molecular and may be third-order under certain conditions. Step 7 of the mechanism proposed in this study is consistent with these arguments. Equation 7 has been discussed on the basis of bonding,[17] and it has been concluded that it would occur with little or no activation energy, similar to the case of the OCl radical.

Reactions 2 and 3, which have been used by previous investigators to describe the pyrolysis mechanism, in all probability contribute significantly to the reaction under the conditions in the present study.[18] However, these steps, when combined with (1) form a first-order nonchain process, or combined with (1) and (5) form a three-halves-order chain process (assuming step 2 produces F atoms). In fact, all mechanisms devised using step 3 as a termination led to orders greater than or equal to one. Thus, although many steps may contribute to the overall reaction, the observed less-than-first-order kinetics strongly indicate that steps 5, 6, and 7 must also be included in the mechanism of the reaction at lower temperatures. In addition, owing to the contributions of steps other than those included in the simple mechanism, i.e., steps 1, 5, 6, and 7, eq 9 is un-

doubtedly overly simplified and k_2' is not equal to $2k_1$ but is made up of a complex group of constants.

The observation that the order increases toward one at higher temperatures implies that the activation energy for the three-halves-order term in the rate law must be lower than that of the second-order term, i.e., less than 39.2 kcal mol^{-1}. Based on presently available thermochemical information (which has a considerable uncertainty) for the reactions in eq 1, 6, and 7, i.e., unless activation energies for steps 1 and 7 are larger than expected and that for step 6 smaller, it is difficult to explain such a low overall activation energy.

In conclusion, it appears that the value for the apparent first-order rate constant for the pyrolysis of OF_2 is reasonably well established. However, it is believed that its significance in terms of elementary steps is still unresolved. The mechanism proposed in this paper is based primarily on the observed low order and does not agree with the relative importance of the steps in the mechanism proposed by Lin and Bauer.[6]

(17) M. Green and J. W. Linnett, *J. Chem. Soc.*, 4959 (1960).
(18) A steady-state treatment of a mechanism which contains all the steps which probably contribute to the reaction yields a solution which is unmanageably complex and experimentally unverifiable. Thus, the results of these calculations are not reported.

Properties and Reactions of 1,3-Oxathiolanes. II. Kinetics, Mechanisms, and Solvent Deuterium Isotope Effects in the Hydrolytic Decomposition of 1,3-Oxathiolane, 2-Methyl-1,3-oxathiolane, and 2,2-Dimethyl-1,3-oxathiolane[1]

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Abstract: The rates of acid-catalyzed hydrolysis of 1,3-oxathiolane and its 2-methyl and 2,2-dimethyl derivatives have been measured in aqueous $HClO_4$ and $DClO_4$ solutions and in several H_2O–D_2O mixtures containing perchloric acid. The activation entropy for the hydrolysis of 2-methyl-1,3-oxathiolane in 2.025 M $HClO_4$ was −14.3 cal mol^{-1} deg^{-1} and that for the hydrolysis of 2,2-dimethyl-1,3-oxathiolane in 0.196 M $HClO_4$ +0.9 cal mol^{-1} deg^{-1}. The hydrolysis of the acetone derivative was found to be sterically hindered, as manifested by its only 57 times higher rate than that of 2-methyl-1,3-oxathiolane. The experiments in mixed water showed that the ratio of the activity coefficients of the transition state and the ground state is dependent on the deuterium atom fraction. All the data and the data for the hydrolysis in moderately concentrated perchloric acid solutions are, however, consistent with an A-1 mechanism in which the ring rupture occurs at the acetal carbon-oxygen bond.

Although the acid-catalyzed hydrolysis of acyclic and cyclic acetals has been thoroughly investigated,[2-6] very little attention has been paid to the de-

tails of the hydrolytic decomposition of cyclic acetals that contain two different heteroatoms.[7-9]

De and Fedor[7] and Fife and Jao[8] reported some results on the acid-catalyzed and mercuric-ion-catalyzed cleavage of 2-(substituted phenyl)-1,3-oxathiolanes. Moreover, Fife and Hagopian[9] also investigated the

(1) Paper I: K. Pihlaja, *Suom. Kemistilehti, B*, **43**, 143 (1970).
(2) K. Pihlaja, *Ann. Univ. Turku., Ser. AI*, No. 114 (1967).
(3) A. Kankaanperä, *ibid.*, No. 95 (1966).
(4) (a) K. Pihlaja and K.-J. Teinonen, *Suom. Kemistilehti, B*, **43**, 206 (1970); (b) K. Pihlaja and K.-J. Teinonen, *Acta Chem. Scand.*, **25**, 323 (1971).
(5) A. Kankaanperä, *Suom. Kemistilehti, B*, **43**, 133 (1970).
(6) See also citations in ref 2-5.

(7) N. C. De and L. R. Fedor, *J. Amer. Chem. Soc.*, **90**, 7266 (1968).
(8) T. H. Fife and L. K. Jao, *ibid.*, **91**, 4217 (1969).
(9) T. H. Fife and L. Hagopian, *ibid.*, **90**, 1007 (1968).

hydrolytic behavior of 2-(substituted phenyl)-3-ethyl-1,3-oxazolidines under different conditions. In acetals containing two different heteroatoms, such as 1,3-oxathiolanes, either the oxygen atom or the sulfur atom may be protonated. It is very interesting to know to which atom the proton adds before the critical transition state is formed, i.e., whether the C–O bond or the C–S bond is broken in the ring cleavage.

De and Fedor[7] concluded that protonation occurs predominantly on the oxygen atom in the acid-catalyzed hydrolysis of 2-(substituted phenyl)-1,3-oxathiolanes which in reality means that the ring cleavage should principally involve the acetal carbon–oxygen bond. Further, these authors proposed the A-2 mechanism for the hydrolysis reaction.

Fife and Jao[8] came to a different conclusion, namely, that the ring rupture proceeds via the sulfur-protonated conjugate acid and hence that the acetal carbon–sulfur bond is broken in the critical transition state. Moreover, they proposed the A-1 mechanism for the hydrolysis reaction. The above two investigations revealed several confusing facts and for this reason additional study was considered justified.

Deductions about the relations in the hydrolysis of a series of compounds may most easily be made by studying suitable simple model compounds. Consequently, unsubstituted 1,3-oxathiolane and its 2-methyl and 2,2-dimethyl derivatives were selected for the study of the basic phenomena in the acid-catalyzed hydrolysis of 1,3-oxathiolanes.

Experimental Section

1,3-Oxathiolane, 2-methyl-1,3-oxathiolane, and 2,2-dimethyl-1,3-oxathiolane were available from a previous study.[1]

Kinetic Measurements. The rates were measured by following the appearance of the aldehydic product with a Beckmann DU quartz spectrophotometer. The reactions were initiated by adding 1.6 μl of the substrate in question to about 3 ml of a perchloric acid solution in a cuvette that had equilibrated at the chosen temperatures. In the case of 1,3-oxathiolane, the hydrolysis rates in HClO$_4$ and DClO$_4$ solutions at 40° were measured by glc using a Perkin-Elmer F 11 gas chromatograph equipped with a column containing 5% Carbowax 20M on Chromosorb G (60/80 mesh). The reference compound in the latter analyses was 1-butanol. The first-order rate coefficients were calculated from equation

$$k = \frac{2.303}{t} \log \frac{D_\infty - D_0}{D_\infty - D_t} \text{ or } k = \frac{2.303}{t} \log \frac{h_0}{h_t}$$

where D_∞ is the observed optical density at the end of the reaction, D_0 that at the beginning of the reaction, and D_t the optical density at time t. Correspondingly, h_0 was the relative peak height at the beginning of the reaction and h_t that at time t. h_∞ was taken to be zero.

Results

The rate coefficients for hydrolysis of 1,3-oxathiolane (1), 2-methyl-1,3-oxathiolane (2), and 2,2-dimethyl-1,3-oxathiolane (3) in aqueous perchloric acid solutions at various temperatures are given in Table I. The presented rate coefficients are mean values for two to three replicate runs.

The values of the activation parameters derived from the rate data by the method of least squares are shown in Table II.

Rate coefficients for the hydrolysis of 2 at 40° and for the hydrolysis of 3 at 25° in various HClO$_4$ solutions are presented in Table III. Figure 1 shows plots
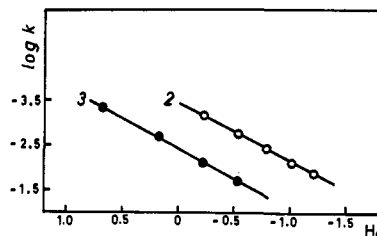

Figure 1. Plots of the logarithms of the first-order rate coefficients vs. H_0 for hydrolysis of 2-methyl-1,3-oxathiolane (2) at 40° and for hydrolysis of 2,2-dimethyl-1,3-oxathiolane (3) at 25°.

of the logarithms of the rate coefficients, k, vs. H_0, the Hammett acidity function.[10] The slopes of the plots are -1.27 for 2 at 40° and -1.34 for 3 at 25°.

Table I. First-Order Rate Coefficients, k, for the Acid-Catalyzed Hydrolysis of 1,3-Oxathiolane (1), 2-Methyl-1,3-oxathiolane (2), and 2,2-Dimethyl-1,3-oxathiolane (3) at Different Temperatures

	1	2	3
		[HClO$_4$], M	
	1.682	2.025	0.196
Temp, °C	10^4k, sec^{-1}	10^4k, sec^{-1}	10^4k, sec^{-1}
25			4.45^a
30		12.4	7.84
35		21.7	13.8
40	0.0121	34.1	26.1
45		52.8	43.7

^{a} In 0.200 M HCl. The standard errors of the rate coefficients did not exceed 2%.

Table II. Second-Order Rate Constants and Arrhenius Activation Parameters for the Hydrolysis of 2-Methyl-1,3-oxathiolane (2) in 2.025 M HClO$_4$ and for the Hydrolysis of 2,2-Dimethyl-1,3-oxathiolane (3) in 0.196 M HClO$_4$^{a}

Temp, °C	2 $k_{H_3O^+}$, M^{-1} sec^{-1}	3 $k_{H_3O^+}$, M^{-1} sec^{-1}
25		0.00222^b
30	0.000611	0.00400
35	0.00107	0.00704
40	0.00168	0.0133
45	0.00261	0.0223
$\Delta H^\ddagger$, kcal/mol	17.85 ± 0.60	21.34 ± 0.33
$\Delta S^\ddagger$, cal mol^{-1} °K^{-1}	-14.3 ± 1.9	$+0.9$ ± 1.1
$\Delta G^\ddagger$, kcal mol^{-1}	22.13 ± 0.03	21.08 ± 0.02

^{a} Solvent water. ^{b} In 0.200 M HCl.

Table III. Rate Coefficients for the Hydrolysis of 2-Methyl-1,3-oxathiolane (2) at 40° and 2,2-Dimethyl-1,3-oxathiolane (3) at Various HClO$_4$ Concentrations in Water

[HClO$_4$], M	$-H_0$	2 10^3k, sec^{-1}	3 10^3k, sec^{-1}
0.200^a	-0.69		0.445
0.494	-0.18		1.922
0.997	0.22	0.693	7.165
1.498	0.53	1.613	18.36
2.025	0.79	3.407	
2.501	1.01	6.892	
2.950	1.21	12.29	

^{a} HCl.

(10) E.g., P. Salomaa, Elfte Nord. Kemistmötet, Berättelse Föredrag, Turku, 338 (1962).
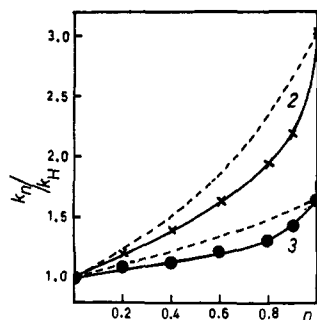
Figure 2. Plots of k_n/k_H vs. deuterium atom fraction (n) for hydrolysis of 2-methyl-1,3-oxathiolane (2) at 40° and for hydrolysis of 2,2-dimethyl-1,3-oxathiolane (3) at 25°. The dotted lines show the theoretical curves calculated from eq 1.

A linear dependence[10] prevails also between (log $k + H_0$) and log a_{H_2O} for the reactions in $HClO_4$ solutions (not shown); the slope is -5.2 for 2.

Rate coefficients for the hydrolysis of 1,3-oxathiolane and 2-methyl-1,3-oxathiolane at 40° and for the hydrolysis of 2,2-dimethyl-1,3-oxathiolane at 25° at various $LClO_4$ concentrations are shown in Table IV.

Table IV. Rate Coefficients for the Hydrolysis of 1,3-Oxathiolane (1) and 2-Methyl-1,3-oxathiolane (2) at 40° and for the Hydrolysis of 2,2-Dimethyl-1,3-oxathiolane (3) at 25° in $HClO_4$-$DClO_4$ Mixtures in L_2O

1					
[LClO4], M	1.68	1.68	1.68	1.70	1.70
n	0	0	0	1	1
$10^6 k$, sec^{-1}	1.22	1.22	1.20	3.06	3.46
k_D/k_H	2.69				
	± 0.22				
2					
[LClO4], M	1.70	1.68	1.69	1.69	1.70
n	0	0.200	0.402	0.605	0.799
$10^8 k$, sec^{-1}	2.22^a	2.66	3.08	3.61	4.33
k_n/k_H	1.00	1.20	1.39	1.63	1.95
[LClO4], M	1.70	1.70	1.70	1.70	
n	0.899	1	1	1	
$10^8 k$, sec^{-1}	4.86	6.77	6.85	6.62	
k_n/k_H	2.19	3.05	3.09	2.98	
	Av 3.04 ± 0.03				
3					
[LClO4], M	0.200^b	0.197	0.198	0.199	0.200
n	0	0.196	0.396	0.595	0.795
$10^8 k_n$, M^{-1} sec^{-1}	2.22	2.43	2.51	2.71	2.91
k_n/k_H	1.00	1.09	1.13	1.22	1.31
[LClO4], M	0.201	0.2015	0.2015	0.2015	
n	0.902	1	1	1	
$10^8 k_n$, M^{-1} sec^{-1}	3.19	3.72	3.61	3.63	
k_n/k_H	1.43	1.67	1.62	1.63	
	Av 1.64 ± 0.02				

^{a} Extrapolated from the plot of log k vs. H_0 in Figure 2. ^{b} HCl.

The ratios k_n/k_H are plotted as a function of n for 2 at 40° and for 3 at 25° in Figure 2. The plots obtained by substituting the different values of n in the equation

$$\frac{k_n}{k_H} = \frac{1 - n + (k_D/k_H)l^3 n}{(1 - n + nl)^3} \quad (1)$$

where $l = 0.703$ at 40° and 0.693 at 25°,[11] are also drawn in Figure 2.

(11) (a) P. Salomaa, L. L. Schaleger, and F. A. Long, J. Amer. Chem. Soc., 86, 1 (1964); (b) K. Pihlaja and M. Seilo, Acta Chem. Scand., 22, 3010 (1968); (c) P. Salomaa and V. Aalto, ibid., 22, 2035 (1966).

Discussion

Effect of Methyl Substitution at the Acetal Carbon on the Hydrolysis Rate. The hydrolysis of 2-methyl-1,3-oxathiolane has a rate coefficient of 2.72×10^{-3} sec^{-1} in 1.68 M $HClO_4$ at 40° (Table IV), whereas that of 1,3-oxathiolane under the same conditions is 1.21×10^{-6} sec^{-1}. Consequently, one methyl group on the acetal carbon increases the hydrolysis rate about 2250-fold. The rate increase in the case of the analogous 1,3-dioxolanes is about 4300-fold.[3] In other words, the accelerating effect of methyl substitution on the acetal carbon is similar in both series of compounds.

Similarly, the hydrolysis of 2-methyl-1,3-oxathiolane has a rate coefficient of 0.456×10^{-4} sec $^{-1}$ in 0.196 M $HClO_4$ at 40°, whereas 2,2-dimethyl-1,3-oxathiolane hydrolyses has a rate of 2.61×10^{-3} sec^{-1} under these conditions. The rate increase due to the second methyl substituent is thus only 57-fold. In the case of the analogous 1,3-dioxolanes the rate increase is only tenfold,[3] but the somewhat smaller steric retardation[3] in 2,2-dimethyl-1,3-oxathiolane is easily understood when it is taken into account that the length of a C–S bond is about 1.82 Å and the length of a C–O bond only about 1.42 Å.

In his thesis, Kankaanperä[3] carefully and reliably pointed out that in the attainment of the critical transition state one of the groups bound by the bonds attached to the acetal carbon in 1,3-dioxolanes is forced to bend inward and the other outward in relation to the ring. The inward bending cannot be achieved without a certain amount of steric interaction with the other ring substituents. This steric retardation appreciably lowers the hydrolysis rate of 2,2-dialkyl-substituted 1,3-dioxolanes and is enough to explain the apparently low rate ratio between, e.g., 2-methyl- and 2,2-dimethyl-1,3-dioxolanes.[3]

In the light of the above discussion, it is evident that the somewhat greater rate ratio between 2-methyl-1,3-oxathiolane and 2,2-dimethyl-1,3-oxathiolane is really due to the difference in the C–S and C–O bond lengths. The interaction between a bending 2-methyl and 4-hydrogen is almost negligible, whereas that between the bending 2-methyl and 5-hydrogen is even initially around 1 kcal/mol.[12]

The rate variation in the studied 1,3-oxathiolanes is thus in accordance with an A-1 mechanism.

Temperature Dependence of the Hydrolysis Rates. The plots of log $k_{H_3O^+}$ against reciprocal temperature for 2 and 3 are linear, and the thermodynamic parameters shown in Table II are quite normal for an A-1-type mechanism.[2,3] Even the relatively low entropy change for the 2-methyl derivative is still within the limits for a hydrolytic decomposition occurring by the A-1 mechanism. In several recent papers it has been shown that the entropy range for reactions occurring by the A-1 mechanism[4,5] may well be 10–20 cal mol^{-1} deg^{-1}.

Hydrolysis in Moderately Concentrated Perchloric Acid Solutions. The plots of log k against H_0 in Figure 2 show an excellent linear dependence with slope -1.27 for 2-methyl-1,3-oxathiolane and -1.34 for 2,2-dimethyl-1,3-oxathiolane; also the plots of (log $k + H_0$) against log a_{H_2O} are linear. Very recently, Guinot[13]

(12) K. Pihlaja and R. Keskinen, estimation confirmed by an independent investigation dealing with the conformations of alkyl-substituted 1,3-oxathiolanes which will be published in near future.

measured rates of hydrolysis of 2,2-dimethyl-1,3-oxa-thiolane in HCl solutions at 25°, and his results yielded for the slope of the plot of log k against H_0 the value -1.30, in close agreement with our value at 40°. Also, these data are consistent with the A-1 mechanism.

In this connection, it is worth mentioning that Fife and Jao[8] studied the hydrolysis of 2-(p-nitrophenyl)-1,3-oxathiolane in a series of HCl solutions at 30°. They reported the value -1.23 for the slope of the plot of log k against H_0. In an earlier paper,[14a] Fife proposed the A-2 mechanism for the hydrolysis of 2-(p-nitrophenyl)-4,4,5,5-tetramethyl-1,3-dioxolane. However, his experimental results seem to be less reliable. If we take into account only the first four of his points in the plots of log k against H_0 and of (log k + H_0) against log a_{H_2O}, the values -1.1 and -1.7 (other points yield -0.7 and $+2.4$; all points give -0.9 and $+1.3$) are derived for the slopes of these relatively linear curves, and these values are well within the limits for normal acetal hydrolysis and the A-1 mechanism. The deviations from these plots at higher HCl concentrations may be due to a change in mechanism, or more probably to a side reaction, since we have also sometimes observed that hydrolysis experiments in over 3-4 M HCl solutions do not give correct results when the spectrophotometric method is used.

In another paper, Fife and Brod[14b] reported the values $\Delta H^\ddagger = 17.5$ kcal/mol and $\Delta S^\ddagger = -15.8$ cal mol^{-1} deg^{-1} for the hydrolysis of 2-(p-nitrophenyl)-4,4,5,5-tetramethyl-1,3-dioxolane. Later, Fife and Jao published a paper on 1,3-oxathiolanes[8] in which they presented the values $\Delta H^\ddagger = 16.8$ kcal/mol and $\Delta S^\ddagger = -13.2$ cal mol^{-1} deg^{-1} for the hydrolytic decomposition of 2-phenyl-1,3-oxathiolane. Despite the similarity of the values of the thermodynamic quantities in both cases, Fife proposed the A-2 mechanism in the former case and the A-1 mechanism in the latter. The proposal of the A-2 mechanism for the hydrolytic decomposition of 2-(para-substituted phenyl)-4,4,5,5-tetramethyl-1,3-dioxolanes was also based on the fact[14] that the replacement of the hydrogen at the acetal carbon by a methyl group in 2-phenyl-4,4,5,5-tetramethyl-1,3-dioxolane produces over a 500-fold rate decrease. However, inspection of models and the understanding of the bending reactions considered by Kankaanperä[3] led to the conclusion that the rate decrease might be due to the increasing steric interaction in the attainment of the critical transition state.

In the opinion of the author, 1,3-dioxolanes generally hydrolyze by an A-1 mechanism, although some of them, e.g., those with highly electronegative substituents, such as a trichloromethyl group on the acetal carbon, may react by a mechanism that more or less resembles the A_{SE}-2-type mechanism.[13] We wish to refer also to the recent arguments against the use of pH values of solvent mixtures and to the attendant serious disadvantages.[15]

Solvent Deuterium Isotope Effects. The measured k_D/k_H ratios were 2.7 for 1 at 40°, 3.0 for 2 at 40°, and 1.64 for 3 at 25°. Fife and Jao[8] reported the ratio 1.93 for the hydrolysis of 2-(p-methoxyphenyl)-1,3-

oxathiolane at 30°, and De and Fedor[7] the value 2.15 for the hydrolysis of 2-phenyl-1,3-oxathiolane under the same conditions. The values observed in this work are high enough to suggest that the hydrolysis occurs via the conjugate acid protonated on the oxygen atom.[8] It thus seems to be the carbon–oxygen bond which is broken in the critical transition state and not the C–S bond, as concluded by Fife and Jao.[8]

Owing to the anomalous dependence of the ratio k_n/k_H on the deuterium atom fraction n (Figure 2), we also determined the free energy change for the transfer of 3 from H_2O to D_2O. The results shown in Table V led to the value $\Delta G^\ddagger = 33.4$ cal/mol, the solubility

Table V. The Solubility of 2,2-Dimethyl-1,3-oxathiolane (3) in H_2O and D_2O at 25° as Indicated by the Refractive Indices of the Substrates and Solutions

	$n_D{}^{25}$		$n_D{}^{25}$
H_2O	1.3322	D_2O	1.3277
H_2O + 3	1.33383	D_2O + 3	1.32929
	$\pm$ 0.00004^a		$\pm$ 0.00006^a
3	1.4725		

^{a} Average of six replicate measurements.

in H_2O being slightly higher. These results confirm that the anomaly in the k_n/k_H curves must be due to the different activity coefficients of the transition states, but not to the different activity coefficients of the ground states in the different waters.[16]

The influence of mixed water on the rate of hydrolysis of 1,3-dioxa compounds has been found generally to be in accordance with the influence expected on the basis of eq 1 because both oxygen atoms have an equal chance to being protonated.[17] However, in the case of 1,3-oxathiolanes, the preequilibrium protonation (A-1 mechanism) occurs both on the oxygen atom and the sulfur atom relative to their basicities,[7] despite the fact that the ring rupture may favor the acetal carbon–oxygen bond fission. Moreover, the C–O bond rupture leads to a carbonium–sulfonium ion in which the sulfur may participate in the solvation phenomena with its d orbitals and, consequently, be responsible for the different activity coefficients of the transition states in H_2O and D_2O. Both of the above-mentioned factors predict an anomalous solvent deuterium isotope effect for the acid-catalyzed hydrolysis of 1,3-oxathiolanes, in agreement with the experimental findings (Table IV and Figure 2).[17]

Further independent evidence for the formation of a carbonium–sulfonium ion is also available. Guinot, Lamaty, and Munsch[18] studied the ring rupture of 2,2-dimethyl-1,3-dioxolane, 2,2-dimethyl-1,3-oxathiolane, and 2,2-dimethyl-1,3-dithiolane in sulfur dioxide and reported that the spectra of both dioxolane and oxa-

(13) F. Guinot, Thesis, University of Montpellier, France, 1970.

(14) (a) T. H. Fife, *J. Amer. Chem. Soc.*, **89**, 3228 (1967); (b) T. H. Fife and L. H. Brod, *J. Org. Chem.*, **33**, 4136 (1968).

(15) P. Salomaa, A. Kankaanperä, and M. Lahti, *J. Amer. Chem. Soc.*, **93**, 2084 (1971).

(16) P. Salomaa, *Acta Chem. Scand.*, **23**, 2095 (1969).

(17) Very recently we observed that the k_D/k_H ratio for 2,2-dimethyl-1,3-dioxolane depends normally on the deuterium atom fraction and that the value of this ratio is greatly dependent on the nature of the heteroatom. Moreover, 1,3-oxathiolanes and 1,3-dioxolanes showed a similar change in the value of k_D/k_H against temperature, whereas the corresponding change for 1,3-dithiolane was nearly doubled. Further evidence for similar ring rupture in the former compounds is the only 60 times greater hydrolysis rate of 2,2-dimethyl-1,3-dioxolane as compared to that of 2,2-dimethyl-1,3-oxathiolane. Details of these studies will be published separately.

(18) F. Guinot, G. Lamaty, and H. Munsch, *Bull. Soc. Chim. Fr.*, 541 (1971).

thiolane recorded in the presence of FSO_3H-SbF_3 catalyst at $-60°$ had a triplet due to the $-OH_2^+$ grouping at 10.9 ppm, whereas the spectrum of dithiolane showed a triplet due to $-SH_2^+$ at 7.3 ppm at $-30°$. Reports on the mass spectrometric fragmentation of 1,3-oxathiolanes[19] and 1,3-oxathianes[20] suggest that sulfur-containing ions are predominantly formed in these fragmentation processes; i.e. the ring splitting occurs mainly at the C–O bond.

Recently, the relative rates of the hydrolytic decomposition of 2,2-dimethyl-1,3-dioxolane, -oxathiolane, and -dithiolane were also determined. The results pointed out that if the relative hydrolysis rate for 2,2-dimethyl-1,3-dithiolane is taken to be unity, then 2,2-dimethyl-1,3-oxathiolane hydrolyzes with a relative rate of 2×10^4 and 2,2-dimethyl-1,3-dioxolane with a relative rate of 1×10^6. The great increase in rate between dithiolane and oxathiolane when compared to the relatively low rate increase between oxathiolane and dioxolane supports also the view of a C–O bond fission in the hydrolysis of 1,3-oxathiolanes.[17,21]
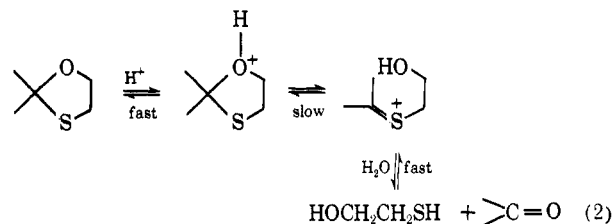
Conclusion

According to the collected data, 1,3-oxathiolanes hydrolyze under acidic conditions by an A-1 mechanism, in which fission of the acetal carbon–oxygen bond oc-

(19) D. J. Pasto, J. Heterocycl. Chem., 6, 175 (1967).
(20) K. Pihlaja and P. Pasanen, Org. Mass Spectrom., 5, 763 (1971).
(21) NOTE ADDED IN PROOF. After the present paper had been submitted, it became clear that the decomposition of 2,2-dimethyl-1,3-dithiolane occurs spontaneously in water but is not at all catalyzed by acids—the decomposition rate remained constant in 0 to 3 M perchloric acid solutions. In addition to this neutral hydrolysis, a relatively mild base catalysis seems to prevail. These findings greatly support the fact that the C–S bond rupture must have a minor role in the oxathiolane hydrolysis.

$$HOCH_2CH_2SH + {>}C{=}O \quad (2)$$

curs predominantly as shown in eq 2. This conclusion confirms the view of Fife and Jao[8] about the A-1 mechanism and that of De and Fedor[7] about selective O protonation, i.e., the fission of the acetal carbon-oxygen bond in the critical transition states. Consequently, contradictions in the previous papers are removed and the experimental results are in general agreement.

The most peculiar feature of the hydrolysis of 1,3-oxathiolanes is the specific solvent deuterium isotope effect; i.e., the rate is much higher when the deuterium atom fraction approaches unity than one would expect. Also, this phenomenon is best understood by assuming that a carbonium–sulfonium intermediate is formed, in which the hybridized p and d orbitals of sulfur play a significant role. This effect is worth additional studies with other model compounds.[17]

Kinetics of the Helix–Coil Transition in Aqueous Poly(L-glutamic acid)

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Abstract: Ultrasonic absorption measurements in dilute aqueous poly(α,L-glutamic acid)(PGA) have been carried out over the frequency range 40 kHz–35 MHz by the resonance, statistical reverberation, and pulse techniques. Data at the two PGA concentrations 2.7×10^{-3} and 1.1×10^{-3} (mol residue)/l. in 0.03 M NaCl at 37° exhibited relaxational absorption over the pH range 4.8–5.6. Both the relaxational amplitude (A) and relaxation time (τ) passed through maximum values at pH 5.21, the midpoint of the helix–coil transition. The maximum values of A and τ were found to be 100×10^{-17} sec^2 cm^{-1} and 1.0 μsec, respectively. The value of the rate constant for helical growth in the Schwarz theory was estimated to be $(8 \pm 5) \times 10^7$ sec^{-1}.

The helix–coil transition of the poly(α,L-amino acids) has long served as a model from which it is hoped to gain insight into the structural and dynamic properties of proteins.[1] About the thermodynamics of the transi-

tion there exists a wealth of information. Very little is known about the kinetics. In fact, prior to this investigation, complete kinetic data had been taken for only one system—poly(α,L-ornithine) in water–methanol mixtures.[2]

(1) For example, see G. D. Fasman in "Poly-α-Amino Acids," G. D. Fasman, Ed., Marcel Dekker, New York, N. Y., 1967.

(2) G. Hammes and P. Roberts, J. Amer. Chem. Soc., 91, 1812 (1969).