[CONTRIBUTION NO. 147 FROM THE GOODYEAR TIRE & RUBBER CO. RESEARCH LABORATORY]

Kinetics of the Hydrolysis of Ethyl Thiolacetate in Aqueous Acetone[1]

BY JOHN R. SCHAEFGEN

A study of the kinetics of the hydrolysis of ethyl thiolacetate at ordinary temperatures was undertaken in order to compare the behavior of thiolesters with esters and to gain further insight into the mechanism of hydrolysis.

Recorded information concerning thiolesterification and the hydrolysis of thiolesters is limited to qualitative observations and some equilibria and rate studies at elevated temperatures.[2] The data reported in this paper give rate constants and activation energies for the acid catalyzed and the alkaline hydrolysis of ethyl thiolacetate in aqueous acetone solutions containing 24.6, 43.0, and 62.0% acetone by weight. Aqueous acetone was selected as the reaction medium because both thiolester and sodium hydroxide were sufficiently soluble for rate studies in such a mixture over a wide range of composition, and, in addition, a comparison with ester kinetic studies in the same medium was possible.[3]

Experimental

Ethyl thiolacetate was prepared in 77% yield (b. p. 112–115°) by treating ethyl mercaptan with acetyl chloride. The thiolester was purified by fractionally distilling it from anhydrous potassium carbonate through a short packed column. A center constant boiling fraction (113.5° (735 mm.)) was used in the rate studies. This fraction had a refractive index $n^{20.6}\text{D}$ 1.4583 and a density d^{20}_4 0.9792. The saponification equivalent was somewhat erratic giving both high and low values depending on the solvent and the length of time allowed for complete hydrolysis. The average value was close to the theoretical, however.

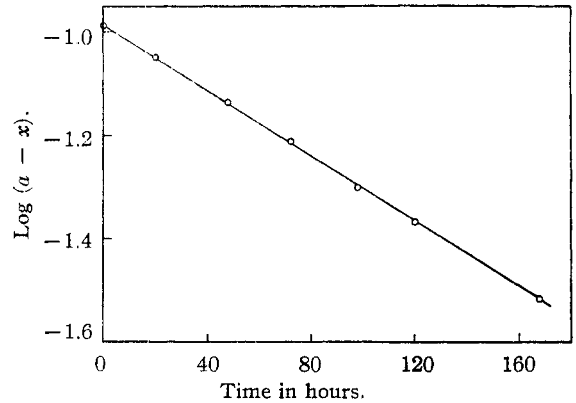

Fig. 1.—The acid catalyzed hydrolysis of ethyl thiolacetate at 40° in 24.6% acetone-water solution: thiolester, 0.1034 *M*; HCl, 0.0985 *M*.

The water–acetone mixtures were made up by weight from boiled distilled water and C. P. acetone dried over and distilled from anhydrous potassium carbonate.

Acid Catalyzed Hydrolysis.—The thiolester solutions were prepared by diluting a weighed quantity of ethyl thiolacetate with aqueous acetone of the desired composition in a volumetric flask. The initial concentration was calculated using the theoretical molecular weight. Appropriate quantities of thiolester and of hydrochloric acid solutions (also in aqueous acetone) were mixed at zero time and the initial concentration of acid was determined by titrating a 10-ml. aliquot with standard 0.1 *N* sodium hydroxide. Additional 10-ml. samples were withdrawn from time to time and titrated to follow the reaction. The mercaptan formed in the reaction interferes with the end-point. Therefore, air freed of carbon dioxide was bubbled through the solution for ten to fifteen minutes to remove mercaptan before a final end-point was determined. The reaction mixture was maintained at constant temperature by means of a thermostat. In some solutions, mainly those high in water content, the mercaptan formed by the hydrolysis separated out as the reaction proceeded. This would tend to make the rate constants low in these cases if much thiolester dissolved in the mercaptan layer.

Alkaline Hydrolysis.—Thiolester solutions were made up the same as for acid catalyzed hydrolysis. Base solutions were prepared by diluting the desired quantity of aqueous carbonate-free sodium hydroxide with acetone until the desired composition was obtained, and making up to volume with aqueous acetone. Appropriate volumes of thiolester and of base solutions were pipetted into separate arms of an inverted Y reaction tube which was partially immersed in a thermostat. The solutions were mixed at zero time by tilting the tube. Samples (10 ml.) were withdrawn from time to time by means of a calibrated free-flowing pipet and were delivered into a slight excess of 0.02 *N* hydrochloric acid solution to stop the reaction. The time of the sample was taken as the time of half delivery. The samples were then back-titrated with 0.02 *N* carbonate-free base solution until a faint phenolphthalein end-point was reached. Air freed of carbon dioxide was bubbled through the solution for ten to fifteen minutes to remove mercaptan before the final end-point was determined just as in acid catalyzed hydrolysis.

Discussion and Results

Acid Catalyzed Hydrolysis.—The rate of the acid catalyzed hydrolysis was found to be first order with respect to thiolester concentration in accord with the rate equation

$$dx/dt = k(a - x)[\mathrm{H}^+] \qquad (1)$$

where a is the original concentration of thiolester and x is the amount of thiolester hydrolyzed in time t. On integration equation (1) becomes

$$2.303 \log (a - x) = -k[\mathrm{H}^+]t + C$$

Graphs of log $(a - x)$ *vs.* t were prepared (such as shown in Fig. 1) to obtain the values of $k[\mathrm{H}^+]$. The data for acid catalyzed hydrolysis are summarized in Table I. The lower value of the rate constant observed in the solution 0.2952 *M* in thiolester may be attributed to the decrease in water content of the solution as the hydrolysis proceeds, and to solution of the thiolester in the mercaptan layer formed during the reaction. The rate of the

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[1] Presented before the Division of Physical and Inorganic Chemistry of the American Chemical Society at the New York Meeting, September, 1947.

[2] W. Michler, *Ann.*, **176**, 177 (1875); E. E. Reid and co-workers, *Am. Chem. J.*, **43**, 489 (1910); THIS JOURNAL, **38**, 2746 (1916); **39**, 1930 (1917).

[3] G. Davies and D. P. Evans, *J. Chem. Soc.*, 339 (1940).

reaction is directly proportional to the hydrogen ion concentration (*i. e.*, initial hydrochloric acid concentration), k therefore being independent of the hydrogen ion concentration. The lower value of the rate constant observed in the case of the 0.2808 *M* hydrochloric acid solution is probably due to experimental error since there is no trend in the values of k with increasing hydrochloric acid concentration.

The activation energy computed from the Arrhenius equation is independent of the composition of the reaction medium within the accuracy of the measurements.

TABLE I

RATE CONSTANTS AND ACTIVATION ENERGIES FOR THE ACID CATALYZED HYDROLYSIS OF ETHYL THIOLACETATE IN AQUEOUS ACETONE SOLUTIONS

Wt. % acetone	Temp. °C. ±0.03	Initial concn. (m./l.) Thiol-ester	HCl	$k[H^+] \times 10^6$ l./m./min.	$k \times 10^4$ l./m./min.	E, cal./mole
24.6	30.00	0.1050	0.0995	4.81	4.83	17,500
	40.00	.1034	.0985	12.1	12.3	
43.0	30.00	.1030	.1025	2.60	2.54	18,000
	30.00	.0986	.2808	6.04	2.15	
	30.00	.0986	.4700	11.5	2.44	
	30.00	.2952	.0998	2.10	2.10	
	40.00	.0975	.1006	6.54	6.50	
62.0	30.00	.0995	.1009	1.35	1.34	18,000
	40.00	.0985	.1007	3.52	3.49	

Alkaline Hydrolysis.—The rate of the alkaline hydrolysis of ethyl thiolacetate in aqueous acetone solution was found to be second order and to proceed according to the equation

$$\begin{array}{ccccccc} CH_3COSC_2H_5 & + & 2OH^- & \longrightarrow & CH_3COO^- & + & C_2H_5S^- + H_2O \\ a - x & & b - 2x & & x & & x \end{array}$$

Integrating the rate expression

$$dx/dt = k(a - x)(b - 2x) \qquad (2)$$

leads to

$$[2.303/(2a - b)] \log [(a - x)/(b - 2x)] = kt + C \ (3)$$

A graph of log $[(a - x)/(b - 2x)]$ is linear with t in agreement with theory up to 60–70% completion of the hydrolysis, as shown in Fig. 2. If $b = 2a$, equation (2) on integration gives

$$1/(a - x) = 2kt + C' \qquad (4)$$

Accordingly, $1/(a - x)$ is linear with t in this case (Fig. 3).

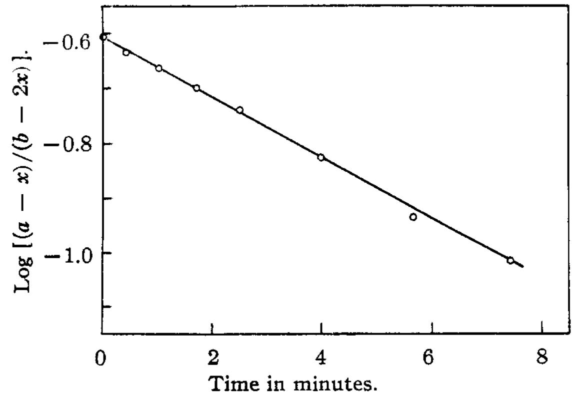


Fig. 2.—The alkaline hydrolysis of ethyl thiolacetate at 20° in 43.0% acetone-water solution: thiolester, 0.0321 *M*; NaOH, 0.1287 *M*.

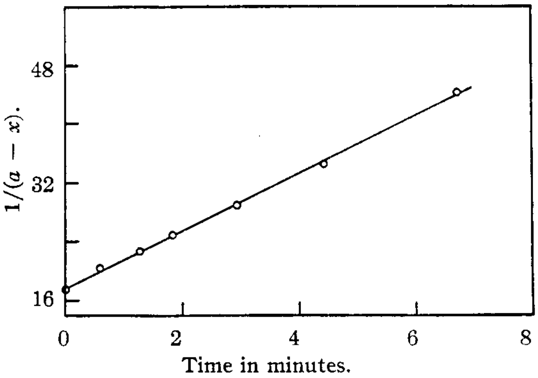


Fig. 3.—The alkaline hydrolysis of ethyl thiolacetate at 20° in 43.0% acetone–water solution: thiolester, 0.0574 *M*; NaOH, 0.1150 *M*.

The data for alkaline hydrolysis are summarized in Table II. The plots from which the energy of activation was determined are shown in Fig. 4. Values of log PZ were calculated from the Arrhenius equation. The rate constant is shown to be independent of thiolester and base concentrations over the small ranges of concentration investigated.

TABLE II

RATE CONSTANTS AND ACTIVATION ENERGIES FOR THE ALKALINE HYDROLYSIS OF ETHYL THIOLACETATE IN AQUEOUS ACETONE SOLUTIONS

Wt. % acetone	Temp. °C. ±0.03	Initial concn. (m./l.) Thiol-ester	NaOH	k (av.)[a] l./mole/min.	E, cal./mole	$\log_{10} PZ$
24.6	10.00	0.0319	0.0637	1.25	13,000	10.2
	20.00	.0369	.0735	2.80		
	30.00	.0319	.0636	5.82		
43.0	10.00	.0570	.1148	0.86	13,800	10.6
	20.00	.0290	.0581	1.91		
	20.00	.0286	.1150	1.98		
	20.00	.0574	.1150	1.98		
	30.00	.0301	.0601	4.39		
62.0	10.00	.0401	.0810	0.638	14,400	10.9
	20.00	.0401	.0802	1.54		
	30.00	.0394	.0795	3.45		

[a] Each of these values is the average of two experiments, the maximum deviation of any value from the mean being 3%.

Comparison with Ester Hydrolysis.—The hydrolysis of ethyl thiolacetate in 62.0% acetone solution is compared to that of ethyl acetate in the same medium in Table III. The rate constant for the acid catalyzed hydrolysis of ethyl acetate at 30° is about thirty times as great as that for ethyl thiolacetate. This difference in k can be attributed almost entirely to the small difference in observed activation energy since the log

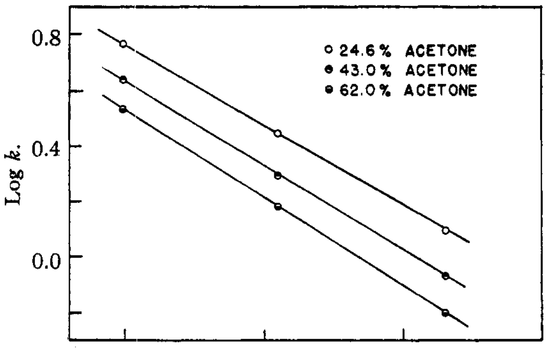


Fig. 4.—The alkaline hydrolysis of ethyl thiolacetate in aqueous acetone. The change of rate constant with temperature.

PZ factor is approximately the same in each case. This would indicate that similar configurational transformations are followed in the acid catalyzed hydrolysis of esters and of thiolesters.

The rate constants for the alkaline hydrolysis of ethyl acetate and of ethyl thiolacetate at room temperature are approximately the same. However, both the activation energy and the log *PZ* factor are much higher for alkaline thiolester hydrolysis than for alkaline ester hydrolysis, indicating that different mechanisms are followed in these two reactions.

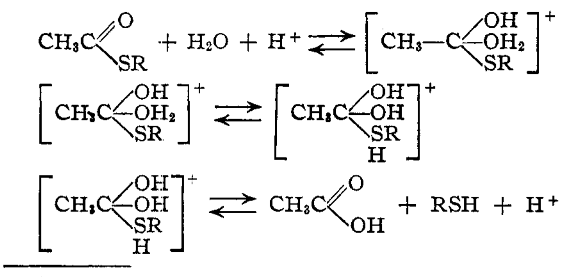
TABLE III

COMPARISON OF THE HYDROLYSIS OF ETHYL ACETATE AND ETHYL THIOLACETATE IN 62% ACETONE SOLUTION

		$CH_3COOC_2H_5$[a]	$CH_3COSC_2H_5$
Acid catalyzed hydrolysis	k at 30°	42.7×10^{-4}	1.34×10^{-4}
	40°	101×10^{-4}	3.49×10^{-4}
	E (kcal./mole)	16.2	17.8
	$\log_{10} PZ$	9.3	9.0
Alkaline hydrolysis	k at 20°	2.13	1.54
	30°	3.74	3.45
	E (kcal./mole)	9.80	14.4
	$\log_{10} PZ$	7.6	10.9

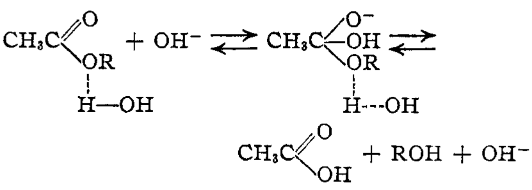
[a] From the data of Davies and Evans, ref. 3.

The mechanism for the acid catalyzed hydrolysis of ethyl thiolacetate is undoubtedly similar to that postulated for ester hydrolysis and may be formulated[4] thus



It should be noted that the addition of the nucleophilic oxygen of the water molecule in the rate controlling first step is favored by polarization of the carbon to sulfur bond; however, the corresponding carbon to oxygen linkage in esters is relatively more polar and the activation energy would therefore be expected to be somewhat lower in the case of ester hydrolysis, in accord with observation (see Table III).

A number of mechanisms have been proposed for alkaline ester hydrolysis, all of which involve an addition of hydroxyl ion at the carbonyl carbon atom in the rate controlling first step with,[5] or without,[6] the aid of a molecule of water to produce the intermediate complex. In the former case the complex then yields the carboxylic acid and the alcohol in a simple decomposition; whereas in the latter case the acid and the alkoxy ion are formed, followed by a second fast reaction with water to produce the alcohol. In view of the work of Kendall,[7] who has demonstrated that solvated ester molecules exist in aqueous solutions of the simple esters, the former mechanism seems more likely, and may be written as follows


(5)

The solvated ester complex, formed by hydrogen bonding as shown, reacts with hydroxyl ion in the rate controlling step to produce the intermediate complex which then decomposes to give the observed products. The addition of hydroxyl ion is aided by the small positive charge induced at the carbonyl carbon atom by the added water molecule. The stretching of the C–OR linkage preparatory to rupture is favored by both addition of hydroxyl ion and the electrophilic attack of the hydrogen atom of the water molecule. Thus the activation energy of the reaction, which may be thought[8] of as the energy necessary to add an hydroxyl ion against a negative environment plus a bond stretching energy necessary to break the C–OR linkage, will be much lower by this mechanism than by one in which the coöperation of a water molecule was not involved.

On the other hand, it is quite unlikely that similar solvated thiolester molecules exist in aqueous solution because of the relative weakness of the S---H—O bond compared to the O---H—O bond.[9]

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[4] T. Lowry, *J. Chem. Soc.*, **127**, 1381 (1925); I. Roberts and H. Urey, THIS JOURNAL, **61**, 2584 (1939); O. Mumm, *Ber.*, **72**, 1874 (1939).

[5] T. Lowry, *J. Chem. Soc.*, **127**, 1381 (1925); W. B. S. Newling and C. N. Hinshelwood, *ibid.*, 1357 (1936).

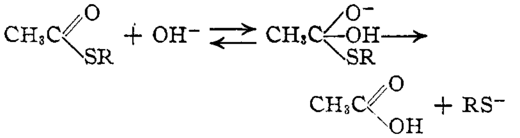
[6] C. K. Ingold and E. H. Ingold, *J. Chem. Soc.*, 756 (1932); J. N. E. Day and C. K. Ingold, *Trans. Faraday Soc.*, **37**, 686 (1941); L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., New York, N. Y., 1940, p. 355.

[7] J. Kendall and C. V. King, *J. Chem. Soc.*, **127**, 1778 (1925); J. Kendall and L. Harrison, *Trans. Faraday Soc.*, **24**, 588 (1928).

[8] C. N. Hinshelwood, K. J. Laidler, and E. W. Timm, *J. Chem. Soc.*, 848 (1938).

[9] E. N. Lassettre, *Chem. Rev.*, **20**, 267 (1937).

Therefore the preferred mechanism for alkaline thiolester hydrolysis is



$$\mathrm{CH_3C}\genfrac{}{}{0pt}{}{/\!\!/\mathrm{O}}{\backslash \mathrm{SR}} + \mathrm{OH^-} \rightleftarrows \mathrm{CH_3C}\genfrac{}{}{0pt}{}{/\mathrm{O^-}}{\genfrac{}{}{0pt}{}{-\mathrm{OH}}{\backslash \mathrm{SR}}} \longrightarrow \mathrm{CH_3C}\genfrac{}{}{0pt}{}{/\!\!/\mathrm{O}}{\backslash \mathrm{OH}} + \mathrm{RS^-} \qquad (6)$$

The activation energy for thiolester hydrolysis by mechanism (6) should be appreciably greater than for ester hydrolysis by mechanism (5) for two reasons: firstly, the coöperation of a water molecule lowers the energy necessary to add hydroxyl ion and to split off alcohol, as pointed out in the preceding paragraph; and secondly, the relatively greater polarization of the C–OR bond in esters compared to the C–SR linkage in thiolesters further lowers the energy necessary for hydroxyl ion addition and bond rupture. The latter reason alone, it should be noticed, is insufficient in itself to account for the large observed difference in activation energies (Table III), since its numerical value will amount to only about 1.6 kcal. as a comparison of acid catalyzed hydrolysis of ester and thiolester reveals (same Table). The steric hindrance to the hydrolysis reaction will be greater for esters (mechanism 5) than for thiolesters (mechanism 6) owing to the shielding effect of the water molecule, thus making the log PZ factor lower for ester than for thiolester hydrolysis, also in accord with observation. On the other hand, the alkaline hydrolyses of ester and of thiolester are similar in that E and log PZ for each reaction both increase with increase in acetone content of the reaction medium[10] (see Table II). The increase of activation energy with change in acetone concentration of the reaction medium is in the expected direction, since a decrease in the dielectric constant of the medium would be expected to decrease the ease of addition of hydroxyl ion at the carbonyl carbon atom.

Acknowledgment.—The author wishes to express his sincere thanks to Dr. Paul J. Flory for his valuable suggestions pertaining to this problem, and to Mr. Daniel Fouser for his assistance in part of the experimental work.

Summary

A kinetic study of the acid catalyzed and the alkaline hydrolysis of ethyl thiolacetate in aqueous acetone has been made. The acid catalyzed hydrolysis is first order with respect to thiolester and with respect to hydrogen ion concentration. The basic hydrolysis is second order. The activation energies are as follows: acid catalyzed hydrolysis 17,800 cal./mole; alkaline hydrolysis 13,000 cal./mole (24.6% acetone solution), 13,800 cal. (43.0% acetone), and 14,400 cal. (62.0% acetone).

A comparison of thiolester and ester hydrolysis has been made, and the mechanisms of hydrolysis have been discussed in view of the results obtained.

[10] R. A. Fairclough and C. N. Hinshelwood, *J. Chem. Soc.*, 538 (1937); C. N. Hinshelwood, K. J. Laidler and E. W. Timm, *ibid.*, 848 (1938); R. A. Harman, *Trans. Faraday Soc.*, **35**, 1336 (1939).

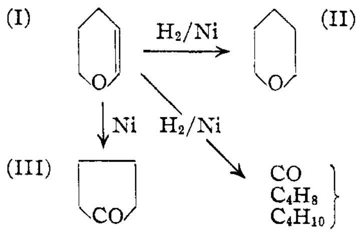
AKRON 16, OHIO RECEIVED NOVEMBER 22, 1947

[COMMUNICATION FROM THE CHEMISTRY DEPARTMENT, UNIVERSITY OF NOTRE DAME]

Reactions of Furan Compounds. IX. Catalyzed Rearrangement of 2,3-Dihydropyran into Cyclopentanone[1]

BY CHRISTOPHER L. WILSON

Experiments described in the present paper have shown that 2,3-dihydropyran (I) can be reduced in good yield to tetrahydropyran (II) by passing the vapor with hydrogen over a nickel catalyst at 100°. This confirms an earlier observation.[2] When the temperature was raised to 200° or above, however, two other reactions were noticed. One was ring fission to butane, butene and carbon monoxide and the other rearrangement to cyclopentanone (III). These two reactions have not been recorded before although reference has been made[2] to the formation of unidentified materials of "high molecular weight." Catalysts of nickel or cobalt and mixtures of each of these with copper were effective. On the other hand, copper chromite failed to induce any change whatever.



The yield of cyclopentanone, calculated on consumed dihydropyran, under favorable circumstances attained almost 30% but the reaction was always accompanied by fission. Replacement of added hydrogen by nitrogen suppressed to some extent both fission and reduction but the rearrangement was only affected to a minor extent. Thus hydrogen does not appear to be essential for this reaction. On the other hand, the catalyst to be active must be so for all three processes and deterioration toward one reaction is accompanied

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[1] This paper was presented before the Organic Division at the New York meeting of the American Chemical Society in September, 1947.

[2] British Patent 565,175, Bremner, Jones and Taylor.