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Mechanism and Reactivity of Hydrolysis of Aliphatic Sulfonate Esters

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It was shown with a five-membered sultone that the hydrolysis of aliphatic sultones in water proceeds substantially by $B_{AL}1$-E1 mechanism, and that it is a nucleophilic substitution reaction caused by hydroxyl ion and water. We carried out a kinetic experiment on the hydrolysis of 1,4-butanesultone and ethyl ethanesulfonate, both in water and in water - acetone mixed solvent. It was found that these aliphatic sulfonate esters were hydrolyzed substantially by $B_{AL}1$-E1 mechanism as in the case of a five-membered sultone, and in particular, ethyl ethanesulfonate was hydrolyzed by complete $B_{AL}1$-E1 mechanism. The results seem to be justified by a tracer experiment with $H_2{}^{18}O$. Namely, the ratios of the C–O fission to the S–O fission in 1,3-propanesultone and ethyl ethanesulfonate were 85.6 : 14.4 and 100 : 0, respectively. In strong alkaline solutions and approtic solvent - water systems, the S_N2 reaction involving attack of the nucleophile on sulfur atom took place partly in sultones, but practically not in linear sulfonate esters. On the other hand, the ratio of relative reaction rates of a five-membered sultone, a six-membered sultone, and a linear sulfonate ester in water is 37 : 1 : 7. Since E_a is nearly the same for these three compounds, the contribution of strain in the molecular structure to the reactivity is small, and in consequence the above ratio seems to be attributed to $\Delta S^{\neq}$.

We reported[1,2] that aliphatic five-membered and six-membered sultones are obtained from sulfonation of long chain alpha olefins with sulfur trioxide and that these sultones are converted into an useful detergent by hydrolysis the mechanism of which is ascribed substantially to $B_{AL}1$-E1. Kinetic data of the hydrolysis in D_2O suggested that the reaction is a nucleophilic substitution reaction by hydroxyl ion and water ($k_H/k_D = 1.03$).[2] However, the sultones used in the tracer experiments on the hydrolysis with $H_2{}^{18}O$ were long chain aliphatic sultones, which gave a mixture of hydroxy alkane sulfonates and alkene sulfonates by hydrolysis, and in consequence, an accurate result could not be expected because of difficulty in purification of the products. In this study, therefore, 1,3-propanesultone which yields only one product by hydrolysis was used in the $H_2{}^{18}O$ tracer experiment, and the previous results were reinvestigated.

Sulfonation of long chain alpha-olefins with sulfur trioxide gives six-membered sultones in addition to five-membered sultones which seem to differ from each other. Studies were thus made on the structural effect on the mechanism of hydrolysis and the reactivity of aliphatic sulfonate esters.

Hydrolysis of linear alkyl sulfonate esters was carried out in $H_2{}^{18}O$, and the results were compared with those obtained in the kinetic study.

Experimental

Materials. Commercial *1,3-propanesultone* (c.p.grade) was distilled under reduced pressure before use:bp 113.0—114.5°C/3 mmHg.

1,4-butanesultone was prepared from tetrahydrofuran according to the method of Truce and Hoerger.[3]: bp 112°C/1.5 mmHg, n_D^{25}1.437.

Found: C, 35.27; H, 5.64; S, 23.33%. Calcd for $C_4H_8SO_3$; C, 35.28; H, 5.92; S, 23.55%.

Ethyl ethanesulfonate was prepared from ethylsulfonyl chloride and ethyl alcohol according to the method of Sekera and Marvel[4]: bp 43°C/1 mmHg and n_D^{25}1.4229.

Found: C, 34.90; H, 7.40; S, 23.11%. Calcd for $C_4H_{10}SO_3$: C, 34.77; H, 7.29; S, 23.20%.

All the solvents used in kinetic experiments were purified by distillation.

Commercial *sodium perchlorate* (c.p.grade) was used.

Water enriched with ^{18}O was obtained from the Yeda Research and Development Co., Ltd. (Israel) and the atomic percentage of ^{18}O was 1.742.

Sodium hydroxide enriched with ^{18}O was prepared in an authentic manner from sodium ethoxide and water enriched with ^{18}O.

Measurement of the Rate of Hydrolysis. 1,4-Butanesultone and ethyl ethanesulfonate were hydrolyzed in water and in 65 vol% of aqueous acetone at room temperature under the following conditions, the pH being kept constant with a pH-stat (manufactured by Toa Electronic Ltd., Model HS-1B). The amount of sultones decomposed was calculated from that of sodium hydroxide required for counterbalancing the decrease of the pH by sulfonic acids formed by the decomposition of sultones.

Hydrolysis was carried out in an atmosphere of nitrogen to eliminate the effect of carbon dioxide in air. Sodium perchlorate was added to maintain the ionic strength of the reaction system constant.

Conditions of Hydrolysis. Concentration of the samples: 0.04 mol/*l*; Solvents: Water and aqueous acetone (65 vol%); Ionic strength: 0, 0.5 and 0.8; Temperatures: 25.0—55.0°C; pH: 3.0—11.3.

Determination of the Reaction Rate Constant (k_1). Using a linear equation, logs $S/(S-S')$ was plotted *versus* time t(sec), where S is the initial amount of sultone and S' is amount of sultone decomposed in time t(sec). k_1 was obtained from the slope of the plots.

Hydrolysis in $H_2{}^{18}O$. *Hydrolysis of 1,3-Propanesultone*: 1,3-Propanesultone (1.954 g, 1.6×10^{-2} mol) was dissolved in a solution containing 750 mg (1.8×10^{-2} mol) of $Na^{18}OH$ in 10 m*l* of $H_2{}^{18}O$, and the solution was heated on a water bath at 70°C for 2.5 hr. The pH of the reaction mixture was greater than 12 at the end of the reaction. The unreacted sultone was removed by extraction with 5 m*l* of petroleum

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[1] M. Nagayama, H. Okada, and S. Tomiyama, *Kogyo Kagaku Zasshi*, **72**, 2248 (1969).

[2] A. Mori, M. Nagayama, and H. Mandai, *ibid.*, **74**, 715 (1971).

[3] W. E. Truce and F. D. Hoerger, *J. Amer. Chem. Soc.*, **76**, 5357 (1954).

[4] V. C. Sekera and C. S. Marvel, *ibid.*, **55**, 345 (1933).

ether carried out four times. The aqueous layer was neutralized with N/10 HCl, and the solvent was evaporated to leave crude sulfonate behind. Recrystallization from 95% ethyl alcohol gave 1.80 g of needles of pure sulfonate. NMR spectral analysis showed that the sulfonate thus obtained contained only sodium 3-hydroxypropanesulfonate.

Pure sulfonate (1 g) was treated with 3 m*l* of dimethylformamide and 40 m*l* of thionyl chloride to give chlorosulfonyl chloride according to the method of Bosshard *et al.*[5] The product was purified by distillation under reduced pressure: yield, 100 mg, bp 65.0°C/3 mmHg; IR spectra, strong SO_2–Cl absorption was observed at 1380 and 1165 cm^{-1}. The atomic percentage of excess ^{18}O in the sulfonate and chlorosulfonyl chloride was measured according to the method of Rittenberg and Ponticorvo[6] and the ratio of the C–O fission to the S–O fission was determined.

Hydrolysis of Ethyl Ethanesulfonate: To a solution of 750 mg (1.8×10^{-2} mol) of Na^{18}OH in 10 m*l* of $H_2{}^{18}O$ was added 2.211 g (1.6×10^{-2} mol) of ethyl ethanesulfonate, and the hydrolysis was carried out with stirring at 80°C for 2 hr on a water bath. The pH of the reaction mixture at the end of the reaction was greater than 12. The unreacted ethyl ethanesulfonate was extracted with ethyl ether, the aqueous layer was neutralized with N/10 hydrochloric acid, the solvent was removed, and NaCl was separated to yield crude sulfonate. Recrystallization from 95% ethanol gave 1.50 g of needles of pure sulfonate. The ratio of the C–O fission to the S–O fission was determined from the atomic percentage of excess ^{18}O in the sulfonate thus obtained and ^{18}O enriched aqueous sodium hydroxide solution used for the hydrolysis.

Results and Discussion

Kinetic Studies of Hydrolysis. Hydrolysis of 1,4-Butanesultone: The relationship between log K_1 and pH in the hydrolysis of 1,4-butanesultone in 65 vol % of aqueous acetone and in water is shown in Fig 1. It is apparent that a six-membered sultone undergoes exactly the same type of reaction as a five-membered sultone. A first-order reaction takes place in water, but in a mixed system consisting of an aprotic solvent and water, a rise is observed in the curve and this tendency becomes slightly less pronounced than in the case of the five-membered sultone on the alkaline side. However, from the rise observed in the curve, it seems that an S_N2-E2 reaction takes place to some extent, although a $B_{AL}1$-E1 reaction predominates.

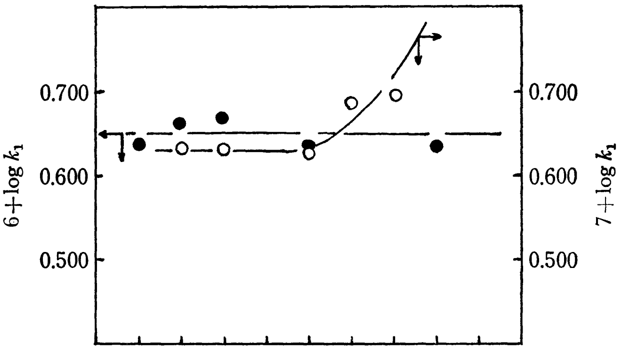

Fig. 1. log k_1 *vs.* pH in the hydrolysis of C_4 1,4-sultone.
○ in 65 vol % acetone, at 50°C, ionic strength 0.5
● in water, at 45°C, ionic strength 0.5

The effect of the ionic strength in 65 vol % of aqueous acetone on the alkaline side, where the reactivity of the S_N2-E2 reaction is large, is shown in Table 1. Here again, the positive salt effect is observed as before, and the increase of electron charge in the transition state, namely the cause of the monomolecular reaction, is detected.

Table 1. Effect of ionic strength on the K_1 value of hydrolysis of C_4 1,4-sultone (at 50°C, pH 9 in 65 vol % Acetone)

Ionic strength	6+log K_1
0	0.629
0.5	0.696
0.8	0.788

Hydrolysis of Ethyl Ethanesulfonate: The relationship between log K_1 and pH in the hydrolysis of ethyl ethanesulfonate in 65 vol % of aqueous acetone and in water is shown in Fig. 2. A clean first-order reaction is observed both in the aqueous acetone and in water. This suggests that, in contrast to sultones, ethyl ethanesulfonate is hydrolyzed completely by the $B_{AL}1$-E1 reaction to the exclusion of the S_N2-E2 reaction. This will be examined later with reference to the analysis of ^{18}O contained in the products of the hydrolysis of ethyl ethanesulfonate in ^{18}O enriched water.

As shown in Fig. 2, the effect of the ionic strength was partly at pH 4 and 10, but only a weak salt effect was observed.

Kinetic Constants of 1,4-Butanesultone and Ethyl Ethanesulfonate: The Arrhenius plots for the hydrolysis of

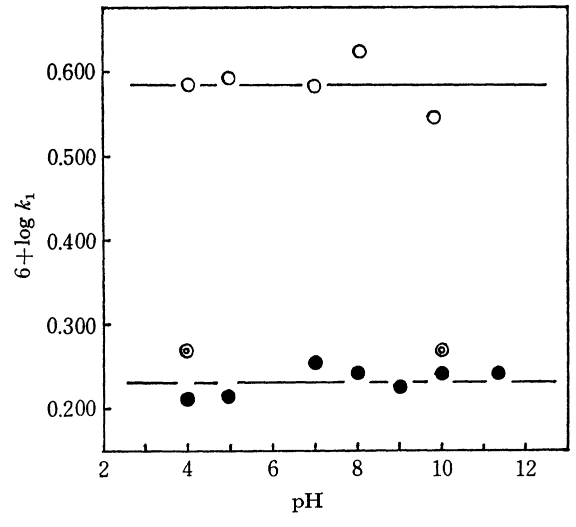

Fig. 2. log k_1 *vs.* pH in the hydrolysis of ethyl ethane sulfonate and effect of ionic strength on the k_1 values.
● in 65 vol % acetone, at 45°C, ionic strength 0.5
◎ in 65 vol % acetone, at 45°C, ionic strength 0.8
○ in water, at 25°C, ionic strength 0.5

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[5] H. H. Bosshard, R. Mory, M. Schmid, and Hch. Zollinger, *Helv. Chim. Acta*, **42**, 1653 (1959).

[6] D. R. Rittenberg and L. Ponticorvo, *J. Appl. Rad. Isotopes*, **1**, 208 (1956).

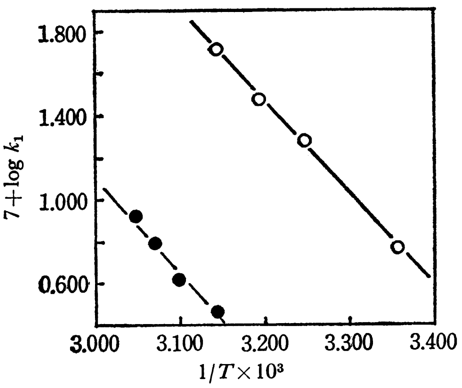


Fig. 3. Arrhenius plots for the C_4 1,4-sultone hydrolysis at pH 7, ionic strength 0.5.
● in 65 vol % acetone ○ in water

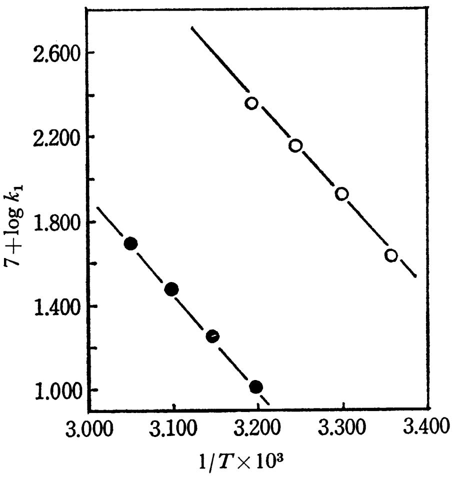


Fig. 4. Arrhenius plots for the ethyl ethane sulfonate hydrolysis at pH 7, ionic strength 0.5.
● in 65 vol % acetone ○ in water

1,4-butanesultone and ethyl ethanesulfonate in 65 vol % of aqueous acetone and in water at pH 7 and ionic strength 0.5 are shown in Figs. 3 and 4, respectively. Table 2 was prepared from these results. For comparison, the data on 1,3-propanesultone reported previously[2)] are also shown.

TABLE 2. KINETIC CONSTANTS (in 65 vol % of aqueous acetone at 25°C, and ionic strength 0.5)

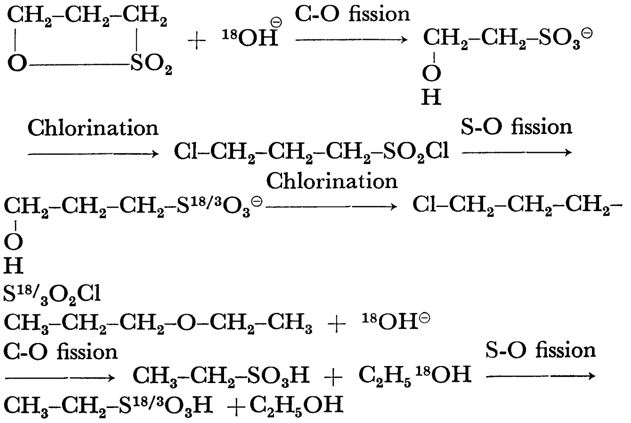
	$K_1 \times 10^7$ (sec^{-1})	E_a (Kcal/mol)	$\Delta S^{\ddagger}$ (e u)
CH_2-CH_2-CH_2 O————SO_2	18.8	20.2	−17.1
	215$^{a)}$		
	130$^{b)}$ (at 20°C)	20.4±0.1$^{b)}$	−13.8$^{b)}$ (at 40°C)
CH_2-CH_2-CH_2-CH_2 O——————SO_2	0.316	20.5	−24.0
	5.76$^{a)}$	20.0$^{a)}$	−20.0$^{a)}$
CH_3-CH_2-SO_2O- CH_2-CH_3	1.88	21.3	−17.9
	42.3$^{a)}$	20.9$^{a)}$	−13.2$^{a)}$

a) in water
b) Bordwell's Data[7)] in water

As shown in Table 2, the ratio of relative reaction rates of a five-membered sultone, a six-membered sultone, and a linear alkyl sulfonate ester in water at pH 7 is 37:1:7. This ratio seems to be the relative rate *via* B_{AL}1-E1 mechanism, because in the relationship between log K_1 and pH the values of log K_1 are constant below pH 10. Since E_a is nearly the same, these compounds can be regarded to undergo practically the same type of reaction. On the other hand, the strain in the ring should depend on the enthalpy term.[8,9)] This term, however, is nearly the same, *viz.*, the difference in free energy of strain between a five-membered ring and a six-membered ring is slight. Consequently, contribution of the strain to the reactivity in the hydrolysis of sultones seems to be small and the reactivity is controlled practically by the entropy term ($\Delta S^{\ddagger}$) alone.

Hydrolysis in $H_2{}^{18}O$. The hydrolysis of sultones and ethyl ethanesulfonate proceed mostly by B_{AL}1-E1 mechanism, but the results of kinetic studies suggest that S_N2-E2 reaction also occurs in the case of sultones. For the sake of confirmation, hydrolysis was carried out in $H_2{}^{18}O$ in a strongly alkaline medium (pH>12), and the atomic percentage of excess ^{18}O in the aqueous sodium hydroxide, hydrolysis products and its chlorinated compound were measured to determine the ratios of the C–O fission to the S–O fission in sultones and ethyl ethanesulfonate.

A previous kinetic study[2)] indicates that both long chain substituted 1,3-sultones and unsubstituted 1,3-sultones undergo the same types of reactions and the ratios of the C–O fission to the S–O fission are nearly the same for the two groups. The samples of long chain substituted sultones for the analysis of ^{18}O present technical problems with respect to purification. Unsubstituted sultones which yield a single component, and are easily purified, seem to give more accurate values for the C–O and S–O fission. Thus, the ratio of the C–O fission to the S–O fission in 1,3-propanesultone seems to be applicable to aliphatic five-membered sultones.



$$\begin{array}{l}CH_2\text{-}CH_2\text{-}CH_2\\ |\qquad\qquad |\\ O\text{————}SO_2\end{array} + {}^{18}\overset{\ominus}{O}H \xrightarrow{\text{C-O fission}} \underset{\underset{H}{|}}{\underset{O}{CH_2}}\text{-}CH_2\text{-}SO_3^{\ominus}$$

$$\xrightarrow{\text{Chlorination}} Cl\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}SO_2Cl \xrightarrow{\text{S-O fission}} \underset{\underset{H}{O}}{CH_2}\text{-}CH_2\text{-}CH_2\text{-}S^{18/3}O_3^{\ominus} \xrightarrow{\text{Chlorination}} Cl\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}S^{18}/{}_3O_2Cl$$

$$CH_3\text{-}CH_2\text{-}CH_2\text{-}O\text{-}CH_2\text{-}CH_3 + {}^{18}OH^{\ominus} \xrightarrow{\text{C-O fission}} CH_3\text{-}CH_2\text{-}SO_3H + C_2H_5{}^{18}OH \xrightarrow{\text{S-O fission}} CH_3\text{-}CH_2\text{-}S^{18/3}O_3H + C_2H_5OH$$

The ratios of the C–O fission to the S–O fission in 1,3-propanesultone and ethyl ethanesulfonate are shown in Table 3.

[7)] F.G. Bordwell, C.E. Osborne, and R.D. Chapman, *J. Amer. Chem. Soc.*, **81**, 2698 (1959).

[8)] F.S. Dainton, T.R.E. Devlin, and P.A. Small, *Trans. Faraday Soc.*, **51**, 1710 (1955).

[9)] P. A. Small, *ibid.*, **51**, 1717 (1955).

Table 3. Atomic percentage of excess ^{18}O and the ratios of the C-O fission to the S-O fission in the hydrolysis of 1,3-propanesultone and ethyl ethanesulfonate

Condition of Hydrolysis \ Sample	1,3-propanesultone	Ethyl ethanesulfonate
	at 70°C, for 2.5 hr above pH 12	at 80°C, for 2 hr above pH 12
$Na^{18}OH$-$H_2{}^{18}O$	1.459 (atom %)	1.503 (atom %)
Resulted Sulfonate	0.351	0.002
Chlorosulfonyl-chloride	0.101	—
C-O fission	85.6 (%)	100 (%)
S-O fission	14.4	0

The hydrolysis of a five-membered sultone occurs *via* scission of the S–O linkage even in water in a strongly alkaline medium. Since the S–O fission *via* monomolecular cleavage is difficult to conceive, the S_N2 reaction seems to be possible. This is reasonable if one considers that $OH^{\ominus}$, a hard base, tends to attack $-^{\oplus}SO_2$ more readily than $C^{\oplus}$ since $-^{\oplus}SO_2$ is a harder acid.

The S_N2 reaction tends to occur in aliphatic sultones when the activity of hydroxyl ion is increased such as in a strong alkaline medium or in a system consisting of an aprotic solvent and water.

On the other hand, in the hydrolysis of ethyl ethanesulfonate not the S_N2 reaction but the $B_{AL}1$-E1 reaction *via* the C–O fission occurs exclusively, both in a strong alkaline medium and in an aprotic solvent-water system. This result agrees with the kinetic results.

The S_N2 reaction seems to occur in six-membered sultones to a slightly less extent than in five-membered sultones, since a rise in the plot of log K_1 *versus* pH in the former sultone in 65 vol % of aqueous acetone is slightly less pronounced.

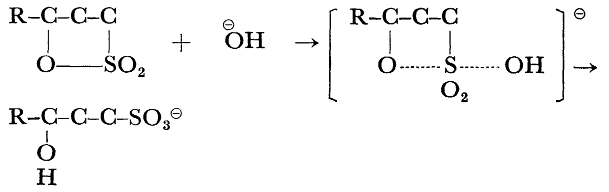
It is obvious that the hydrolysis of sultones proceeds by $B_{AL}1$-E1 mechanism. It is considered that in ordinary hydrolysis systems, where the activity of hydroxyl ion is not very high, only the $B_{AL}1$-E1 reaction occurs as in the case of ethyl ethanesulfonate. Consequently, the ratio of K_1 of a five-membered sultone, a six-membered sultone, and ethyl ethanesulfonate in water at pH 7 shows the relative reactivity of hydrolysis by the $B_{AL}1$-E1 reaction.

We thus conclude that in the reactions of hydrolysis of aliphatic alkyl sulfonate esters which proceed by the $B_{AL}1$-E1 reaction *via* the cleavage of C–O bond, the contribution of a ring strain to reactivity is very small, and the reactivity seems to be decided essentially by the entropy term ($\Delta S^{\neq}$).

The S_N2 reaction which follows a fission of S–O bond only occurs when the sultones are reacted in a solvent where the activity of hydroxyl ion is very high. This reaction seems to occur more easily in a five-membered sultone than a six-membered sultone.

However, in straight chain alkyl sulfonate ester which has no ring strain, the S_N2 reaction was not observed. It is obvious that in this reaction, contribution of the ring strain to the reactivity is very large. This tendency is consistent with the observation by Kaiser *et al.*[10] on aliphatic five-membered, six-membered and straight chain alkyl sulfates.

It is very interesting to compare these observations with the study by Müller *et al.*[11] with regard to the reactions of hydrolysis of aromatic sultones, in which only the S_N2 reaction can occur. Even in this case, contribution of the ring strain is also very large.



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[10] E. T. Kaiser, M. Panar, and F. H. Westheimer, *J. Amer. Chem. Soc.*, **85**, 602 (1963).

[11] P. Müller, D. F. Mayers, O. R. Zaborsky, and E. T. Kaiser, *ibid.*, **91**, 6732 (1969).