

# Synthesis of 5, 5'-Oxydivaleric Acid from 1, 1, 1, 5-Tetrachloropentane

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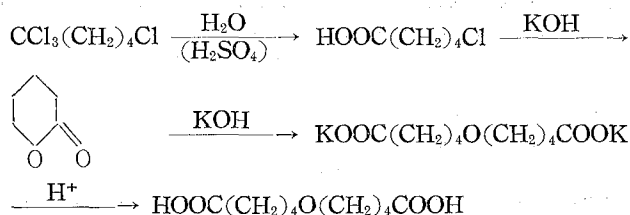
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The synthesis of 5, 5'-oxydivaleric acid from 1, 1, 1, 5-tetrachloropentane via  $\delta$ -valerolactone was attempted and the formation of the acid from the lactone with alkali was examined in detail. It has been found that the rate of the formation is affected with the molar ratio of alkali to the lactone to a great extent. At a temperature of 270°, the rate was maximum at the ratio of 0.7 : 1 and it became very slow at the ratio of 1 : 1.

## INTRODUCTION

5, 5'-Oxydivaleric acid which would be a raw material for making polyamides or plasticizers, was synthesized from ethylene telomer by the following routes.



Since the formation of 4, 4'-oxydibutyric acid from  $\gamma$ -butyrolactone with alkali was found by Reppe,<sup>1)</sup> several investigations<sup>2-5)</sup> including dimerization of  $\gamma$ - or  $\delta$ -lactone to the corresponding  $w, w'$ -oxydicarboxylic acid have been reported. No details, however, were known. In the present paper we report the results on the formation of 5, 5'-oxydivaleric acid from  $\delta$ -valerolactone with potassium hydroxide by using gas chromatography to clarify the optimum conditions and propose the mechanism of the reaction.

## EXPERIMENTAL

**1, 1, 1, 5-Tetrachloropentane.** A shaking stainless steel autoclave of 1.2 l. capacity was filled with 576 g. of carbon tetrachloride, 100 g. of water and 10 g. of azobisisobutyronitril. The autoclave was evacuated, pressed to 39 kg./cm<sup>2</sup>. with ethylene at 18°. When the temperature of reaction mixture had been raised to 80°, the maximum pressure of 72 kg./cm<sup>2</sup>. was observed. After heating at 90° for five hours, the final pressure showed 35 kg./cm<sup>2</sup>. The water layer of the

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product was separated from the organic layer, and the latter was washed with water. It was then dried over anhydrous calcium chloride. Carbon tetrachloride was removed from the product in the stripping still and careful fractional vacuum distillation of the residue gave 250 g. of 1, 1, 1, 5-tetrachloropentane, b.p.  $72^{\circ}/7$  mm.,  $n_D^{20}$  1.4482 (lit.<sup>6)</sup> b. p.  $112^{\circ}/24$  mm.,  $n_D^{20}$  1.4482).

Found: C, 28.44; H, 4.15, Calcd. for  $C_5H_8Cl_4$ : C, 28.60; H, 3.84%

**$\delta$ -Chlorovaleric Acid.** According to Takagi's procedure,<sup>7)</sup> a 1 l. three necked flask, containing 210 g. of 1, 1, 1, 5-tetrachloropentane, 525 g. of 98% sulfuric acid, and 50 g. of water, was fitted with a stirrer, a thermometer, and condenser with a gas exhaust tube. The temperature was then slowly raised with stirring. At about  $80^{\circ}$ , the reaction occurred with a vigorous evolution of hydrogen chloride. After the temperature was kept at  $90^{\circ}$  for two hours, the reaction mixture was cooled, poured onto 800 g. of cracked ice, and extracted several times with carbon tetrachloride. The extract was washed with water. After drying with anhydrous calcium chloride, carbon tetrachloride was removed, and the residue was distilled to give 116 g. of  $\delta$ -chlorovaleric acid (84%), b.p.  $101-102^{\circ}/3$  mm.,  $n_D^{20}$  1.4541 (lit.<sup>7)</sup> b.p.  $124^{\circ}/9$  mm.,  $n_D^{25}$  1.4529).

Found: C, 43.97; H, 6.64, Calcd. for  $C_5H_9ClO_2$ : C, 43.85; H, 6.70%.

**$\delta$ -Valerolactone.** According to Jouce's procedure,<sup>8)</sup> a solution of  $\delta$ -chlorovaleric acid in 100 ml. of methanol was placed in a 1 l. three necked flask equipped with a stirrer, thermometer and dropping funnel. The solution was cooled to  $5^{\circ}$  and a solution of potassium hydroxide in methanol (300 ml., 5N) was added, maintaining the temperature below  $10^{\circ}$  with stirring. The resulting solution was made neutral to phenolphthalein by further addition of potassium hydroxide solution and was refluxed for two hours. It was then cooled and filtered. The methanol was removed from the filtrate in a stripping still and the residue was distilled through a precision column to give 121 g. of  $\delta$ -valerolactone (80%), b.p.  $69-72^{\circ}/3$  mm.,  $n_D^{25}$  = 1.4545 (lit.  $92^{\circ}/8$  mm.,  $n_D^{25}$  = 1.4550).

Found: C, 59.98; H, 8.37, Calcd. for  $C_5H_8O_2$ : C, 59.98; H, 8.05%.

$\delta$ -Valerolactone gave a hydrazide melting at  $105-6^{\circ}$  (lit.<sup>9)</sup>  $105-6^{\circ}$ ).

**Examination of Reaction Conditions for Formation of 5, 5'-Oxydivaleric Acid.** In a 30 ml. flask equipped with an air condenser and a thermometer, 15 g. of  $\delta$ -valerolactone and necessary amount of potassium hydroxide\* were heated to  $160-180^{\circ}$ . Then exothermic reaction occurred. After the reaction mixture became homogeneous, it was cooled and was solidified. The resulting product was divided to ten portions. Each of them was weighed exactly and was placed in a 5 ml long necked flask. The flasks were placed in an oil bath which had been heated to the settled temperature. Nitrogen gas was supplied into the mouths of the flasks to exclude air. At every accurately determined time interval, the product was cooled, dissolved in 20 ml. of methanol and then acidified with 10 ml. of methanolic sulfuric acid (3N). About 1 g. of sebacic acid (as the internal

\* The potassium hydroxide was commercial material of the highest available purity and had a purity of 86% by acid titration.

standard substance) weighed exactly was added into the methanol solution and the mixture was refluxed for four hours. Then 10 ml. of the resulting mixture was made neutral by adding 3 g. of sodium bicarbonate with stirring for ten minutes. The methanol solution thus obtained was analysed gaschromatographically.

**Gaschromatographic Analysis.** Hitachi model F6D gaschromatograph attached with Golay-type capillary column and hydrogen flame ionization detector was used. Separation was made in a 45 m column coated with butanediol succinate polyester. The column was operated at 150° with a carrier nitrogen gas pressure of 1.5 kg./cm<sup>2</sup>. Characteristic retention times of  $\delta$ -valerolactone and the esters follow:  $\delta$ -valerolactone, 6 min., dimethyl sebacate, 17 min., and dimethyl 5, 5'-oxydivalate, 30 min.

**5, 5'-Oxydivaleric Acid.** In a 100 ml. flask fitted with an air condenser, was placed 30 g. of  $\delta$ -valerolactone and 17.5 g. of potassium hydroxide. Nitrogen gas was supplied into the top of the condenser to exclude air. When the mixture was heated to about 160°, vigorous exothermic reaction occurred suddenly and potassium hydroxide dissolved. Then the flask was heated at 270° for five hours in an oil bath. The reaction mixture was cooled and acidified with 50 ml. of 6N sulfuric acid. The water was removed and organic residue was extracted with ether to separate inorganic salt. Vacuum distillation of the ether extract under nitrogen atmosphere gave 8 g. of unreacted  $\delta$ -valerolactone and 20.7 g. of residue, crude 5, 5'-oxydivaleric acid. Recrystallization from benzene gave 16.9 g of 5, 5'-oxydivaleric acid (yield 70%): m.p. 89° (lit.<sup>10</sup> 89°).

Found: C, 55.29; H, 8.59. Calcd. for C<sub>10</sub>H<sub>18</sub>O<sub>5</sub>: C, 55.03; H, 8.31%.

Hydrazide was obtained by heating 4 g. of dimethyl 5, 5'-oxydivalate with 4 ml. of 85% aq. hydrazine hydrate for four hours in ethanol. m.p. 151°.

Found: C, 48.56; H, 8.81; N, 22.73. Calcd. for C<sub>10</sub>H<sub>22</sub>N<sub>4</sub>O<sub>3</sub>:  
C, 48.76; H, 9.00; N, 22.75%.

## RESULT AND DISCUSSION

Table 1. Effect of Reaction Temperature. (1)

Temp.: 250°

KOH:  $\delta$ -valerolactone=0.8: 1 (mole)

| Reaction<br>time (min) | Lactone (g)<br>used | Yield* |      | Lactone (g)<br>recovered | Conversion<br>(%) |
|------------------------|---------------------|--------|------|--------------------------|-------------------|
|                        |                     | (g)    | (%)  |                          |                   |
| 60                     | 0.906               | 0.230  | 23.5 | 0.724                    | 20.1              |
| 120                    | 0.942               | 0.378  | 36.5 | 0.571                    | 39.4              |
| 180                    | 0.854               | 0.449  | 48.2 | 0.396                    | 53.6              |
| 240                    | 0.806               | 0.491  | 55.8 | 0.298                    | 63.1              |
| 300                    | 0.948               | 0.657  | 63.6 | 0.251                    | 73.5              |
| 360                    | 0.908               | 0.638  | 64.4 | 0.209                    | 77.0              |
| 420                    | 0.979               | 0.712  | 66.7 | 0.193                    | 80.2              |
| 480                    | 0.997               | 0.738  | 68.0 | 0.143                    | 85.6              |
| 540                    | 0.805               | 0.618  | 70.4 | 0.110                    | 86.7              |

\* The yield was based upon the amount of  $\delta$ -valerolactone used.

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Table 2. Effect of Reaction Temperature. (2)

Temp. : 270°

KOH :  $\delta$ -valerolactone=0.8 : 1 (mole)

| Reaction time (min) | Lactone (g) used | Yield |      | Lactone (g) recovered | Conversion (%) |
|---------------------|------------------|-------|------|-----------------------|----------------|
|                     |                  | (g)   | (%)  |                       |                |
| 10                  | 0.958            | 0.099 | 9.5  | 0.868                 | 9.5            |
| 20                  | 0.965            | 0.172 | 16.4 | 0.782                 | 19.0           |
| 40                  | 0.873            | 0.303 | 31.6 | 0.559                 | 36.0           |
| 90                  | 0.912            | 0.491 | 49.4 | 0.336                 | 59.8           |
| 120                 | 0.954            | 0.583 | 56.7 | 0.294                 | 69.2           |
| 180                 | 0.841            | 0.582 | 63.5 | 0.144                 | 82.9           |
| 240                 | 0.852            | 0.620 | 67.6 | 0.124                 | 85.5           |
| 300                 | 0.825            | 0.612 | 68.0 | 0.080                 | 90.8           |
| 360                 | 0.949            | 0.707 | 68.4 | 0.072                 | 92.2           |
| 420                 | 0.892            | 0.667 | 68.5 | 0.059                 | 93.4           |

Table 3. Effect of Reaction Temperature. (3)

Temp. : 290°

KOH :  $\delta$ -valerolactone=0.8 : 1 (mole)

| Reaction time (min) | Lactone (g) used | Yield |      | Lactone (g) recovered | Conversion (%) |
|---------------------|------------------|-------|------|-----------------------|----------------|
|                     |                  | (g)   | (%)  |                       |                |
| 10                  | 0.903            | 0.219 | 22.2 | 0.654                 | 27.8           |
| 20                  | 0.903            | 0.384 | 39.1 | 0.474                 | 47.5           |
| 40                  | 0.683            | 0.387 | 52.0 | 0.218                 | 68.1           |
| 60                  | 0.781            | 0.505 | 59.4 | 0.136                 | 82.5           |
| 120                 | 0.986            | 0.650 | 60.6 | 0.056                 | 94.2           |
| 240                 | 0.951            | 0.645 | 62.8 | 0.018                 | 98.1           |

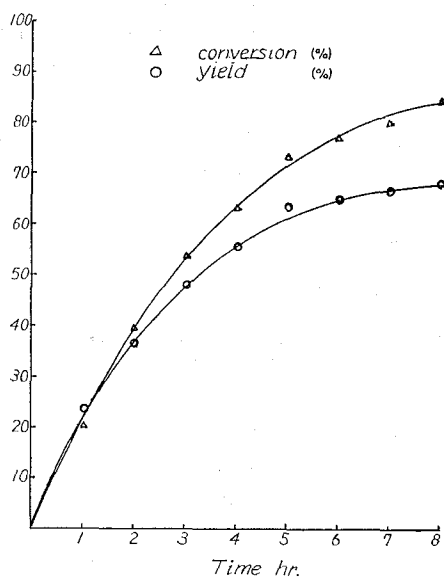


Fig. 1. Effect of Temperature. (1)  
Temperature : 250°  
Molar Ratio=0.8 : 1

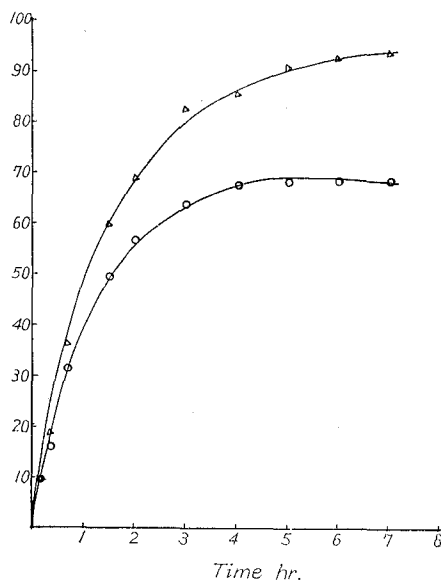


Fig. 2. Effect of Temperature (2)  
Temperature : 270°  
Molar Ratio=0.8 : 1

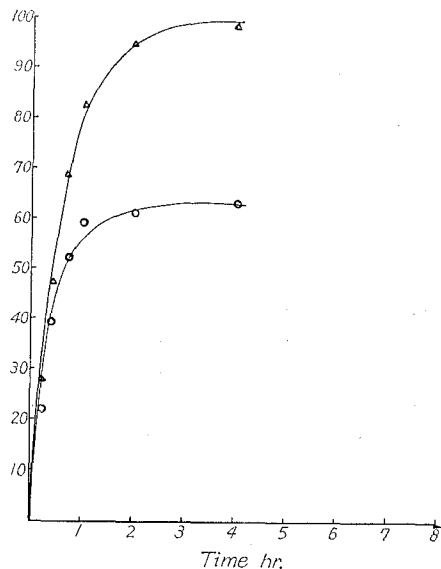


Fig. 3. Effect of Temperature. (3)  
 Temperature : 290°  
 Molar Ratio=0.8 : 1

The synthesis of 5,5'-oxydivaleric acid from  $\delta$ -valerolactone was studied according to the procedure described in the experimental part and obtained the following results.

**Effect of the Reaction Temperature.** The results obtained in the range of 250~290° with a molar ratio of alkali to the lactone of 0.8 : 1 are shown in Tables 1~3 and Figures 1~3. The reaction rate increased with elevation of the reaction temperature. The ultimate yield was hardly affected with temperature in the range of 250~270°. At above 290°, however, it decreased probably owing to undesirable decomposition.

**Effect of the Molar Ratio of Potassium Hydroxide to  $\delta$ -Valerolactone.** In the previous reports,<sup>1-5)</sup> potassium hydroxide and lactones were used in a ratio of

Table 4. Effect of Molar Ratio. (1)  
 Temp. : 270°  
 KOH :  $\delta$ -valerolactone=0.6 : 1 (mole)

| Reaction<br>time (min) | Lactone (g)<br>used | Yield |      | Lactone (g)<br>recovered | Conversion<br>(%) |
|------------------------|---------------------|-------|------|--------------------------|-------------------|
|                        |                     | (g)   | (%)  |                          |                   |
| 10                     | 0.880               | 0.050 | 5.3  | 0.819                    | 6.9               |
| 20                     | 1.000               | 0.117 | 10.8 | 0.847                    | 15.3              |
| 40                     | 0.905               | 0.281 | 28.6 | 0.553                    | 38.6              |
| 60                     | 0.924               | 0.383 | 38.0 | 0.463                    | 49.8              |
| 90                     | 0.936               | 0.456 | 44.7 | 0.356                    | 62.0              |
| 120                    | 0.920               | 0.467 | 47.0 | 0.275                    | 70.3              |
| 180                    | 1.042               | 0.545 | 48.1 | 0.232                    | 77.8              |
| 240                    | 0.105               | 0.577 | 48.0 | 0.163                    | 86.0              |

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Table 5. Effect of Molar Ratio. (2)

Temp. : 270°

KOH :  $\delta$ -valerolactone=0.7 : 1 (mole)

| Reaction<br>time (min) | Lactone (g)<br>used | Yield |      | Lactone (g)<br>recovered | Conversion<br>(%) |
|------------------------|---------------------|-------|------|--------------------------|-------------------|
|                        |                     | (g)   | (%)  |                          |                   |
| 10                     | 0.960               | 0.124 | 11.9 | 0.814                    | 9.5               |
| 20                     | 0.968               | 0.229 | 21.7 | 0.722                    | 19.0              |
| 40                     | 0.912               | 0.349 | 35.1 | 0.534                    | 36.0              |
| 60                     | 0.887               | 0.423 | 43.8 | 0.393                    | 59.8              |
| 90                     | 0.916               | 0.517 | 51.7 | 0.308                    | 69.2              |
| 120                    | 0.952               | 0.569 | 54.8 | 0.276                    | 82.9              |
| 180                    | 0.880               | 0.555 | 58.0 | 0.149                    | 85.5              |
| 240                    | 0.868               | 0.560 | 59.2 | 0.128                    | 90.8              |
| 300                    | 0.814               | 0.515 | 58.0 | 0.084                    | 93.4              |

Table 6. Effect of Molar Ratio. (3)

Temp. : 270°

KOH :  $\delta$ -valerolactone=0.9 : 1 (mole)

| Reaction<br>time (min) | Lactone (g)<br>used | Yield |      | Lactone (g)<br>recovered | Conversion<br>(%) |
|------------------------|---------------------|-------|------|--------------------------|-------------------|
|                        |                     | (g)   | (%)  |                          |                   |
| 10                     | 0.849               | 0.059 | 6.4  | 0.760                    | 9.6               |
| 20                     | 0.919               | 0.114 | 11.4 | 0.776                    | 15.4              |
| 40                     | 0.899               | 0.213 | 21.8 | 0.654                    | 27.2              |
| 60                     | 0.890               | 0.324 | 33.4 | 0.541                    | 39.2              |
| 90                     | 0.880               | 0.394 | 41.2 | 0.445                    | 49.4              |
| 120                    | 0.836               | 0.455 | 49.9 | 0.348                    | 58.4              |
| 180                    | 0.954               | 0.575 | 56.0 | 0.309                    | 67.6              |
| 240                    | 0.954               | 0.677 | 65.1 | 0.201                    | 78.7              |
| 300                    | 0.866               | 0.640 | 68.0 | 0.121                    | 86.1              |
| 360                    | 0.695               | 0.540 | 71.3 | 0.080                    | 88.4              |
| 480                    | 0.841               | 0.663 | 72.4 | 0.060                    | 92.9              |

Table 7. Effect of Molar Ratio. (4)

Temp. : 270°

KOH :  $\delta$ -valerolactone=0.95 : 1 (mole)

| Reaction<br>time (min) | Lactone (g)<br>used | Yield |      | Lactone (g)<br>recovered | Conversion<br>(%) |
|------------------------|---------------------|-------|------|--------------------------|-------------------|
|                        |                     | (g)   | (%)  |                          |                   |
| 10                     | 1.118               | 0.028 | 2.3  | 1.095                    | 2.1               |
| 20                     | 0.996               | 0.064 | 5.9  | 0.928                    | 6.8               |
| 60                     | 0.939               | 0.160 | 15.7 | 0.769                    | 18.2              |
| 120                    | 0.894               | 0.245 | 25.3 | 0.616                    | 31.1              |
| 180                    | 0.885               | 0.311 | 32.8 | 0.546                    | 38.2              |
| 240                    | 0.897               | 0.358 | 36.5 | 0.484                    | 46.1              |
| 300                    | 0.868               | 0.405 | 42.0 | 0.401                    | 53.8              |
| 420                    | 1.003               | 0.449 | 41.1 | 0.401                    | 60.0              |

Table 8. Effect of Molar Ratio. (5)

Temp. : 270°

KOH :  $\delta$ -valerolactone=1.0 : 1 (mole)

| Reaction time (min) | Lactone (g) used | Yield |     | Lactone (g) recovered | Conversion (%) |
|---------------------|------------------|-------|-----|-----------------------|----------------|
|                     |                  | (g)   | (%) |                       |                |
| 60                  | 0.923            | 0.015 | 1.4 | 0.672                 | 27.2           |
| 120                 | 0.923            | 0.018 | 1.8 | 0.547                 | 40.5           |
| 180                 | 0.931            | 0.021 | 2.1 | 0.437                 | 53.0           |
| 240                 | 0.911            | 0.024 | 2.4 | 0.380                 | 58.2           |
| 390                 | 0.936            | 0.034 | 3.4 | 0.235                 | 75.1           |
| 480                 | 0.908            | 0.045 | 4.3 | 0.192                 | 80.3           |

1:1. The results obtained at 270° with a ratio of from 0.6:1 to 1:1 are shown in Table 4~8 and Figures 4~8. It has been found that the ratio affects both reaction rate and yield of 5,5'-oxydivaleric acid. The initial rate was maximum at a ratio of 0.7:1. The ultimate yield was maximum at a ratio of 0.9:1. It is interesting that at a ratio of 1:1, the formation of the acid was hardly observed even at conversion of 70% as shown in Table 8 and Figure 8. In this case it seems to be likely that an unknown side reaction occurs instead of the formation of the acid.

**Reaction mechanism.** In order to interpret the above results, the following mechanism is proposed.

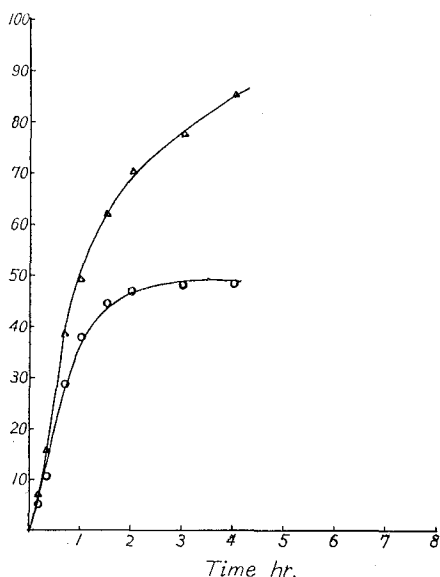
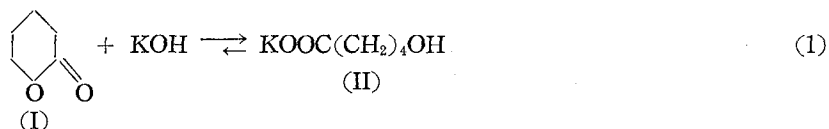


Fig. 4. Effect of Molar Ratio. (1)  
Temperature : 270°  
Molar Ratio=0.6 : 1

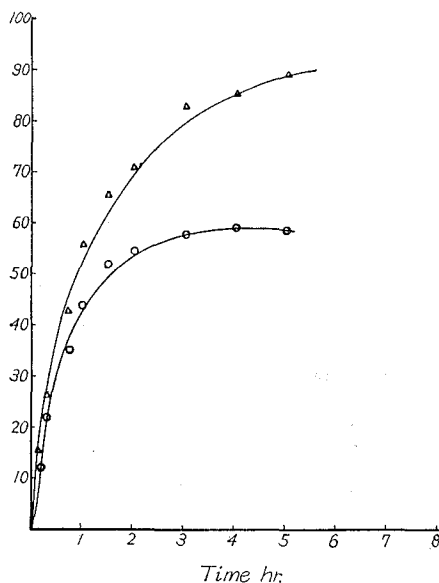


Fig. 5. Effect of Molar Ratio. (2)  
Temperature : 270°  
Molar Ratio=0.7 : 1

# Synthesis of 5, 5'-Oxydivaleric Acid

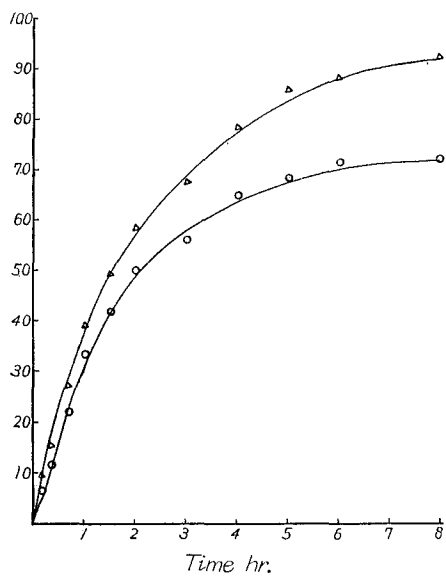


Fig. 6. Effect of Molar Ratio. (3)  
Temperature : 270°  
Molar Ratio ≈ 0.9 : 1

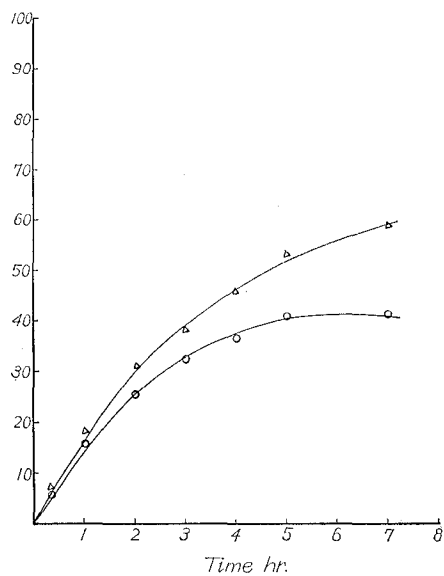


Fig. 7. Effect of Molar Ratio. (4)  
Temperature : 270°  
Molar Ratio = 0.95 : 1

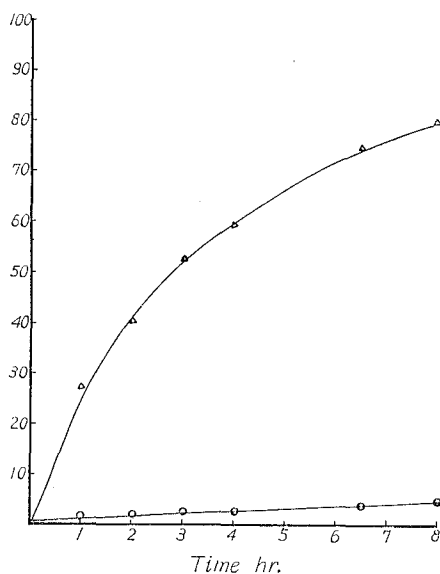
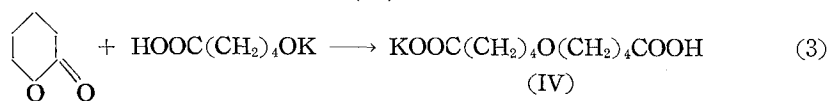
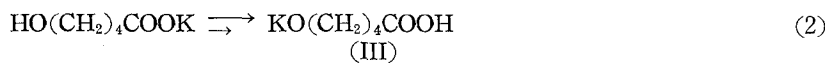
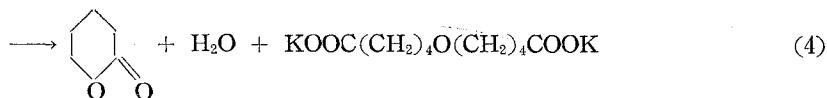


Fig. 8. Effect of Molar Ratio. (5)  
Temperature : 270°  
Molar Ratio = 1 : 1







Step 1 occurs with evolution of heat when  $\delta$ -valerolactone (I) and potassium hydroxide are heated at 150~160°. The equilibrium is thought to be almost in favor of the right side under the reaction conditions. In step 2, a very small equilibrium concentration of alcoxide of  $\delta$ -hydroxyvaleric acid (III) is rapidly formed from potassium  $\delta$ -hydroxyvalerate (II).

In step 3, (III) reacts with (I) slowly to give monopotassium 5',5'-oxydivalerate (IV). In step 4, (IV) reacts with (II) rapidly to give dipotassium, 5,5'-oxydivalerate (V) and regenerate (I). Since the rate of formation of (V) is thought to be equal to that of step 3, the rate is given by following equation.

$$\frac{d[\text{C}_{10}\text{H}_{16}\text{O}_5\text{K}_2]}{dt} = k \left[ \text{C}_6\text{H}_{10}\text{O}_5 \right] [\text{KO}(\text{CH}_2)_4\text{COOH}]$$

The amount of the lactone which exists during the reaction is constant and it is nearly equal to the remainder obtained by subtracting the amount of potassium hydroxide used from the amount of the lactone used. The fact that at the ratio of 1 : 1 the rate of formation of the dibasic acid is very slow can be explained as being due to small concentration of the lactone. Since the ultimate yield depends upon the initial amount of (II) which is nearly equal to the amount of potassium hydroxide used, it is reasonable that at a ratio of 0.9 : 1, the yield was maximum in spite of relatively slow reaction rate. Due to difficulty of calculating the concentration of the alcoxide it is not determined accurately that what ratio gives the maximum reaction rate. However the result that at a ratio of 0.7 : 1 the initial rate was maximum seems to be in harmony with the above mechanism.

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