

## 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) phthalate 와 2-ethyl hexanol 의 反應에 의한 bis(2-ethylhexyl) phthalate 合成에서 黃酸을 觸媒로 使用했을 경우의 反應速度를 測定하여 反應機構를 究明하였다.

黃酸觸媒使用時 위 反應에서의 反應次數는 mono(2-ethylhexyl) phthalate 에 關하여 1 次이고 2-ethyl hexanol 에 關하여도 1 次이며 따라서 全次數는 2 次이었다.

이 反應의 活性化에너지 값은 13 kcal/mole 이었다.

黃酸觸媒의 濃度 및 反應溫度에 따르는 反應速度定數는 다음式으로 表示할 수 있었다.

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

또한 약간의 反應機構에 대한 考察을 행하였다.

### 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.

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

Some discussion of the catalytic reaction mechanism was also given.



Table 1. Reaction of 2-ethyl hexanol and sulfuric acid (0.378 % H<sub>2</sub>SO<sub>4</sub>)

Temp. [°C]	Time [min]	Sample [g]	Equivalent of 1 N NaOH [ml]	Original H <sub>2</sub> SO <sub>4</sub> [m-mole]	Remaining H <sub>2</sub> SO <sub>4</sub> [m-mol]	Combined H <sub>2</sub> SO <sub>4</sub> [%]	Apparent milliequivalent [m·eq]
120	1/2	1.28	0.088	0.0492	0.0388	21.2	54.9
	1	1.46	0.075	0.0563	0.0187	66.9	73.7
	2	1.38	0.063	0.0532	0.0098	81.7	82.9
	20	1.32	0.061	0.0507	0.0103	79.7	81.5
	30	1.77	0.077	0.0682	0.0088	87.1	86.9
140	1/2	1.96	0.120	0.0756	0.0444	41.3	61.8
	1	1.65	0.074	0.0638	0.0105	83.5	84.2
	2	1.51	0.066	0.0583	0.0768	86.8	86.7
	15	1.38	0.077	0.0705	0.0064	90.8	89.8
	20	1.80	0.078	0.0694	0.0087	87.5	87.2
155	30	1.54	0.067	0.0594	0.0076	87.1	86.9
	1/2	1.79	0.104	0.0690	0.0351	49.1	65.0
	1	1.59	0.074	0.0613	0.0129	79.0	81.1
	2	1.47	0.065	0.0568	0.0082	85.4	85.6
	5	1.57	0.074	0.0604	0.0137	77.4	80.0
170	10	1.63	0.072	0.0628	0.0093	85.1	85.4
	15	1.76	0.074	0.0679	0.0061	90.9	89.9
	1/2	3.05	0.150	0.1180	0.0327	72.2	75.2
	1	1.24	0.058	0.0480	0.0101	79.0	79.4
	2	1.45	0.067	0.0559	0.0112	80.0	80.0
180	5	1.65	0.070	0.0636	0.0065	89.8	87.2
	15	1.48	0.064	0.0571	0.0070	87.7	85.6
	20	1.16	0.053	0.0448	0.0083	81.5	81.1
	1/2	1.36	0.066	0.0526	0.0135	74.3	76.5
	1	1.59	0.077	0.0612	0.0139	77.3	78.3
180	2	1.42	0.075	0.0548	0.0073	86.7	84.8
	10	1.60	0.072	0.0618	0.0103	83.3	82.4
	15	1.91	0.080	0.0735	0.0066	91.0	88.1
	20	1.31	0.058	0.0506	0.0075	85.2	83.7
	30	1.41	0.062	0.0545	0.0076	86.1	84.3

Table 2. Reaction rate equation data

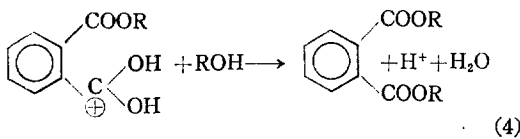
Catalyst correction [%]	Time [min]	Free acidity [%]	Actual monoester [%]	Monoester converted [mole·l <sup>-1</sup> ]	$\frac{1}{C_{M0}-C_{A0}} \ln \frac{C_{A0}(C_{M0}-C_B)}{C_{M0}(C_{M0}-C_B)}$ [l·mole <sup>-1</sup> ]
$C_C = 0.768 \times 10^{-2}$ (0.0867 %), 120 °C, $C_{A0}/C_{M0} = 11$ , $C_{M0} = 0.526$					
$(278/86) \times 0.0867$ $= 0.2803$	2	16.1	15.8	0.015	0.0048
	5	15.9	15.6	0.021	0.0068
	10	15.9	15.6	0.022	0.0073
	15	15.5	15.2	0.034	0.0115
	20	15.2	14.9	0.044	0.0152
	30	14.4	14.1	0.069	0.0245
	40	14.2	13.9	0.077	0.0275
	60	13.1	12.8	0.110	0.0410
	90	11.9	11.6	0.151	0.0592

Catalyst correction	Time	Free acidity	Actual monoester	Monoester converted	$\frac{1}{C_{M0}-C_{A0}} \ln \frac{C_{A0}(C_{M0}-C_B)}{C_{M0}(C_{M0}-C_B)}$
(%)	(min)	(%)	(%)	(mole·l <sup>-1</sup> )	(l·mole <sup>-1</sup> )
	120	10.9	10.6	0.182	0.0744
	$C_C = 0.86 \times 10^{-2}$ ( $\Rightarrow 0.0937\%$ ), 120 °C, $C_{A0}/C_{M0} = 4$ , $C_{M0} = 1.13$				
(278/86) × 0.0937	2	34.3	34.0	0.026	0.0050
= 0.303	10	33.3	33.0	0.060	0.0124
	15	32.6	32.3	0.083	0.0174
	20	32.1	31.8	0.100	0.0208
	30	30.0	29.7	0.166	0.0362
	40	29.1	28.8	0.195	0.0429
	60	27.2	26.9	0.258	0.0594
	90	24.4	24.1	0.347	0.0850
	120	22.6	22.3	0.405	0.1038
	$C_C = 1.46 \times 10^{-2}$ ( $\Rightarrow 0.159\%$ ), 120 °C, $C_{A0}/C_{M0} = 5.01$ , $C_{M0} = 0.968$				
(278/86) × 0.159	5	29.1	28.6	0.042	0.0092
= 0.514	10	28.7	28.2	0.055	0.0210
	15	27.1	26.6	0.107	0.0243
	20	26.2	25.7	0.136	0.0315
	30	23.8	23.3	0.216	0.0502
	40	22.7	22.2	0.250	0.0630
	60	20.5	20.0	0.324	0.0836
	90	17.6	17.1	0.415	0.1211
	120	15.4	14.9	0.486	0.1633
	$C_C = 2.49 \times 10^{-2}$ ( $\Rightarrow 0.272\%$ ), 120 °C, $C_{A0}/C_{M0} = 4$ , $C_{M0} = 1.13$				
(278/86) × 0.272	2	34.2	33.3	0.048	0.0099
= 0.879	5	33.4	32.5	0.076	0.0158
	10	31.3	30.4	0.144	0.0308
	15	29.3	28.4	0.209	0.0466
	20	27.3	26.4	0.272	0.0634
	30	25.4	24.5	0.333	0.0812
	40	22.8	21.9	0.417	0.1080
	60	19.4	18.5	0.528	0.1505
	90	16.1	15.2	0.634	0.1997
	120	13.6	12.7	0.716	0.2475
	$C_C = 4.59 \times 10^{-2}$ (0.500 %), 120 °C, $C_{A0}/C_{M0} = 4$ , $C_{M0} = 1.13$				
(278/86) × 0.500	2	32.9	31.3	0.115	0.0240
= 1.62	5	31.2	29.6	0.169	0.0366
	10	29.0	27.4	0.241	0.0549
	15	26.7	25.1	0.316	0.0756
	20	24.7	23.1	0.380	0.0955
	30	21.5	19.9	0.482	0.1316
	40	19.3	17.7	0.554	0.1611
	60	15.9	14.3	0.665	0.2165
	90	12.7	11.1	0.768	0.2826
	120	10.8	9.12	0.832	0.3354
	$C_C = 4.59 \times 10^{-2}$ ( $\Rightarrow 0.500\%$ ), 120 °C, $C_{A0}/C_{M0} = 6$ , $C_{M0} = 0.841$				
(278/86) × 0.500	2	24.8	23.2	0.099	0.0251
= 1.62	5	24.6	23.0	0.105	0.0267
	10	22.2	20.6	0.183	0.0496
	15	20.6	19.0	0.234	0.0663
	20	19.7	18.1	0.262	0.0762

Catalyst correction [%]	Time [min]	Free acidity [%]	Actual monoester [%]	Monoester converted [mole·l <sup>-1</sup> ]	$-\frac{1}{C_{M0}-C_{A0}} \ln \frac{C_{A0}(C_{M0}-C_B)}{C_{M0}(C_{M0}-C_B)}$ [l·mole <sup>-1</sup> ]
	30	17.6	16.0	0.331	0.1027
	40	15.9	14.3	0.384	0.1262
	60	13.1	11.5	0.472	0.1727
	90	10.2	8.6	0.567	0.2383
	120	8.3	6.7	0.626	0.2918
$C_C = 4.59 \times 10^{-2}$ (= 0.500 %), 120 °C, $C_{A0}/C_{M0} = 9$ , $C_{M0} = 0.604$					
(278/86) × 0.500	2	18.7	17.1	0.067	0.0216
= 1.62	5	18.1	16.5	0.086	0.0286
	10	16.6	15.0	0.131	0.0455
	15	15.5	13.9	0.167	0.0603
	20	14.5	12.9	0.197	0.0741
	30	13.0	11.4	0.247	0.0993
	40	11.8	10.2	0.283	0.1198
	60	9.6	8.0	0.357	0.1704
	90	7.8	6.2	0.411	0.2193
	120	6.3	4.7	0.458	0.2752
$C_C = 4.73 \times 10^{-2}$ (= 0.516 %), 120 °C, $C_{A0}/C_{M0} = 4$ , $C_{M0} = 1.13$					
(278/86) × 0.516	2	34.8	33.1	0.054	0.0108
= 1.69	10	29.8	28.1	0.216	0.0484
	15	26.8	25.1	0.313	0.0746
	20	24.8	23.1	0.379	0.0951
	40	19.1	17.4	0.564	0.1657
	60	15.5	13.8	0.681	0.2250
	90	12.0	10.3	0.794	0.3021
	120	9.9	8.2	0.861	0.3640
	180	7.8	6.1	0.928	0.4437
	240	6.3	4.6	0.979	0.5274
$C_C = 9.34 \times 10^{-2}$ (= 1.02 %), 120 °C, $C_{A0}/C_{M0} = 4$ , $C_{M0} = 1.13$					
(278/86) × 1.02	5	31.2	27.9	0.213	0.0477
= 3.297	10	26.7	23.4	0.358	0.0891
	15	23.0	19.7	0.481	0.1311
	20	20.1	16.8	0.576	0.1709
	30	17.0	13.7	0.679	0.2245
	40	14.3	11.0	0.688	0.2295
	60	10.8	7.6	0.882	0.3860
	90	7.7	4.4	0.983	0.5346
	120	6.9	3.6	1.010	0.5942
$C_C = 0.768 \times 10^{-2}$ (= 0.0867 %), 140 °C, $C_{A0}/C_{M0} = 11$ , $C_{M0} = 0.527$					
(278/86) × 0.0867	2	16.4	16.1	0.004	0.0014
= 0.280	5	16.0	15.7	0.019	0.0064
	10	15.5	15.2	0.035	0.0119
	15	14.6	14.3	0.063	0.0219
	20	14.2	13.9	0.076	0.0269
	30	12.9	12.6	0.118	0.0443
	40	12.2	11.9	0.142	0.0551
	60	10.6	10.3	0.194	0.0806
	90	9.0	8.7	0.244	0.1097
	120	6.9	6.6	0.313	0.1568

Catalyst correction	Time	Free acidity	Actual monoester	Monoester converted	$\frac{1}{C_{M0}-C_{A0}} \ln \frac{C_{A0}(C_{M0}-C_B)}{C_{M0}(C_{M0}-C_B)}$
(%)	(min)	(%)	(%)	(mole·l <sup>-1</sup> )	(l·mole <sup>-1</sup> )
$C_C = 1.46 \times 10^{-2}$ (= 0.159 %), 140 °C, $C_{A0}/C_{M0} = 5.01$ , $C_{M0} = 0.968$					
(278/86) × 0.159	2	29.7	29.2	0.023	0.0049
= 0.514	5	29.1	28.6	0.043	0.0094
	10	27.4	26.9	0.098	0.0212
	15	26.0	25.5	0.145	0.0343
	20	23.3	22.8	0.230	0.0572
	30	20.5	20.0	0.321	0.0861
	40	18.0	17.5	0.403	0.1162
	60	13.8	13.3	0.539	0.1791
	90	10.2	9.7	0.655	0.2533
	120	7.6	7.1	0.738	0.3279
$C_C = 0.768 \times 10^{-2}$ (= 0.0867 %), 155 °C, $C_{A0}/C_{M0} = 11$ , $C_{M0} = 0.527$					
(278/86) × 0.0867	2	16.2	15.9	0.012	0.0040
= 0.280	5	15.7	15.4	0.029	0.0099
	10	14.0	13.7	0.082	0.0294
	15	12.7	12.4	0.125	0.0471
	20	11.9	11.6	0.150	0.0585
	30	10.1	9.8	0.209	0.0891
	40	8.6	8.3	0.259	0.1198
	60	6.1	5.8	0.338	0.1837
	90	4.1	3.8	0.402	0.2601
	120	3.3	3.0	0.430	0.3607
$C_C = 1.46 \times 10^{-2}$ (= 0.159 %), 155 °C, $C_{A0}/C_{M0} = 5.01$ , $C_{M0} = 0.968$					
(278/86) × 0.159	2	29.3	28.8	0.038	0.0011
= 0.514	5	26.9	26.4	0.113	0.0259
	10	22.2	21.7	0.268	0.0687
	15	18.3	17.8	0.394	0.1126
	20	16.5	16.0	0.452	0.1364
	30	11.7	11.2	0.607	0.2191
	40	9.7	9.2	0.672	0.2668
	60	6.4	5.9	0.778	0.3731
	90	5.2	4.7	0.816	0.4292
	120	4.6	4.1	0.835	0.4626
$C_C = 0.768 \times 10^{-2}$ (= 0.0867 %), 170 °C, $C_{A0}/C_{M0} = 11$ , $C_{M0} = 0.527$					
(278/86) × 0.0867	5	16.0	15.7	0.019	0.0064
= 0.280	10	13.3	13.1	0.104	0.0384
	15	12.4	12.1	0.136	0.0518
	20	10.5	10.3	0.195	0.0812
	30	7.2	6.9	0.303	0.1524
	40	6.7	6.4	0.320	0.1665
	60	4.4	4.1	0.394	0.2479
	90	2.6	2.3	0.451	0.3527
	120	1.7	1.4	0.480	0.4658
$C_C = 1.46 \times 10^{-2}$ (= 0.159 %), 170 °C, $C_{A0}/C_{M0} = 5.01$ , $C_{M0} = 0.968$					
(278/86) × 0.159	2	29.6	29.1	0.028	0.0058
= 0.514	5	27.5	27.0	0.095	0.0215
	10	21.3	20.8	0.296	0.0778
	15	16.7	16.2	0.445	0.1337

Catalyst correction [%]	Time [min]	Free acidity [%]	Actual monoester [%]	Monoester converted [mole·l <sup>-1</sup> ]	$\frac{1}{C_{M0}-C_{A0}} \ln \frac{C_{A0}(C_{M0}-C_B)}{C_{M0}(C_{A0}-C_B)}$ [l·mole <sup>-1</sup> ]
	20	13.5	13.0	0.549	0.1846
	30	9.6	9.1	0.674	0.2685
	40	6.8	6.3	0.765	0.3573
	60	4.5	4.0	0.838	0.4675
	90	3.8	3.3	0.862	0.5197
	120	3.7	3.2	0.865	0.5253
$C_C = 0.768 \times 10^{-2}$ (= 0.0867 %) 180 °C, $C_{A0}/C_{M0} = 11$ , $C_{M0} = 0.527$					
(278/86) × 0.0867	2	15.5	15.2	0.036	0.0122
= 0.280	5	14.6	14.3	0.064	0.0226
	10	11.5	11.2	0.163	0.0647
	15	9.5	9.2	0.228	0.1002
	20	7.9	7.6	0.281	0.1350
	30	5.8	5.5	0.349	0.1940
	40	3.9	3.5	0.411	0.2742
	60	2.5	2.2	0.456	0.3640
	90	1.5	1.2	0.486	0.4696
	120	1.3	1.0	0.494	0.5096
$C_C = 1.46 \times 10^{-2}$ (= 0.159 %). 180 °C, $C_{A0}/C_{M0} = 5.01$ , $C_{M0} = 0.968$					
(278/86) × 0.159	2	28.9	28.4	0.051	0.0110
= 0.514	5	25.2	24.7	0.169	0.0403
	10	18.7	18.2	0.380	0.1701
	15	13.4	12.8	0.552	0.1859
	20	9.4	8.9	0.680	0.2734
	30	6.3	5.8	0.781	0.3786
	40	5.1	4.6	0.820	0.4361
	60	3.9	3.4	0.858	0.5102
	90	3.4	2.9	0.874	0.5484
	120	3.3	2.8	0.879	0.5640



但 R는  $\text{C}_4\text{H}_9\text{CH}(\text{C}_2\text{H}_5)\text{CH}_2$ -기를 표시한다.

Monoester의 카르보닐기가 쉽게 프로톤을 취하여 평형에 도달될 수 있기 때문에 (3)식은 다음의 평衡式이 된다.

$$K = \frac{C_{MH^+}}{C_{H^+}(C_{M0}-C_B-C_{MH^+})} \quad (5)$$

따라서 (4)식이 이反應의 속도를 결정 한다고 볼 수 있으므로 反應速度式은 다음과 같이 된다.

$$\frac{dC_B}{dt} = k' C_{MH^+} (C_{A0} - C_B) \quad (6)$$

(5)식을 (6)에 대입하면

$$\frac{dC_B}{dt} = K k' C_{H^+} (C_{M0} - C_B) (C_{A0} - C_B) / (1 + K C_{H^+}) \quad (7)$$

$K C_{H^+} \ll 1$  이고  $C_{H^+} \approx 2 C_C$  라면

$$\begin{aligned} \frac{dC_B}{dt} &= \frac{1}{2} K k' C_C (C_{M0} - C_B) (C_{A0} - C_B) \\ &= k'' C_C (C_{M0} - C_B) (C_{A0} - C_B) \end{aligned} \quad (8)$$

따라서

$$k'' C_C t = k t = \frac{1}{C_{M0} - C_{A0}} \ln \frac{C_{A0}}{C_{M0}} \cdot \frac{(C_{M0} - C_B)}{(C_{A0} - C_B)} \quad (9)$$

한편 實驗 데이터로부터 黃酸의 濃도가 0.159 %이고 monoester와 2-ethyl hexanol의 물비가 1:5인 경우에 (9)식을 Fig. 1에 플롯하였다.

Fig. 1에서 보는바와 같이 좋은 直線이 얻어지므로 (6)식이 잘 適用됨을 알 수 있다. 따라서 앞에서 假定한 反應機構中 monoester와 프로톤의 反應은 대단히 빠른 平衡이며 反應速度를 支配하는것은 (4)식이라고 할 수 있다.

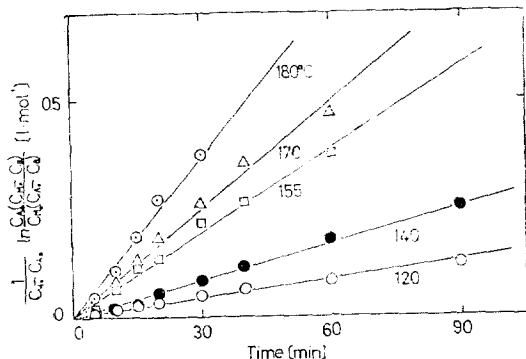


Fig. 1. Plot of equation (9) for the case of  $C_{A0}/C_{M0} = 5$  and  $C_C = 1.46 \times 10^{-2}$ .

즉, 一般의인 에스테르화反應에서처럼 黃酸에서 생긴 푸로톤이 monoester의 칼복실기에 受容되며 이것이 알코올과 錯物을 만드는 것이 速度를 支配한다고 볼 수 있다. 따라서 (4)式的 反應은 다음과 같이 進行되리라 생각된다.

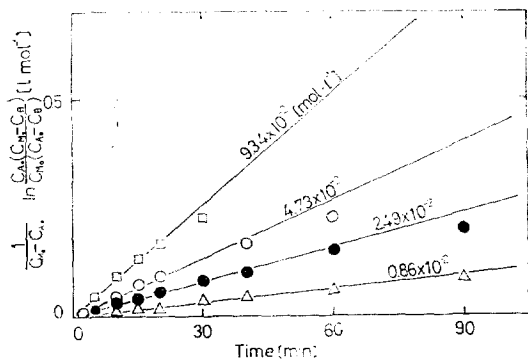
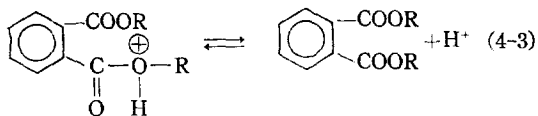
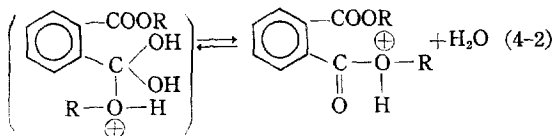
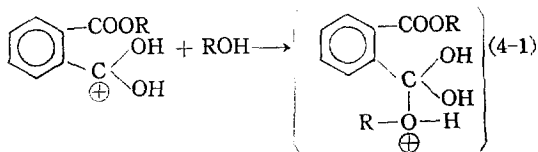


Fig. 2. Plot of equation (9) with variation of catalyst concentration for the case of  $120^\circ\text{C}$  and  $C_{A0}/C_{M0} = 4$ .

反應溫度가  $120^\circ\text{C}$ 이고 黃酸觸媒의 濃度를 달리했을 때의 結果를 Fig. 2에 表示하였다.

여기서 보던 觸媒의 濃度가 增加함에 따라 反應速度는 상승하며 모든 점이 거의 直線上에 있는 것으로 보아 diester의 生成反應에 있어 反應次數는 monoester에 대해 1次이며 2-ethyl hexanol에 대해 1次로서 全次數가 2次이다. 또한 monoester와 2-ethyl hexanol의 物 比를 變化 시키고 黃酸觸媒濃度는 0.5%로 一定히하여 反應溫度  $120^\circ\text{C}$ 에서 反應시킨 結果를 Fig. 3에 표시하였다.

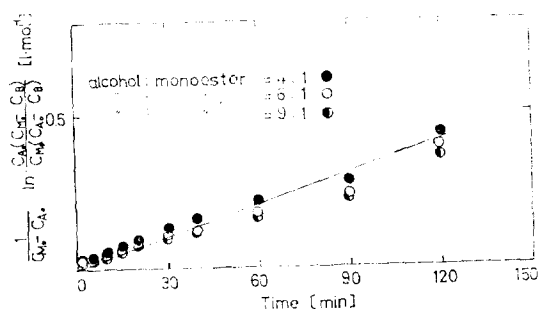


Fig. 3. Plot of equation (9) with variation of  $C_{A0}/C_{M0}$  for the case of  $120^\circ\text{C}$  and  $C_C = 4.59 \times 10^{-2}$ .

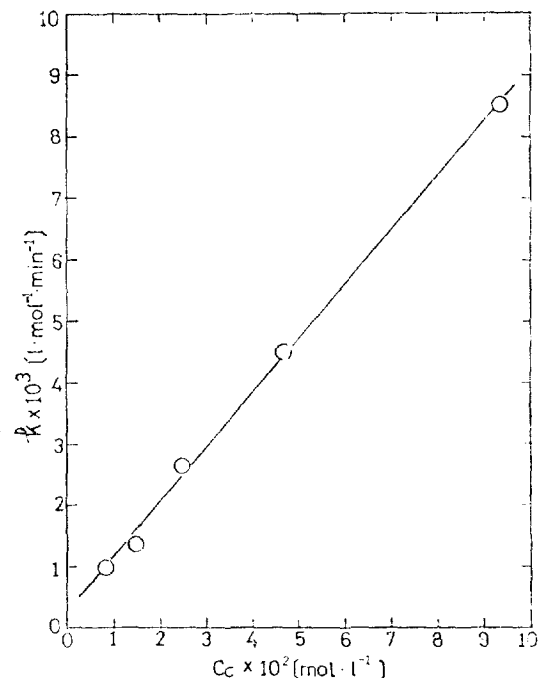


Fig. 4. Catalyst concentration dependence of rate constant.

여기서 보면 monoester와 2-ethyl hexanol의 몰비의 변화에는 관계 없이 한 직선에 있다는 것은 이反應機構의 假定의 타당성을 보여 주고 있다.

Monoester對 2-ethyl hexanol의 몰비가 1:4 일 때의 黃酸觸媒의 濃度變化에 대한  $k$ 값을 Fig. 4에 플롯하였는데 좋은 직선이 얻어진다.

이 結果로부터 Arrhenius 플롯 한것이 Fig. 5이다. 여기서 求한 活性化에너지값이 13 kcal/mole이며 이 값은 無觸媒에서의 活性化에너지값 18 kcal/mole에

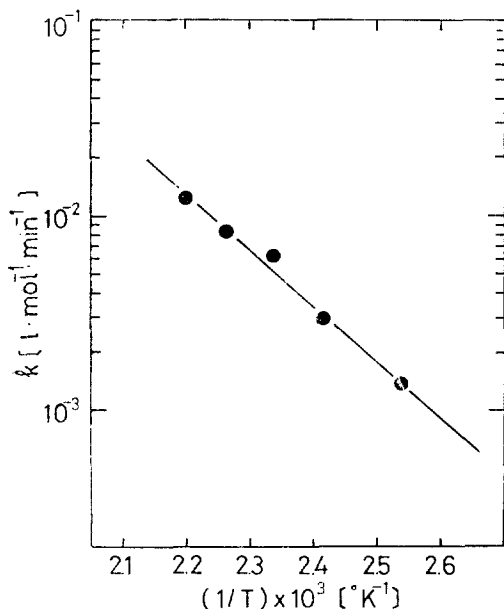


Fig. 5. Temperature dependence of rate constant.

비하면 5 kcal/mole 적은 것이다.

速度定數와 觸媒濃度 및 反應溫度的 關係를 알기 위하여 Fig. 6에  $k/e^{-13000/RT}$ 를 縱軸에 酸觸媒濃도를 橫軸에 플롯하였으며 좋은 직선이 됨으로 다음식이 成立한다.

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

따라서 황산은 定量的으로 촉매 反應에 關여 함을 알 수 있다.

## 結 論

黃酸를 觸媒로 使用하여 monoester로부터 2-ethyl hexanol에 의하여 diester이 생길때 速度式은 monoester와 알코올에 대하여 모두 1次로 表示된다.

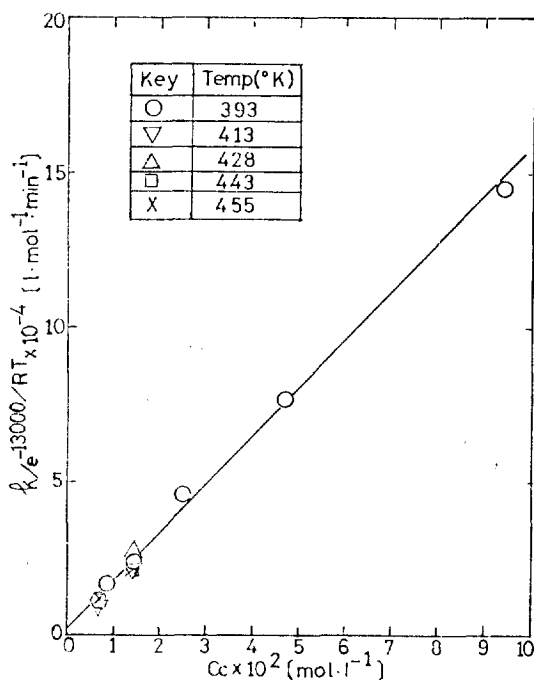


Fig. 6.  $k/e^{-13,000/RT}$  vs. catalyst concentration.

이 式으로부터 얻어진 活性化에너지 값은 13 kcal/mole로서 無觸媒의 18 kcal/mole 보다 5 kcal/mole 적었다.

이 反應의 速度定數는 溫度가 一定할 때 觸媒濃도에 比例하며 본 연구의 使用 觸媒濃度 範圍에서는 黃酸으로부터 주어지는 프로톤 이 反應에 定量的으로 關與한다.

## Nomenclature

- A: Weight of sample [g]
- $C_{A0}$ : Initial concentration of 2-ethyl hexanol ( $\text{mol} \cdot \text{l}^{-1}$ )
- $C_B$ : Concentration of bis(2-ethylhexyl) phthalate ( $\text{mol} \cdot \text{l}^{-1}$ )
- $C_C$ : Concentration of sulfuric acid catalyst ( $\text{mol} \cdot \text{l}^{-1}$ )
- $C_{H^+}$ : Concentration of hydrogen ion ( $\text{mol} \cdot \text{l}^{-1}$ )
- $C_{M0}$ : Initial concentration of mono(2-ethylhexyl) phthalate ( $\text{mol} \cdot \text{l}^{-1}$ )
- $C_{MH^+}$ : Concentration of protonated mono(2-ethylhexyl) phthalate ( $\text{mol} \cdot \text{l}^{-1}$ )
- $E_q$ : Apparent milliequivalent to correct [m.eq]
- $k$ :  $k = 2C_C k' K$  ( $\text{l} \cdot \text{mol}^{-1} \text{min}^{-1}$ )
- $k'$ : Rate constant in equation (6) ( $\text{l} \cdot \text{mol}^{-1} \text{min}^{-1}$ )

- $k''$ :  $k''=2k'K$  [ $l^2 \cdot \text{mol}^{-2} \cdot \text{min}^{-1}$ ]  
 $K$ : Equilibrium constant for equation (3) [ $l \cdot \text{mol}^{-1}$ ]  
 $L$ : Volume of consumption of 1 N NaOH aq. solution for the titration [mL]  
 $M_1$ : Moles of original sulfuric acid in sample  
 $M_1 = AP_2/9.808$  [m·mol]  
 $M_2$ : Moles of remaining sulfuric acid in sample  
 $M_2 = N_1 - M_1$  [m·mol]
- $N_1$ : Titration equivalent weight of 1 N NaOH aq. solution used  $N_1 = N_2 L$  [m·mol]  
 $N_2$ : Normality of 1 N NaOH aq. solution used for the titration [N]  
 $P_1$ : Percentage of sulfuric acid combined  
 $P_1 = (M_1 - M_2) 100/M_1$  [%]  
 $P_2$ : Percentage of total sulfuric acid in sample [%]

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