} = 11 \), \( C_{MB} = 0.527 \)

(278/86) × 0.0867

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<th>Time (min)</th>
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<th>( \frac{1}{C_{M0} - C_B} )</th>
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HWAHAHK KONGHAK Vol. 12, No. 4, August 1974
\( C_{C} = 1.46 \times 10^{-2} \) (equals 0.159 %)

140 °C, \( C_{A0}/C_{M0} = 5.01 \), \( C_{M0} = 0.968 \)

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<th>Actual monoester (%)</th>
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<th>( \frac{1}{C_{M0}-C_{A0}} \ln \frac{C_{A0}(C_{M0}-C_{B})}{C_{M0}(C_{M0}-C_{B})} ) (mole⁻¹)</th>
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\( C_{C} = 0.768 \times 10^{-2} \) (equals 0.0867 %)

155 °C, \( C_{A0}/C_{M0} = 11 \), \( C_{M0} = 0.527 \)

<table>
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<th>Actual monoester (%)</th>
<th>Monoester converted (mole⁻¹)</th>
<th>( \frac{1}{C_{M0}-C_{A0}} \ln \frac{C_{A0}(C_{M0}-C_{B})}{C_{M0}(C_{M0}-C_{B})} ) (mole⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>16.2</td>
<td>15.9</td>
<td>0.012</td>
<td>0.0040</td>
</tr>
<tr>
<td>5</td>
<td>15.7</td>
<td>15.4</td>
<td>0.029</td>
<td>0.0099</td>
</tr>
<tr>
<td>10</td>
<td>14.0</td>
<td>13.7</td>
<td>0.082</td>
<td>0.0294</td>
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<tr>
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<td>12.4</td>
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<tr>
<td>20</td>
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<td>11.6</td>
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<td>30</td>
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<td>9.8</td>
<td>0.209</td>
<td>0.0891</td>
</tr>
<tr>
<td>40</td>
<td>8.6</td>
<td>8.3</td>
<td>0.259</td>
<td>0.1198</td>
</tr>
<tr>
<td>60</td>
<td>6.1</td>
<td>5.8</td>
<td>0.338</td>
<td>0.1837</td>
</tr>
<tr>
<td>90</td>
<td>4.1</td>
<td>3.8</td>
<td>0.402</td>
<td>0.2601</td>
</tr>
<tr>
<td>120</td>
<td>3.3</td>
<td>3.0</td>
<td>0.430</td>
<td>0.3607</td>
</tr>
</tbody>
</table>

\( C_{C} = 1.46 \times 10^{-2} \) (equals 0.159 %)

170 °C, \( C_{A0}/C_{M0} = 5.01 \), \( C_{M0} = 0.968 \)

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>Free acidity (%)</th>
<th>Actual monoester (%)</th>
<th>Monoester converted (mole⁻¹)</th>
<th>( \frac{1}{C_{M0}-C_{A0}} \ln \frac{C_{A0}(C_{M0}-C_{B})}{C_{M0}(C_{M0}-C_{B})} ) (mole⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>29.3</td>
<td>28.8</td>
<td>0.038</td>
<td>0.0011</td>
</tr>
<tr>
<td>5</td>
<td>26.9</td>
<td>26.4</td>
<td>0.113</td>
<td>0.0259</td>
</tr>
<tr>
<td>10</td>
<td>22.2</td>
<td>21.7</td>
<td>0.268</td>
<td>0.0687</td>
</tr>
<tr>
<td>15</td>
<td>18.3</td>
<td>17.8</td>
<td>0.394</td>
<td>0.1126</td>
</tr>
<tr>
<td>20</td>
<td>16.5</td>
<td>16.0</td>
<td>0.452</td>
<td>0.1364</td>
</tr>
<tr>
<td>30</td>
<td>11.7</td>
<td>11.2</td>
<td>0.607</td>
<td>0.2191</td>
</tr>
<tr>
<td>40</td>
<td>9.7</td>
<td>9.2</td>
<td>0.672</td>
<td>0.2668</td>
</tr>
<tr>
<td>60</td>
<td>6.4</td>
<td>5.9</td>
<td>0.778</td>
<td>0.3731</td>
</tr>
<tr>
<td>90</td>
<td>5.2</td>
<td>4.7</td>
<td>0.816</td>
<td>0.4292</td>
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<tr>
<td>120</td>
<td>4.6</td>
<td>4.1</td>
<td>0.835</td>
<td>0.4626</td>
</tr>
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</table>

\( C_{C} = 0.768 \times 10^{-2} \) (equals 0.0867 %)

170 °C, \( C_{A0}/C_{M0} = 11 \), \( C_{M0} = 0.527 \)

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>Free acidity (%)</th>
<th>Actual monoester (%)</th>
<th>Monoester converted (mole⁻¹)</th>
<th>( \frac{1}{C_{M0}-C_{A0}} \ln \frac{C_{A0}(C_{M0}-C_{B})}{C_{M0}(C_{M0}-C_{B})} ) (mole⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>16.0</td>
<td>15.7</td>
<td>0.019</td>
<td>0.0064</td>
</tr>
<tr>
<td>10</td>
<td>13.3</td>
<td>13.1</td>
<td>0.104</td>
<td>0.0384</td>
</tr>
<tr>
<td>15</td>
<td>12.4</td>
<td>12.1</td>
<td>0.136</td>
<td>0.0518</td>
</tr>
<tr>
<td>20</td>
<td>10.5</td>
<td>10.3</td>
<td>0.195</td>
<td>0.0812</td>
</tr>
<tr>
<td>30</td>
<td>7.2</td>
<td>6.9</td>
<td>0.303</td>
<td>0.1524</td>
</tr>
<tr>
<td>40</td>
<td>6.7</td>
<td>6.4</td>
<td>0.320</td>
<td>0.1665</td>
</tr>
<tr>
<td>60</td>
<td>4.4</td>
<td>4.1</td>
<td>0.394</td>
<td>0.2479</td>
</tr>
<tr>
<td>90</td>
<td>2.6</td>
<td>2.3</td>
<td>0.451</td>
<td>0.3527</td>
</tr>
<tr>
<td>120</td>
<td>1.7</td>
<td>1.4</td>
<td>0.480</td>
<td>0.4658</td>
</tr>
</tbody>
</table>

\( C_{C} = 1.46 \times 10^{-2} \) (equals 0.159 %)

170 °C, \( C_{A0}/C_{M0} = 5.01 \), \( C_{M0} = 0.968 \)

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>Free acidity (%)</th>
<th>Actual monoester (%)</th>
<th>Monoester converted (mole⁻¹)</th>
<th>( \frac{1}{C_{M0}-C_{A0}} \ln \frac{C_{A0}(C_{M0}-C_{B})}{C_{M0}(C_{M0}-C_{B})} ) (mole⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>29.6</td>
<td>29.1</td>
<td>0.028</td>
<td>0.0058</td>
</tr>
<tr>
<td>5</td>
<td>27.5</td>
<td>27.0</td>
<td>0.095</td>
<td>0.0215</td>
</tr>
<tr>
<td>10</td>
<td>21.3</td>
<td>20.8</td>
<td>0.296</td>
<td>0.0778</td>
</tr>
<tr>
<td>15</td>
<td>16.7</td>
<td>16.2</td>
<td>0.445</td>
<td>0.1337</td>
</tr>
</tbody>
</table>
\[
C_{C} = 0.768 \times 10^{-2} \quad (= 0.0867 \%) \quad 180 \, {\circ}C, \quad C_{M_{0}}/C_{M_{0}} = 11, \quad C_{M_{0}} = 0.527
\]
\[
(C_{78}/86) \times 0.0867 \quad 2 \quad 15.5 \quad 15.2 \quad 0.036 \quad 0.0122
\]
\[
= 0.280 \quad 5 \quad 14.6 \quad 14.3 \quad 0.064 \quad 0.0226
\]
\[
10 \quad 11.5 \quad 11.2 \quad 0.163 \quad 0.0647
\]
\[
15 \quad 9.5 \quad 9.2 \quad 0.228 \quad 0.1002
\]
\[
20 \quad 7.9 \quad 7.6 \quad 0.281 \quad 0.1350
\]
\[
30 \quad 5.8 \quad 5.5 \quad 0.349 \quad 0.1940
\]
\[
40 \quad 3.9 \quad 3.5 \quad 0.411 \quad 0.2742
\]
\[
60 \quad 2.5 \quad 2.2 \quad 0.456 \quad 0.3640
\]
\[
90 \quad 1.5 \quad 1.2 \quad 0.486 \quad 0.4696
\]
\[
120 \quad 1.3 \quad 1.0 \quad 0.494 \quad 0.5096
\]
\[
C_{C} = 1.46 \times 10^{-2} \quad (= 0.159 \%) \quad 180 \, {\circ}C, \quad C_{M_{0}}/C_{M_{0}} = 5.01, \quad C_{M_{0}} = 0.968
\]
\[
(C_{78}/86) \times 0.159 \quad 2 \quad 26.9 \quad 28.4 \quad 0.051 \quad 0.0110
\]
\[
= 0.514 \quad 5 \quad 25.2 \quad 24.7 \quad 0.169 \quad 0.0443
\]
\[
10 \quad 18.7 \quad 18.2 \quad 0.380 \quad 0.1701
\]
\[
15 \quad 13.4 \quad 12.8 \quad 0.552 \quad 0.1859
\]
\[
20 \quad 9.4 \quad 8.9 \quad 0.680 \quad 0.2734
\]
\[
30 \quad 6.3 \quad 5.8 \quad 0.781 \quad 0.3786
\]
\[
40 \quad 5.1 \quad 4.6 \quad 0.820 \quad 0.4361
\]
\[
60 \quad 3.9 \quad 3.4 \quad 0.858 \quad 0.5102
\]
\[
90 \quad 3.4 \quad 2.9 \quad 0.874 \quad 0.5848
\]
\[
120 \quad 3.3 \quad 2.8 \quad 0.879 \quad 0.5640
\]

\[
\begin{align*}
\text{RCOOH} + \text{HOH} & \rightarrow \text{RCOO} + \text{H}^+ + \text{H}_2\text{O} \\
& \text{(4)}
\end{align*}
\]

\[
KC_{H^+} \leq 1 \text{이고}\quad C_{H^+} \approx 2 C_{C}\quad \text{러만}
\]
\[
\frac{dC_{B}}{dt} = \frac{1}{2} k' k' C_{C} (C_{M_{0}} - C_{B}) (C_{A_{0}} - C_{B})
\]
\[
= k'' C_{C} (C_{M_{0}} - C_{B}) (C_{A_{0}} - C_{B})
\]

따라서
\[
k'' C_{C} dt = \int \frac{1}{C_{M_{0}} - C_{A_{0}}} \ln \frac{C_{A_{0}}}{C_{M_{0}}} \frac{(C_{M_{0}} - C_{B})}{(C_{A_{0}} - C_{B})} \text{d}t
\]

\[
\text{한편 실험 결과로부터 추정의 속도가 0.159}\%\text{이고 monoester와 2-ethyl hexanol의 농도가 1:5인 경우 때}\]
\[
\text{는}\text{Fig. 1} \text{에 플로트하였다.}
\]
\[
\text{Fig. 1에서 보는바와 같이 좋은 직선이 얻어지므로}\text{의}\text{가 끝 점을 알 수 있다.}\text{따라서 앞에서}\text{산정한}\text{적 영역 중 monoester와}\text{의}\text{반응은}\text{태영해 깔려}\text{平衡이며}\text{적 극한을}\text{에}\text{하는}\text{은}\text{의}\text{라고}\text{할}\text{수}\text{있다.}
\]

HWAHAH KONGHAK Vol. 12, No.4, August 1974
Fig. 1. Plot of equation (9) for the case of \( C_{A0}/C_{M0} = 5 \) and \( C_C = 1.46 \times 10^{-2} \).

즉, 일반적인 에스테르화 반응에서 얻는 액산에서 생긴 주된 반응은 monoester의 결합을 통해 붙이며 이것에 알코올과 합물을 만드는 것이 반응을 합성하고 분해할 수 있다. 따라서 (4)식의 반응은 다음과 같이 진행 되리라 생각된다.

\[
\text{COOR} + \text{OH} \rightarrow \text{COOR}
\]

\[
\text{C} + \text{OH} \rightarrow \text{COOR}
\]

\[
\text{C} + \text{OH} \rightarrow \text{COOR} + \text{H}_2\text{O}
\]

\[
\text{COOR} + \text{H} \rightarrow \text{COOR}
\]

Fig. 2. Plot of equation (9) with variation of catalyst concentration for the case of 120°C and \( C_{A0}/C_{M0} = 4 \).

반응온도가 120°C이고 액산의 총수를 달리는 편의에 따른 결과는 Fig. 2에 보다하였다.

여기서 보던 반응은 액산의 종류가 증가함에 따라 반응속도는 상승하며 오른쪽 위의 점선을 위의 것으로 보아 diester의 생성속도에 있어 반응속도는 monoester에 대해 1배이며 2-ethyl hexanol에 대해 1배로서 전체가 2배이다. 또한 monoester와 2-ethyl hexanol의 용액을 변화시키고 액산량은 0.5%로 일정하여 반응온도 120°C에서 반응시간 결과는 Fig. 3에 표시하였다.

Fig. 3. Plot of equation (9) with variation of \( C_{A0}/C_{M0} \) for the case of 120°C and \( C_C = 4.59 \times 10^{-2} \).

\[
K \times 10^3 \text{[mol g]^{-1}} \]

Fig. 4. Catalyst concentration dependence of rate constant.

화학공학 제12권 제4호 1974년 8월
여기서 보면 monoester와 2-ethyl hexanol의 몰비의
변화에 관계 없이 한 질량기에 있다고 있는 이 반응
기구의 예측의 전달성을 보여 주고 있다.

Monoester에서 2-ethyl hexanol의 몰비가 1:4일 때
의 황산 간계의 강도 변화에 대한 k값을 Fig. 4에 도
모트 하였는데 좋은 직선이 얻어졌다.

이 결과로부터 Arrhenius 슬로프 하루가 Fig. 5이
다. 여기서 임의의 활성화에너지 값이 13 kcal/mole이며
이 값은 두 항목에서의 활성화에너지 값 18 kcal/mole에
비하면 5 kcal/mole 작은 것이다.

황산 크리스탈 및 황산 간계의 관계를 알기 위
하여 Fig. 6에 $k/e^{13000/RT}$와 황산 크리스탈의 크리
스탈의 크리스탈로 같은 직선이 되므로 다음과이 성
립한다.

$$k = (3 \times 10^7 + 1.5 \times 10^6 C_C) e^{-13000/RT} \tag{10}$$

이로서 관계가 정확적으로 증명 된다. 관계를 얻을
수 있다.

결론

황산 크리스탈과 식별하여 monoester로부터 2-ethyl
hexanol에 의하여 diester이 생성할 때 이식된 식은 mono-
ester와 연관되어 전체 1차로 표시된다.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{fig5.png}
\caption{Temperature dependence of rate constant.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{fig6.png}
\caption{$k/e^{-15,000/KT}$ vs. catalyst concentration.}
\end{figure}

이 식을로부터 얻어진 활성화에너지 값은 13 kcal/
mole로서 두 항목의 18 kcal/mole보다 5 kcal/mole 적
이다.

이 반응의 활성화에너지는 높은 값을 확신하여 본 연구의 활성
화에 클리스탈 유의한 연구에서는 황산으로
로부터 주어지는 두 부분이 반응에 영향을 주는 것으로 관찰한
다.

Nomenclature

\begin{itemize}
  \item $A$: Weight of sample [g]
  \item $C_{AS}$: Initial concentration of 2-ethyl hexanol [mol·l$^{-1}$]
  \item $C_B$: Concentration of bis(2-ethylhexyl) phthalate [mol·l$^{-1}$]
  \item $C_C$: Concentration of sulfuric acid catalyst [mol·l$^{-1}$]
  \item $C_{H^+}$: Concentration of hydrogen ion [mol·l$^{-1}$]
  \item $C_{MS}$: Initial concentration of mono(2-ethylhexyl)
  phthalate [mol·l$^{-1}$]
  \item $C_{MSH^+}$: Concentration of protonated mono(2-ethyl-
  hexyl) phthalate [mol·l$^{-1}$]
  \item $E_Q$: Apparent milliequivalent to correct (m eq)
  \item $k$: $k = 2C_Ck'(1 \text{·} \text{mol}^{-1} \text{·} \text{min}^{-1})$
  \item $k'$: Rate constant in equation (6) (1·mol$^{-1}$·min$^{-1}$)
\end{itemize}

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\[ k'' = 2k' K \left( \text{P} \cdot \text{mol}^{-1} \cdot \text{min}^{-1} \right) \]

\[ K = \text{Equilibrium constant for equation (3)} \left( \text{l} \cdot \text{mol}^{-1} \right) \]

\[ L = \text{Volume of consumption of 1 N NaOH aq. solution for the titration (mL)} \]

\[ M_1 = \text{Moles of original sulfuric acid in sample} \]
\[ M_1 = \frac{AP_s}{9.808} \text{ (m} \cdot \text{mol)} \]

\[ M_2 = \text{Moles of remaining sulfuric acid in sample} \]
\[ M_2 = N_1 - M_1 \text{ (m} \cdot \text{mol)} \]

\[ N_1 = \text{Titrination equivalent weight of 1 N NaOH aq. solution used} N_1 = N_2L \text{ (m} \cdot \text{mol)} \]

\[ N_2 = \text{Normality of 1 N NaOH aq. solution used for the titration (N)} \]

\[ P_1 = \text{Percentage of sulfuric acid combined} \]
\[ P_1 = \frac{(M_1 - M_2)}{M_1} \times 100 \text{ (%)} \]

\[ P_2 = \text{Percentage of total sulfuric acid in sample (%)} \]

**Literature Cited**

2. A.I. Kutepova, S.M. Lokte, N.I., Grishko and O.A. Shtekker, **Plast. Massy**, No. 5, 47 (1967)
4. 古川勝, 成智聖司, 千葉大 工研報, No. 13, 23 (1962)
5. F. X. Weber, (B.F. Goodrich Co.), **Ger.** 1, 083, 265 (1960)
7. U. Roje and S. Trumbic, **Kem. Ind. (Zagreb)**, 15(11), 677 (1966)
8. S. Berman, A.A. Melnyehunk and D.F., Othmer, **Ind. Eng. Chem.**, 40, 1312 (1948)
10. C.E. Leyes and D.F. Othmer, **Ind. Eng. Chem.**, 37(10), 968 (1945)