[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF ROCHESTER]

THE KINETICS OF BASIC HYDROLYSIS OF SOME γ-LACTONES AND γ-THIOLACTONES IN AQUEOUS ACETONE[1]

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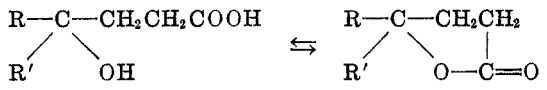
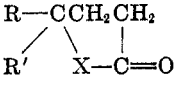
Measurements of rates of lactonization of γ-hydroxyacids show that the rate increases as the hydroxyl group changes from primary to secondary to tertiary (1, 2). This order, which is the reverse of that observed for esterification of alcohols (primary hydroxyls being esterified more rapidly than secondary or tertiary), suggests that the lactonization may proceed by a carbonium ion mechanism when the hydroxyl is tertiary, and conversely, that acid hydrolysis of lactones with a tertiary C—O bond may proceed by alkyl-oxygen cleavages, the $A_{AL}1$ category in Ingold's classification (3). *tert*-Butyl acetate is known to hydrolyze in acid solution by this mechanism (4–6), although γ-butyrolactone (I) is hydrolyzed by the normal acyl oxygen cleavage ($A_{AC}2$) (3, 7), which is usual for esters derived from primary and secondary alcohols.



Earlier work on the comparison of sulfur and oxygen compounds showed (6) that with thiol esters, RCOSR′, only when R′ was trityl did the $A_{AL}1$ mechanism appear. Studies by Schjanberg (9) on hydrolysis of some γ- and δ-thiolactones revealed some interesting points from the mechanistic side, but he did not examine any thiolactones with a tertiary C—S bond. We therefore undertook a comparative study of lactones and thiolactones derived from primary, secondary, and tertiary hydroxy- or mercapto-acids. The present paper reports the preparation and a study of the kinetics of the aklaline hydrolysis in 43% acetone-water of γ-butyrolactone (I), γ-valerolactone (II), γ-isocaprolactone (III), and the corresponding thiolactones (IV, V, VI). It is hoped to study acid-catalyzed hydrolysis later.



I, R = R′ = H, X = O
II, R = CH_3, R′ = H, X = O
III, R = R′ = CH_3, X = O
IV, R = R′ = H, X = S
V, R = CH_3, R′ = H, X = S
VI, R = R′ = CH_3, X = S

It was thought that γ-thioisocaprolactone (VI) should be most readily accessible by the Markownikoff addition of hydrogen sulfide in the presence of sulfur (10) to 4-methyl-4-pentenoic acid (VII), which could be made through the cor-

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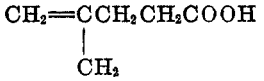
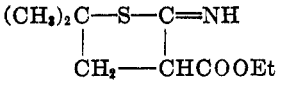
responding malonic acid. It was found impractical to hydrolyze and decarboxylate diethyl β-methylallylmalonate to VII, because of the very great ease of lac-



VII

tonization to γ-isocaprolactone (III); a mixture of the lactone and the acid VII was always obtained, and in fact the lactone was most readily prepared pure this way. Many runs on the addition of hydrogen sulfide to a mixture of the acid VII and isocaprolactone, to the malonic acid, or to the malonic ester corresponding to VII did not give a useful yield of the thiolactone VI.

This compound was finally prepared by alkylating ethyl cyanoacetate with isobutylene sulfide to give VIII, following Snyder and Alexander (11); hydrolysis and decarboxylation of VIII yielded the desired thiolactone VI, which has not been previously described.

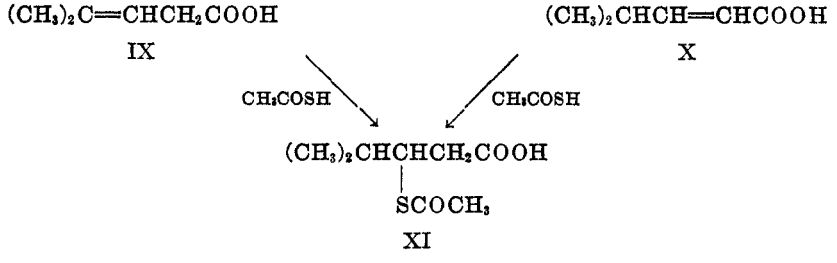


VIII

The thiolactones IV and V were prepared by the addition of thioacetic acid to 4-pentenoic acid and 4-hexenoic acid, followed by hydrolysis of the acetylmercapto group and lactonization (12, 13). One point in these synthetic experiments is of some theoretical interest.

Schjanberg (13) observed that with β,γ- and γ,δ-unsaturated *straight chain* acids, thioacetic acid added to the carbon atom more distant from the carboxyl group, giving γ- and δ-acetylmercapto acids from β,γ- and γ,δ-unsaturated acids respectively. It is difficult to see a theoretical basis for this behavior.

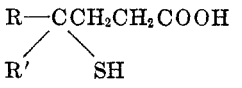
It is known that the addition of thioacetic acid to an unsymmetrically substituted double bond is anti-Markownikoff (14); in the addition of thioacetic acid to 4-methyl-3-pentenoic acid (IX), these two effects, the "proximity" factor of Schjanberg and the anti-Markownikoff orientation, are in competition. It was found actually that the anti-Markownikoff orientation prevailed, and that addition of thioacetic acid to both IX and X led to the same adduct XI.



The identity of XI was apparent from its saponification equivalent, its hydrolysis to a mercapto acid giving a color test for a primary or secondary mercapto

group (15), and the failure of the mercapto acid to lactonize on heating or to give the known (11) crystalline γ,γ'-dithio-bis-isocaproic acid on oxidation.

The γ-mercapto acids



derived from the thiolactones IV, V, and VI, do not lactonize nearly as readily as the corresponding γ-hydroxy acids, but require elevated temperatures for complete lactonization. This is in agreement with earlier observation on the position of the equilibrium between carboxylic acids and mercaptans (16). It was shown in the present work that basic hydrolysis of the tertiary thiolactone VI goes with acyl-sulfur cleavage to form the tertiary mercapto acid, from which the thiolactone can be regenerated.

The kinetic results of the basic hydrolysis runs, which were obtained conductometrically, are given in Tables I and II; the former shows two representative runs in detail.

A comparison of the values in Table II with the values previously obtained (5)

TABLE I

RATE OF ALKALINE HYDROLYSIS OF LACTONES AND THIOLACTONES IN 43% ACETONE BY WEIGHT AT 30.0° C

t (min.)	Conductivity (mho × 10^{-5})	k (l $mole^{-1}$ $min.^{-1}$)
A. γ-ISOCAPROLACTONE[a]		
0	2.591	—
4.60	2.057	7.20
8.90	1.876	6.89
11.70	1.805	6.83
15.00	1.745	6.80
19.00	1.689	6.92
30.00	1.610	6.95
60.00	1.536	7.48
∞	1.088	—
B. γ-THIOISOCAPROLACTONE[b]		
0	2.597	—
3.00	2.358	3.63
5.60	2.242	3.32
8.00	2.160	3.14
11.50	2.066	3.14
17.00	1.957	3.22
35.00	1.786	3.40
∞	1.548	—

[a] Lactone, 0.02252 M; base, 0.02762 M.

[b] Thiolactone, 0.01299 M; base, 0.02762 M.

TABLE II

RATE CONSTANTS, ACTIVATION ENERGIES, AND PREËXPONENTIAL TERMS FOR ALKALINE HYDROLYSIS IN 43% ACETONE OF LACTONES AND THIOLACTONES, R—C(R′)(X)—CH_2CH_2—C(=O)

R	R′	T, C.°	k^a l/mole^{-1} min^{-1}	E kcal./mole	$\log_{10}A$
A. LACTONES (X = oxygen)					
H	H	10.0	14.9		
H	H	20.0	30.0	12.0	10.4
H	H	30.0	60.7		
CH_3	H	10.0	5.57		
CH_3	H	20.0	11.7	12.3	10.2
CH_3	H	30.0	23.6		
CH_3	CH_3	10.0	1.89		
CH_3	CH_3	20.0	3.79	11.4	9.07
CH_3	CH_3	30.0	7.17		
B. THIOLACTONES (X = sulfur)					
H	H	10.0	1.59		
H	H	20.0	3.35	12.8	10.1
H	H	30.0	7.14		
CH_3	H	10.0	0.971		
CH_3	H	20.0	2.15	13.3	10.2
CH_3	H	30.0	4.60		
CH_3	CH_3	10.0	0.651		
CH_3	CH_3	20.0	1.62	14.2	10.8
CH_3	CH_3	30.0	3.45		

[a] Rate constants are the mean of at least two and usually more separate determinations.

for alkaline hydrolysis of a series of acetates, CH_3COOR, and thiolacetates, CH_3COSR, shows that the rates of hydrolysis of the lactones and of the open-chain esters are of the same order of magnitude. However, the rates for the open-chain compounds are much more sensitive to changes in structure than are the rates for the lactones and thiolactones. Thus, *tert*-butyl acetate, $CH_3COOC(CH_3)_3$ hydrolyzes about 100 times more slowly than ethyl acetate (5); with the corresponding lactones, γ-butyrolactone (I) shows a rate only 8 times that of the "tertiary" lactone III. A similar situation exists for the thiolesters and the thiolactones. Furthermore, the activation energies and the preëxponential terms vary much less with the degree of substitution in the lactone and thiolactone series than they do in the ester-thiolester series. Apparently the cyclic structure of the lactones tends to diminish the steric effects of increasing substitution around the alkyl oxygen or sulfur; the ring system holds the lactone carbonyl groups in a relatively fixed position, and its vulnerability to attack is not much diminished by one or two additional methyl groups. In the open-chain esters, increas-

ing substitution on the alkyl carbon reduces markedly the accessibility of the carbonyl carbon. It would be expected that the six-membered δ-lactones would show a greater effect on the rate of hydrolysis by increasing substitution than do the γ-lactones.

EXPERIMENTAL[3]

Diethyl β-methylallylmalonate. Sodium (23 g.) was dissolved in 800 cc. of absolute ethanol (dried by distilling from sodium directly into the reaction flask) in a 3-neck flask protected from moisture, and 376 g. of diethyl malonate was added, with refluxing for 10 min. Redistilled β-methylallyl chloride (100 g.) was added as rapidly as possible, and the mixture was refluxed for 2 hr., at which point it was neutral to phenolphthalein. About 650 cc. of the alcohol was removed by distillation, 400 cc. of water was added to the reaction mixture to dissolve the sodium chloride, and the layers were separated. The aqueous layer was extracted with three portions of benzene, and the combined benzene extracts and organic layers were distilled. Two distillations yielded 161 g. (75%) of the product b.p. 94–96° (5 mm.) n_D^{25} 1.4340. The product has been reported to have b.p. 113–116° (14–17 mm.), n_D^{25} 1.4341, but no analysis was given (17).

Anal. Calc'd for $C_{11}H_{18}O_4$: C, 61.66; H, 8.47; Sapon. equiv., 107.1.
Found: C, 61.97; H, 8.50; Sapon. equiv., 107.7.

The ester was characterized by conversion to the corresponding barbituric acid, m.p. 184–189°; the reported m.p. for this compound which is a hemihydrate (17) is 187–189°.

β-Methylallylmalonic acid (VIII). This compound was obtained in essentially quantitative yield by acid or alkaline hydrolysis of the above ester. Crystallization from benzene-hexane gave colorless plates, m.p. 97–98°.

Anal. Calc'd for $C_7H_{10}O_4$: C, 53.16; H, 6.37; Neut. equiv., 79.1.
Found: C, 53.36; H, 6.27; Neut. equiv., 79.6.

γ-Isocaprolactone (III). Diethyl β-methylallylmalonate (21.4 g.) was refluxed with 25% aqueous hydrochloric acid with stirring for 1 hr. at 110–120°; the mixture became homogeneous during this period. The flask was fitted with a condenser and trap for downward distillation, and stirring and heating were continued. After about 80 cc. of distillate had been collected, the temperature of the heating bath was slowly raised; decarboxylation began at 140°, and was completed in about 30 min. at 160–180°. The temperature was raised briefly to 195° to complete the decarboxylation-cyclization reaction. The distillate (10.5 g., 92%) was redistilled, giving lactone with the following properties: b.p. 74–76° (5–6 mm.), n_D^{20} 1.4335, d_4^{20} 1.0122. Glickman and Cope (18) give n_D^{25} 1.4315 for lactone prepared from isobutylene oxide and ethyl cyanoacetate. Isocaprolactone prepared by us by the action of the methyl Grignard on ethyl levulinate (19) showed n_D^{20} 1.4351, and had an unpleasant odor, in contrast to the material prepared above, which had a coconut-like odor.

The γ-isocaprolactone was converted to γ-hydroxyisocaproamide, m.p. 98–99°, as reported (18).

Addition of thioacetic acid to 4-methyl-2-pentenoic acid. 4-Methyl-3-acetylmercaptopentanoic acid (XI). 4-Methyl-2-pentenoic acid was prepared by condensation of isobutyraldehyde with malonic acid in the presence of pyridine and piperidine (20), and showed the reported properties. Thioacetic acid was prepared in poor and variable yield by the action of hydrogen sulfide on acetic anhydride (22); the reason for the variability was not found. Unless both the unsaturated acid and the thioacetic acid were freshly distilled, little or no addition occurred.

4-Methyl-2-pentenoic acid (11.4 g.) and 10 g. of thioacetic acid were allowed to stand at room temperature for 24 hr., were heated on the steam-bath for 2 hr., and after 30 hr. more at room temperature were distilled. After a forerun of thioacetic acid, the main

[3] Microanalyses are by Miss Claire King; melting points are not corrected.

fraction (10.3 g., 54%) was collected at 128–139° (2–3 mm.). After redistillation, it showed the following properties: b.p. 136–139° (3 mm.); n_D^{20} 1.4892; d_4^{20} 1.1178.

Anal. Calc'd for $C_8H_{14}O_3S$: Sapon. equiv., 95.1; Neut. equiv., 190.3; M_D, 49.27.
Found: Sapon. equiv., 95.2; Neut. equiv., 191.8; M_D 49.14.

The ultraviolet spectrum (in 95% alcohol) showed λ_{max} 233 mμ, ϵ_{max} 4.69 × 10^3.

3-Mercapto-4-methylpentanoic acid. Alkaline hydrolysis at room temperature for 24 hr. of the above 3-acetylmercapto-4-methylpentanoic acid, followed by distillation of the product, yielded the 3-mercapto acid, with the following properties: b.p. 99–100° (1.5 mm.); n_D^{20} 1.4810; d_4^{20} 1.0799.

Anal. Calc'd for $C_6H_{12}O_2S$: Neut. equiv., 148.2; M_D, 39.52.
Found: Neut. equiv., 148.8; M_D, 39.06.

The compound gave a positive test for a mercaptan grouping on a primary or secondary carbon (15) and was oxidized to a colorless oil by iodine-potassium iodide.

Addition of thioacetic acid to 4-methyl-3-pentenoic acid (IX). *4-Methyl-3-acetylmercaptopentanoic acid* (XI). 4-Methyl-3-pentenoic acid, prepared by isomerization of 4-methyl-2-pentenoic acid with concentrated potassium hydroxide (23) was treated with thioacetic acid under the conditions described above. There was marked heat evolution, in contrast to the preceding case. The acetylmercapto compound and the mercapto compound obtained from it by hydrolysis had properties identical with those of the products described above.

γ-Thiobutyrolactone (IV). This compound was prepared (12) by the addition of thioacetic acid to 3-butenoic acid (24), followed by hydrolysis to 4-mercaptobutanoic acid, and lactonization by slow distillation (12). The sample used for the kinetic runs had b.p. 56–57° (4 mm.), n_D^{20} 1.5240, d_4^{20} 1.1750, λ_{max} 235 mμ, ε 3600, in good agreement with the reported values (12).

γ-Thiovalerolactone (V). This was also prepared, following Schjanberg (13), by addition of thioacetic acid to 3-pentenoic acid (25), followed by hydrolysis and lactonization of the resulting 4-mercaptopentanoic acid. The sample used in the kinetic runs had the following properties, in good agreement with the literature (13): b.p. 70–71° (6 mm.), n_D^{20} 1.5031, d_4^{20} 1.0962, λ_{max} 234 mμ, ε 3600.

The thiovalerolactone was also prepared, in 44% yield of pure material, by the action of sulfur and hydrogen on levulinic acid at 200° in the presence of a cobalt polysulfide catalyst, following Farlow, Lazier, and Signaigo (26).

The thiolactone was obtained in 9% yield by the action of phosphorous pentasulfide on valerolactone at 60–80° (27).

2-Imino-3-carbethoxy-5,5-dimethylthiophane (VIII). The procedure of Snyder and Alexander (11) was modified as follows: Redistilled ethyl cyanoacetate (15 g.) was added to a solution prepared from 2.3 g. of sodium and 200 cc. of absolute ethanol, in a 3-neck flask protected from atmospheric moisture, and the mixture was stirred for 2 hr. Isobutylene sulfide (28) (9 g.) then was added dropwise to the stirred solution at 30° in the course of 1 hr., and the solution was allowed to stand at room temperature for 24 hr. During this period, the solution took on a red color and deposited a sizable amount of solid material. The mixture was filtered and the filtrate was concentrated to about 50 cc. by removing the ethanol under reduced pressure. The solution was poured into 100 cc. of ice-water, the mixture was cooled in an ice-bath, and the lustrous white crystals which formed were collected. The yield of air-dried product, m.p. 53–54°, as reported (11) was 9.1 g. (45%). The preparation was tried in more concentrated and in more dilute solutions, but the above procedure gave the best yields.

γ-Thioisocaprolactone (VI). 2-Imino-3-carbethoxy-5,5-dimethylthiophane (8 g.) was refluxed for 10 hr. with 50 cc. of 10% sodium hydroxide solution, at which point ammonia evolution had stopped. The small amount of insoluble material was removed, the alkaline solution was acidified to *p*H 1 with 4 *N* hydrochloric acid, and was extracted with four portions of ether. The extracts were dried, the solvent was removed, and the residual pale yellow liquid was heated in a Claisen flask at atmospheric pressure, using an oil-bath. After the decarboxylation reaction appeared to be over, cyclization was completed under

100 mm. pressure. The resulting yellow liquid was steam-distilled, and the product was obtained from the steam-distillate by ether extraction. The γ-thioisocaprolactone was obtained from the ether extracts by distillation in 77% yield (4.0 g.) with the following properties: b.p. 55–56° (3 mm.), n_D^{29} 1.4992, d_4^{20} 1.0577: λ_{max} 235 mμ, ε 3600.

Anal. Calc'd for $C_6H_{10}OS$: C, 55.34; H, 7.74; Sapon. equiv., 130; M_D 35.85.

Found: C, 55.33; H, 7.67; Sapon. equiv., 130; M_D 36.16.

The thiolactone developed a positive test for the tertiary mercaptan grouping (green in the nitrous acid test, ref. 15); hydrolysis, neutralization, and oxidation with iodine-potassium iodide solution yielded γ,γ′-dithiodiisocaproic acid, m.p. (from aqueous ethanol) 84–85°, in agreement with the reported value (11).

Hydrolysis and recyclization of γ-thioisocaprolactone. A sample of the thiolactone (2.6 g.) was dissolved in 60 cc. of 1 *N* sodium hydroxide by swirling at room temperature, and was allowed to stand 4 days. It formed a clear colorless solution. It was then acidified to *p*H 1 with 4 *N* hydrochloric acid, and there was no odor of hydrogen sulfide when acidification occurred. The solution was extracted with several portions of ether, and the extracts were dried and distilled. The product nearly all distilled, and 1.56 g. (60%) of the lactone was obtained, with b.p. 45–47° (0.5 mm.), n_D^{29} 1.4992.

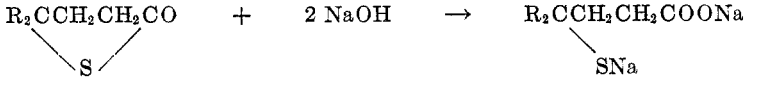
Kinetic measurements. The three thiolactones used in the kinetic work were prepared and purified as described above.

γ-Butyrolactone (from Cliffs Dow Chemical Co.) was redistilled; the sample used had b.p. 70–71° (5 mm.); n_D^{29} 1.4365, d_4^{20} 1.1256, in good agreement with the literature.

γ-Valerolactone (from Monsanto Chemical Co.) had b.p. 75–76° (6 mm.), n_D^{29} 1.4336, d_4^{20} 1.0536, likewise in good agreement with reported values.

γ-Isocaprolactone was prepared as above from the decarboxylation-cyclization of β-methylallylmalonic acid. Preliminary experiments showed that following the reaction by titration was unsatisfactory, and it was therefore done conductometrically, using 43% acetone–57% water (by weight) as solvent, in order to give results comparable to those reported previously (5, 6).

The reaction therefore was followed conductometrically, using the general procedures employed by earlier workers (19, 20). The cells were of Pyrex or Kimble glass, with fixed platinized electrodes about 1 cm. square and 1–5 cm. apart, of 30–80 cc. volume; they could be closed to protect the solutions against the air. The resistances were measured by direct reading oscillator bridges, with cathode ray null point indicators. Solutions were made up by the standard procedures, with suitable precautions to prevent access of carbon dioxide. Concentrations were in the range of 0.025 *M*, and a slight excess of sodium hydroxide was used. The equation for the lactone hydrolyses was assumed to be the usual one, with the reaction involving one equivalent each of lactone and sodium hydroxide; with the thiolactones, the reaction was assumed to be the following (5) and the rate constant in these cases was calculated from the



equation

$$k = \frac{1}{t(b - 2a)} \ln \frac{a(b - 2x)}{b(a - x)}$$

where k is the constant in m/l/min., a is concentration of lactone, and b is concentration of hydroxyl. The rate constants for a single run usually varied over a range of about 10%; typical runs are shown in Table I. The results for the six compounds studied are collected in Table II, which tabulates also the Arrhenius activation energies and the preëxponential factor $\log_{10}$ A, obtained in the usual way.

SUMMARY

Rates of alkaline hydrolysis for three γ-lactones and three γ-thiolactones in 43% acetone–57% water have been measured conductometrically. The lac-

tones and thiolactones show much smaller effects on the rate from increasing alkyl substitution around oxygen (or sulfur) than do the open-chain acetates and thiolacetates. A number of methods of synthesizing γ-isocaprolactone and the corresponding thiolactone have been evaluated. The addition of thioacetic acid to 4-methyl-3-pentenoic acid is anti-Markownikoff, yielding 4-methyl-3-acetylmercaptopentanoic acid, which is also obtained from 4-methyl-2-pentenoic acid.

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