# A Comparison of Acid-Catalysed Hydrolysis of 2-Aryl-1,3-dithiolane in Aqueous Perchloric Acid with those of Its Analogous Dithianes

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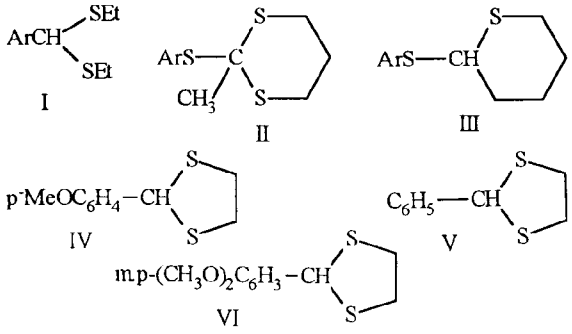
**Summary**: The behaviour of 2-Aryl-1,3-dithiolanes hydrolysis catalysed by perchloric acid have been studied kinetically. The effect of changes in aryl substituent, acid concentration, temperature, and isotopic solvent on the rate of hydrolysis show that the hydrolyses in 6.0 to 9.0 mol $dm^{-3}$ of the acid proceed via A2 mechanism. The results for the dithiolanes seerve to confirm the pattern of behaviour obtained for the dithianes.

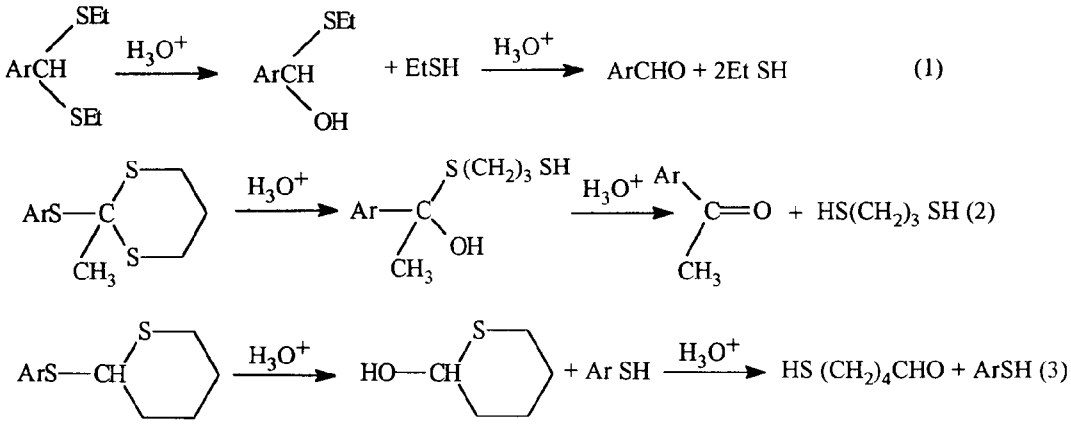
## Introduction

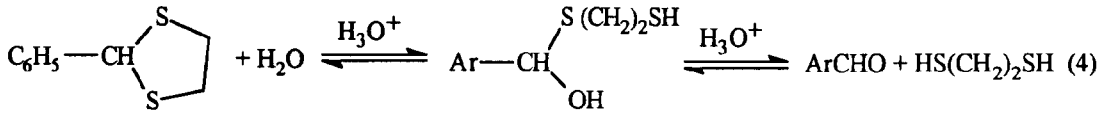
Little is known about the kinetics and mechanism of the Bronsted acid-catalysed hydrolysis of S,S-acetals [1], however, we have recently reported [2-4] on the behaviour of open chain (I), cyclic (II), and open chain-cyclic (III) S,S-acetals derived from substituted benzaldehydes and acetophenones.




These S,S-acetals hydrolyse according to equations (1), (2) and (3).

The hydrolysis of S,S-acetals is much slower than O,O-analogues. The O,S-acetals occupy an intermediate position. Due to less reactivity the hydrolysis of S,S-acetals require relatively concentrated solutions of Bronsted acids to have convenient rates at 25°C. Using initial concentrations of ca. $10^{-5}$ mol $dm^{-3}$ the hydrolysis of I,II and III in aqueous acid leads to effectively quantitative yield of the coresponding aldehyde or ketone. The hydrolysis of S,S-acetal proceeds via first order process with no significant build up of hemithioacetal intermediate [2,3]. However in the hydrolysis of 2-Aryl-1,3-dithianes, it was noticed [4] that the build-up of intermediate, hemithioacetal, is significant. The significant build-up of hemithioacetal is also found for IV, V, and VI i.e. at such initial concentrations the hydrolysis does not always lead to a quantitative yield of aldehyde there is evidence [5] that the reverse reaction is significant equation (4).






## Results and Discussion

Our results are illustrated in Tables (1-4) and the Figure. The hydrolysis of IV shows different behaviour at different concentrations. The results at lower initial concentration, 5 x $10^{-6}$ mol $dm^{-3}$, and relatively higher initial concentration, 5 x $10^{-5}$ mol dm-3, are discussed below.

*(i) Reactions at lower initial concentration*

At lower concentration, 5 x $10^{-6}$ mol $dm^{-3}$, the hydrolysis is relatively straight forward and a high yield of aldehyde is obtained. The reverse reaction of the products can be ignored as a first approximation. There is not obvious build up of hemithioacetal; this is expected if the reverse of step (2) is relatively slow at these low concentrations, since the known relative reactivities of cyclic S,S-acetal [1,3] and open-chain O,S-acetals make it very likely that $k_2 > k_1$. For equation (4) under such condition $k_{obs} = k_1k_2/(k_{-1} + k_2)$. It is difficult to predict the relative magnitude of $k_{-1}$ and $k_2$; $k_{-1}$ (which reflects an intramolecular route) is probably large, but if $k_{-1} > k_2$ it is unlikely

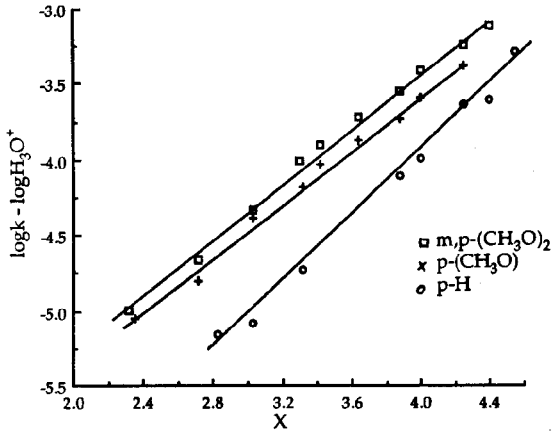



Fig. 1: The X* plots for 2-aryl-1,3-dithiolanes at 298K

*X is an acidity function called excess acidity and X plot means the plot of logK - log[$H_3O^+$] vs X

that hemithioacetal would accumulate even under concentration conditions when the reverse reaction of the product is significant. If we assume that $k_2 > k_{-1}$ then $k_{obs} = k_1$. The slope [6] ($m^*m^*$) of a plot of log $k_{obs}$ - log [$H_3O^+$] against the excess acidity X (as shown in the Fig. ) is 0.76 using $m^* = 1.3$ for the S,S-acetal). The (qualitative) relative reactivities of the other dithiolanes (Tables 2-4) reveal a quite small effect of substituents ($\rho = 0.9$) on the rate of hydrolysis at fixed [$H_3O^+$] compared with that found ($\rho = 3.0$) for the A1 and ASE2 hydrolyses of I and II. If $k_{obs} = k_1$, these results are suggestive [7,8] of an A2 mechanism for step one. Fife and Natarjan [9] have suggested an A2 scheme for a similar cyclic O,S-acetal. The present series of compounds are much less reactive than the acetals I and less reactive than the acetals II, (Ar = 4-$NO_2C_6H_4$), the least reactive of the acetophenone derivatives was also assigned an A2 mechanism and the activation parameters for p-$CH_3OC_6H_4$) Table-2 are more similar to those found for II (R=4-$NO_2$) than to those of the other S,S-acetals we have studied. The relatively slow rate of hydrolysis of the present 1,3-Dithiolane arises from a more negative entropy of activation. Whatever combination of rate constants $k_{obs}$ really represents, step (1) seems unlikely to involve an A1 mechanism [1,2,8].

*(ii) Reactions at higher initial concentration*

It appears that the reactions in both directions, equation (3), proceed first to an equilibrium position depending on the initial concentration of the reactant. The subsequent slow increase of aldehyde absorption may be due to oxidation of the free thiol which may allow the equilibrium to shift to the right. The finding of incomplete hydrolysis of these systems was unexpected and were also observed in case of 1,3-dithianes [4]. No similar effects are found for II when $[S,S\text{-acetal}]_{initial}$ 5 x $10^{-5}$ mol $dm^{-3}$, ketones are, however, known to react with alcohols less readily than do aldehydes, which could explain the results with II. No doubt the opportunity for intramolecular interaction accounts for the larger amount of acetal. (We have found similar effect using ethane-1,2-dithiol). Assuming for acetal formation that, as a first approximation, either the dithioacetal or the

hemithioacetal is the dominant acetal species at equilibrium.

Table-1: Effect of temperature on k*obs* for 2(m,p-Dimethoxyphenyl)-1,3-dithiolane using 7.20 mol $dm^{-3}$ perchloric acid.

| T K | $10^4 k_{obs}$ $S^{-1}$ | 10/T $k^{-1}$ | $10^6 k_{obs}/T$ | $\ln(k_{obs})/T$ |
|---|---|---|---|---|
| 298.1 | 5.80 | 33.54 | 1.94 | -13.15 |
| 303.3 | 9.70 | 32.97 | 3.19 | -12.65 |
| 310.3 | 14.5 | 32.22 | 4.68 | -12.27 |
| 314.7 | 22.3 | 31.77 | 7.08 | -11.85 |

Table-2: Values of $k_{obs}$ for various concentrations of perchloric acid with 2-(m,p-dimethoxyphenyl)-1,3-dithiolane ($5x10^{-5}$ and $dm^{-3}$ in 1% dioxane-water at 298K.

| $[HClO_4]$ mol $dm^{-3}$ | $10^4 k_{obs}$ $s^{-1}$ | X | logk | $\log\{H_3O^+\}$ | $\log k_{obs} - \log[H_3O^+]$ |
|---|---|---|---|---|---|
| 6.00 | 0.60 | 2.31 | -4.22 | 0.77 | -4.99 |
| 6.60 | 1.44 | 2.71 | -3.84 | 0.82 | -4.66 |
| 7.20 | 3.39 | 3.03 | -3.47 | 0.86 | -4.33 |
| 7.50 | 7.59 | 3.30 | -3.12 | 0.88 | -4.00 |
| 7.80 | 9.85 | 3.42 | -3.00 | 0.89 | -3.89 |
| 8.20 | 15.9 | 3.64 | -2.80 | 0.91 | -.371 |
| 8.4 | 23.9 | 3.88 | -2.62 | 0.92 | -3.54 |
| 8.60 | 34.0 | 4.00 | -2.47 | 0.93 | -3.40 |
| 9.0 | 52.1 | 4.25 | -2.28 | 0.95 | -3.23 |
| 9.20 | 71.8 | 4.40 | -2.14 | 0.96 | -3.10 |
| 9.60 | 120 | 4.54 | -1.92 | 0.98 | -2.90 |

Table-3: Values of $k_{obs}$ for various concentrations of perchloric acid with 2-phenyl-1,3-dithiolane ($5x10^{-5}$ mol $dm^{-3}$ in 1% dioxane-water at 298K.

| $[HClO_4]$ mol $dm^{-3}$ | $10^4 k_{obs}$ $s^{-1}$ | X | logk | $\log\{H_3O^+\}$ | $\log k_{obs} - \log[H_3O^+]$ |
|---|---|---|---|---|---|
| 6.80 | 0.47 | 2.82 | -4.32 | 0.83 | -5.15 |
| 7.20 | 0.60 | 3.03 | -4.22 | 0.86 | -5.08 |
| 7.50 | 1.41 | 3.31 | -3.85 | 0.87 | -4.72 |
| 8.4 | 6.64 | 3.88 | -3.18 | 0.92 | -4.10 |
| 8.60 | 8.91 | 4.00 | -3.05 | 0.93 | -3.98 |
| 9.00 | 21.0 | 4.25 | -2.68 | 0.95 | -3.63 |
| 9.40 | 23.9 | 4.40 | -2.62 | 0.97 | -3.59 |
| 9.60 | 51.3 | 4.54 | -2.29 | 0.98 | -3.27 |

Table-4: Values of $k_{obs}$ for various concentrations of perchloric acid with 2-(Methoxyphenyl-1,3-dithiolane ($5x10^{-5}$ mol $dm^{-3}$ in 1% dioxane-water at 298K.

| $[HClO_4]$ mol $dm^{-3}$ | $10^4 k_{obs}$ $s^{-1}$ | X | logk | $\log\{H_3O^+\}$ | $\log k_{obs} - \log[H_3O^+]$ |
|---|---|---|---|---|---|
| 6.00 | 0.53 | 2.35 | -4.27 | 0.78 | -5.05 |
| 6.60 | 1.03 | 2.71 | -3.98 | 0.82 | -4.80 |
| 7.20 | 2.95 | 3.03 | -3.53 | 0.85 | -4.38 |
| 7.50 | 5.00 | 3.31 | -3.30 | 0.87 | -4.17 |
| 7.80 | 7.30 | 3.42 | -3.13 | 0.89 | -4.02 |
| 8.20 | 11.2 | 3.64 | -2.95 | 0.91 | -3.86 |
| 8.4 | 15.8 | 3.88 | -2.80 | 0.92 | -3.72 |
| 8.60 | 22.1 | 4.00 | -2.65 | 0.93 | -3.58 |
| 9.0 | 38.2 | 4.25 | -2.42 | 0.95 | -3.37 |

There have been very few studies of Bronsted acid catalysed S,S-acetal hydrolysis apart from our own but, perhaps significantly, Pihlaja has reported [10] strange (and unexplained) kinetic behaviour for some S,S-acetals derived from acetones.

## Experimental

*Materials*

The dithiolanes were prepared from the corresponding benzaldehyde and ehtane-1,2-dithiol by the method described previously [3]. They were purified by recrystallisation from ethanol. All had appropriate nmr spectra and hydrolysis in dil. acid in the presence of $Hg^{2+}$ ions led to > 90% yield of the parent aldehyde. Perchloric acid was AnalaR (Aldrich) grade and 1,4-dioxane was of spectroscopic grade (Aldrich).

*Kinetics*

Reactions were initiated, as before [2,3] by adding to the aqeuous acid a small volume of a stock solution of the dithiolane in 1,4-dioxane. Reaction mixtures contained 1% (v/v) 1,4-dioxane. The dithiolanes (and the ethane-dithiol product) absorb weakly, but the absorption of aldehydes is intense between 250 to 300 nm. The progress of the reaction was followed by observing the increase in absorbance in this region using repeated scans. A Perkin Elmer Lambda 5 spectrophotometer was used for the studies.

For the initial concentrations of the dithiolane $< 5 \times 10^{-5}$ mol $dm^{-3}$, the hydrolysis proceeded to give more than 90% of the aldehyde in a first order process and the value of $k_{obs}$, the observed first order rate constant, were reproducible to within ± 10%. This reaction was studied over a range of perchloric acid concentrations and at four temperatures at significantly higher initial dithiolane concentrations (e.g. $2\text{-}5x10^{-5}$ mol $dm^{-3}$) the reaction was not accurately first order, slowing down noticeably towards the end, but usually providing eventually a high yield of aldehyde. Under these conditions, the hydrolysis appeared to proceed in two (partly overlapping) stagtes, the extent of the first stage being greater at lower initial concentration. First order plots of the initial part of the reaction, using a computed infinity value gave rate constants (reproducible to with ± 15%) similar to those obtained at the lower initial concentrations. The

behaviour of artificial product mixture of aldehyde and dithiol corresponding to different initial dithiolane concentrations was qualitatively compatible with these observations. This behaviour was also found for analogous dithianes. When [aldehyde] = [dithiol] 5 x $10^{-6}$ mole $dm^{-3}$ the aldehyde absorption is little affected, but at higher concentrations, there occurs a relatively rapid fall in aldehyde absorption depending upon the concentration. When [aldehyde] = [dithiol] = 5 x $10^{-5}$ mole $dm^{-3}$ the absorption falls to ca. 50 to 60% of that expected for the usually recovered over a period of hours. These types of kinetic and spectroscopic effect were found with all the dithiolanes used as was observed for corresponding dithianes [4]. We conclude that at high initial concentrations the hydrolysis proceeds first to an equilibrium position (eqn (4) involving ≤ 100% aldehyde formation. Unfortunately it was difficult to study this equilibrium quantitatively since the absorption of the hemiacetal is unknown, and because of the final slow increase in aldehyde absorption (see Discussion). For the p-$CH_3O$, p-$CH_3$, and m.p.-$(CH_3O)_2$, it is necessary to use [dithiolane]initial $10^{-6}$ mol $dm^{-3}$ to obtain a high yield of aldehyde during hydrolysis. Since it was inconvenient to use such low concentration in kinetic runs, approximate reactivities of these dithiolanes were obtained from the initial parts of their hydrolyses at higher concentration. For the p-$CH_3O$ derivative when hydrolysed at 5 x $10^{-5}$ mol $dm^{-3}$, qualitative tests towards the end of the first stages of the reactions revealed the presence of a singificant amount of hemithioacetal (> 10% of original acetal). This findings is in keeping with the conclusion that the hydrolyses, equation (4) do not lie far to the right at these concentrations.

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