The Synthesis of Lactones from ω-Chlorocarboxylic Acids

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Various intermediates for polymers have been prepared by Russian authors¹⁾ from ω-chlorocarboxylic acids, which are the basic derivatives from the tetrachloroalkanes obtained by the telomerization of ethylene with carbon tetrachloride. However, the hydrolysis of these ω-chlorocarboxylic acid has been little studied.

In the present work, the author will report on the kinetics of the hydrolysis of δ-chlorovaleric and ω-chloroheptanoic acids in an aqueous solution. Joyce et al.²⁾ derived δ-valerolactone from δ-chlorovaleric acid by heating it with sodium hydroxide in methanol. δ-Chlorovaleric acid is easily hydrolyzed in an aqueous alkaline solution to δ-hydroxyvaleric acid, which is then immediately converted to δ-valerolactone by neutralizing the solution. When an aqueous solution of sodium δ-chlorovalerate is heated, the oily layer of δ-valerolactone appears. On the other hand, the hydrolysis product from sodium ω-chloroheptanoate in an aqueous solution remains ω-hydroxyheptanoic acid. Its polyester is produced by removing water from the solution.

The dimeric lactone of ω-hydroxyheptanoic acid was obtained by the thermal decomposition of the polyester according to the method of Spangel and Carothers.³⁾ The monomeric

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1) R. Kh. Freidlina and Sh. A. Karapetyan, "Telomerization and New Synthetic Materials," Pergamon Press (1961).

2) R. M. Joyce, W. E. Hanford and J. Harmon, *J. Am. Chem. Soc.*, **70**, 2529 (1948).

3) E. W. Spangel and W. H. Carothers, ibid., **57**, 929 (1935).

TABLE I. THE THERMAL DECOMPOSITION OF THE POLYESTER-NaCl MIXTURE
$Cl(CH_2)_6COOH$, 82.5 g. Catalyst, 1.0 g.

Catalyst	Temp. (bath) °C	Distillate g.	Frac. I g.	Frac. II g.	Residue g.	Crystals g.
——	310～330	49.5	14.0	28.5	6.5	12.5
$MgCl_2\cdot 6aq.$	300～310	55.0	19.5	28.0	7.0	23.5
$SnCl_2\cdot 2aq.$	310～320	53.0	18.0	27.5	7.0	22.0
$FeCl_2\cdot 4aq.$	310～320	53.5	18.5	27.5	7.5	23.0
$CoCl_2\cdot 6aq.$	320～330	50.0	17.5	25.0	7.0	15.5
$MnCl_2\cdot 4aq.$	300～310	51.0	19.5	26.0	3.0	19.0
Mg powder	290～300	40.0	19.0	16.5	3.5	9.0
MgO	300～310	44.0	25.0	11.0	6.5	7.0
$MgCO_3$	300～310	45.5	24.0	14.0	4.0	7.5
$PbCl_2$	310～320	36.0	16.0	16.5	3.0	12.0
$ZnCl_2$	310～320	55.0	26.0	24.0	4.5	19.0

lactone was also isolated from the lower-boiling by-products. Stoll and Rouve[4] early obtained the dimeric lactone by treating ω-hydroxyheptanoic acid in a large amount of benzene (the dilution method).

Practical methods for the preparation of δ-valerolactone from δ-chlorovaleric acid were investigated on the basis of the kinetic studies.

Experimental

The Hydrolysis of ω-Chlorocarboxylic Acids.—Sample solutions were prepared by neutralizing δ-chlorovaleric and ω-chloroheptanoic acids with a dilute aqueous solution of sodium hydroxide, using phenolphthalein as an indicator, while stirring and cooling the solutions with ice-water. The fresh solution was diluted to a given concentration and immediately subjected to the reaction in a thermostat. In the case of ω-chloroheptanoic acid, the reaction was carried out in a sealed ampoule. As the reaction proceeded, a portion of the solution was taken up and titrated with a standard solution of silver nitrate.

The Preparation of δ-Valerolactone.—1) A mixture of δ-chlorovaleric acid (136.5 g.) and an equivalent aqueous sodium hydroxide was heated while evaporating water with an aspirator. After the removal of the water, the residue was distilled under reduced pressure to afford δ-valerolactone; yield 92.0 g. (92%). Repeated distillation gave an analytically pure sample of δ-valerolactone; b. p. 75～76°C/3 mmHg, n_D^{25} 1.4555, d_4^{20} 1.0988 (lit. b. p. 88°C/4 mmHg, n_D^{20} 1.4600, 1.4503, d_4^{20} 1.0794, 1.094). The above sample was easily polymerized in the presence of acid catalysts. Its infrared spectrum shows, at 1725 cm^{-1}, a strong absorption band attributable to $C=O$ stretching in lactone. 2) An aqueous solution (400 ml.) of sodium δ-chlorovalerate (1.0 mol.) was refluxed for 2 hr. After it had been cooled, the reaction mixture was extracted three times with benzene. The extract was distilled under reduced pressure to give δ-valerolactone; yield 92.5 g. (92.5%).

The Thermal Decomposition of a Polyester-Sodium Chloride Mixture.—A solid mixture of the polyester and sodium chloride was prepared by evaporating water from the aqueous solution of sodium ω-chloroheptanoate. The mixture was decomposed by heating it with a niter-bath above 300°C under reduced pressure (1 mmHg) in the presence of various catalysts. By the repeated distillation of the decomposition product, two fractions were obtained: fraction I, b. p. 45～70°C/1 mmHg; fraction II, b. p. 115～130°C/1 mmHg. White crystals were precipitated by cooling the methanol solution of the fraction II with dry ice-methanol. Recrystallization from methanol afforded the dimeric lactone of ω-hydroxyheptanoic acid; m. p. 46°C (lit.[4] m. p. 41°C).

Found: C, 65.77; H, 9.37. Calcd. for $C_{14}H_{24}O_4$: C, 65.59; H, 9.44%.

This 16-membered dimeric lactone has a fairly strong musk odor. Its infrared spectrum indicates the characteristic absorption band at 1725 cm^{-1} due to the lactonic carbonyl. From these results, the crystalline product was proved to be the dimeric lactone of ω-hydroxyheptanoic acid.

The fractional distillation of fraction I afforded a liquid; b. p. 96～98°C/10 mmHg, n_D^{20} 1.4520. This was treated with potassium permanganate in an aqueous alkaline solution. The manganese dioxide produced was filtered out. From the ether extract of the filtrate, a crystalline product identified with pimelic acid (m. p. 103～104°C) was obtained.

The infrared spectrum of this fraction is similar to that of the dimeric lactone and shows the characteristic band at 1720 cm^{-1} due to the lactonic carbonyl. The above sample, after being allowed to stand for a few days, was converted into a polymer which was identified analytically with the polyester from ω-hydroxyheptanoic acid. These results indicate this fraction to be the monomeric lactone of ω-hydroxyheptanoic acid. Details of the reaction are shown in Table I.

The Thermal Decomposition of the Polyester.—A mixture of ω-chloroheptanoic acid (329 g.), potassium acetate (300 g.) and glacial acetic acid (400 ml.) was refluxed for 16 hr. The reaction mixture was then diluted with water and extracted with benzene. After being washed several times with water, the ether extract was distilled

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[4] M. Stoll and A. Rouve, *Helv. Chim. Acta*, **18**, 1087 (1935).

TABLE II. THE THERMAL DECOMPOSITION OF THE POLYESTER

Polyester, 64 g. Catalyst, 1.0 g.

Catalyst	Temp. (bath) °C	Distillate g.	Frac. I g.	Frac. II g.	Residue g.	Crystals g.
$\mathrm{MgCl_2\cdot 6aq.}$	300∼310	38.5	10.0	22.0	6.0	12.5
$\mathrm{SnCl_2\cdot 2aq.}$	310∼320	24.5	9.5	12.0	3.0	7.0
MgO	300∼310	35.0	20.5	9.5	4.0	4.5

TABLE III. RATE CONSTANTS ($\mathrm{min^{-1}}$) IN THE HYDROLYSIS OF δ-CHLOROVALERIC ACID

$A=1.0$ mol./l.

Time	Temp., 50°C		Temp., 55°C		Temp., 60°C		Temp., 65°C	
min	conv. %	$k\cdot 10^2$	conv. %	$k\cdot 10^2$	conv. %	$k\cdot 10^2$	conv. %	$k\cdot 10^2$
10	—	—	—	—	24.3	2.87	34.1	4.30
15	13.6	0.99	—	—	—	—	52.6	4.96
20	18.5	1.02	30.8	1.84	49.0	3.37	62.0	4.83
25	—	—	—	—	—	—	67.6	4.51
30	27.8	1.09	42.6	1.85	62.7	3.29	74.9	4.61
40	36.0	1.12	53.3	1.90	70.2	3.03	—	—
50	42.9	1.12	61.2	1.89	75.6	2.84	—	—
60	49.0	1.12	66.2	1.80	—	—	—	—
70	54.9	1.14	—	—	—	—	—	—
(average)*		(1.12)		(1.86)		(3.06)		(4.67)

* In calculating the average values we neglected those in the initial stage of the reaction.

TABLE IV. RATE CONSTANTS ($\mathrm{min^{-1}}$) IN THE HYDROLYSIS OF ω-CHLOROHEPTANOIC ACID

$A=1.0$ mol./l.

Time	Temp., 90°C		Temp., 95°C		Temp., 100°C		Temp., 105°C	
min.	conv. %	$k\cdot 10^2$	conv. %	$k\cdot 10^2$	conv. %	$k\cdot 10^2$	conv. %	$k\cdot 10^2$
30	12.5	0.441	—	—	23.3	0.888	31.7	1.20
60	21.0	0.393	28.9	0.568	34.1	0.698	47.1	1.06
90	28.2	0.369	37.2	0.518	43.0	0.623	57.7	0.954
120	33.0	0.337	44.3	0.490	52.1	0.614	64.5	0.863
150	37.4	0.312	49.3	0.457	—	—	70.6	0.817
180	41.7	0.300	53.7	0.428	—	—	—	—
(average)		(0.359)		(0.490)		(0.706)		(0.979)

under reduced pressure to give ω-acetoxyheptanoic acid (b. p. 147∼150°C/1 mmHg, n_D^{20} 1.4430). The product (335 g.) was saponified with a small excess of sodium hydroxide in an aqueous methanol solution. The solution was acidified with hydrochloric acid and extracted with ether. The polyester of ω-hydroxyheptanoic acid was prepared by evaporating ether from the extract and by heating the residue a further 3 hr. under reduced pressure (about 3 mmHg). The polyester was decomposed as in the previous experiments. The results are given in Table II.

Results and Discussion

The Hydrolysis of ω-Chlorocarboxylic Acids. —The rate of hydrolysis was expressed by the following first-order equation:

$$dx/dt=k(A-x)$$

where A represents the initial concentration of the reactant, and x denotes the concentration of sodium chloride produced. The results are summarized in Tables III and IV.

In Table III, the rate constants at each temperature are calculated with a good constancy except for those at the beginning of the reaction. In the case of ω-chloroheptanoic acid, however, the rate constants tend to decrease as the reaction proceeds. Since the reaction product is in an equilibrium between δ-hydroxyvaleric acid and δ-valerolactone, a large change in pH valne, which is considered to affect the reaction rate, is prevented in the course of the reaction. On the other hand, the reaction solution of ω-chloroheptanoic acid becomes weakly acidic as the reaction proceeds.

The decrease in pH during the reaction, at any rate, is rather small, for the reaction system is a buffer solution. Therefore, the average values were employed for the calculation of rate constants.

The relation between the temperature and

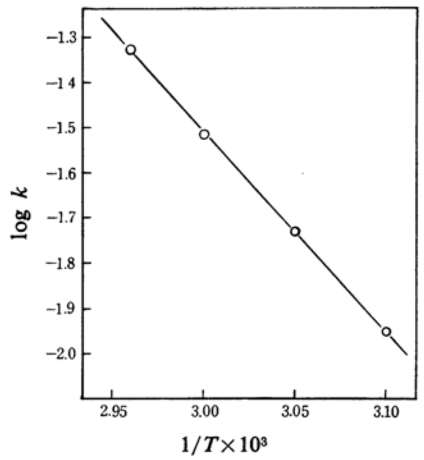


Fig. 1. Arrhenius plot for the hydrolysis of δ-chlorovaleric acid.
$E=19900$ cal./mol.

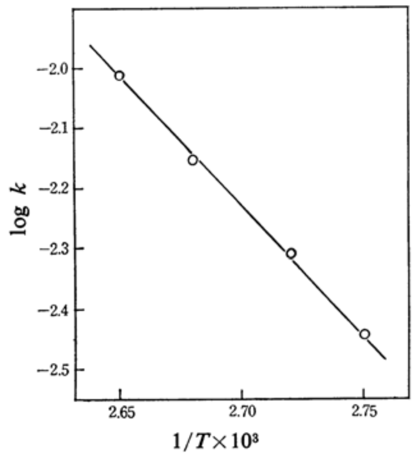


Fig. 2. Arrhenius plot for the hydrolysis of ω-chloroheptanoic acid.
$E=19700$ cal./mol.

the rate constants is plotted in Figs. 1 and 2.

The energies and entropies of the activation in these reactions are calculated as: $E=19900$ cal./mol., $\Delta S^{\ne}=-14$ e.u. (δ-chlorovaleric acid); and $E=19700$ cal./mol., $\Delta S^{\ne}=-24$ e.u. (ω-chloroheptanoic acid). The rate equations are expressed as follows:

for δ-chlorovaleric acid:

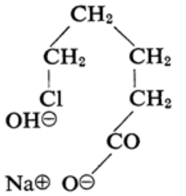
$$dx/dt=3.5\cdot10^{11}\cdot e^{-19900/RT}(A-x) \quad (\text{mol. l}^{-1}\text{min}^{-1})$$

for ω-chloroheptanoic acid:

$$dx/dt=2.6\cdot10^{9}\cdot e^{-19700/RT}(A-x) \quad (\text{mol. l}^{-1}\text{min}^{-1})$$

While an equal value is obtained for the activation energies in these two reactions, a large difference is obterved between the activation entropies.

These facts suggest that the chlorine atom in δ-chlorovaleric acid is far more accessible to hydroxyl ions than that in ω-chloroheptanoic acid. The chlorine atom at the δ-position is considered to be located close to the ion-pair ($-COO^{\ominus}$ $Na^{\oplus}$), which accelerates the hydrolysis as below:



The large difference between the activation entropies in these reactions may be realized by the above explanation.

Summary

1) The kinetics of the hydrolysis of δ-chlorovaleric and of ω-chloroheptanoic acids in an aqueous solution of their sodium salts has been studied. The reason for the difference between the activation entropies has been discussed.

2) The methods for the preparation of δ-valerolactone from δ-chlorovaleric acid have been established.

3) By the thermal decomposition of the polyester from ω-hydroxyheptanoic acid, the dimeric lactone of the acid has been prepared, and the formation of the monomeric lactone has also been ascertained.

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