Kinetics of Hydrolysis of 2-Aryl-2-phenyl-1,3-dithianes in 10% (v/v) Dioxane–Water, Containing Perchloric Acid. Acidity Functions in this Solvent and the Reactivity of α-Thio Carbocations

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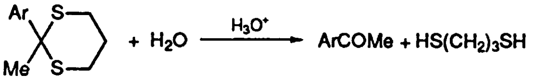
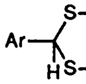
The acid-catalysed hydrolysis of 2-aryl-2-phenyl-1,3-dithianes in 10% (v/v) dioxane–water occurs at a convenient rate at 25 °C in the presence of 5–8 mol dm^{-3} perchloric acid. The effect on the rate of changes in substituents, acidity and temperature, and of the use of a deuteriated solvent are described. Measurements of the H_0 and X acidity functions for the solvent are reported; their values are very similar to those found for pure water over most of the acidity range. The mechanism of hydrolysis is believed to change from an $A\text{S}_E2$ scheme for the most reactive dithianes to an A2-like scheme for the least reactive. In very concentrated acid solutions the dithianes (and other suitable *S,S*-acetals) lead to stoichiometric amounts of the α-thio carbocations often postulated as low-concentration intermediates in *S,S*-acetal hydrolysis. The kinetics of the reaction of these ions with water to give the benzophenone (or corresponding carbonyl compound) are described, and compared with findings for similar α-oxo carbocations. Previous views on the mechanism of this reaction are criticised.

We reported recently[1–3] on the kinetics and mechanism of the hydrolysis in aqueous acid [*e.g.* eqn. (1)] of the *S,S*-acetals **1–3**. For **3** we found evidence[2] for hydrolysis *via* the $A\text{S}_E2$ mechanism. This mechanism is shown[4,5] by a variety of *O,O*-acetals but had not previously been identified for *S,S*-acetals. 2,2-Diaryl-1,3-dioxolanes are believed[6] to exhibit the $A\text{S}_E2$ mechanism of hydrolysis; we therefore considered that the compounds **4** might provide another example of it amongst *S,S*-acetals. Acetals **1–3** can be studied using a 1% (v/v) dioxane–water solvent, but acetals **4** are less soluble, and we have therefore used a 10% (v/v) dioxane–water mixture to ensure homogeneous solutions. Strongly acidic mixtures are required to hydrolyse most *S,S*-acetals at convenient rates[1–3] and a knowledge of the corresponding acidity functions is useful for interpreting these rates. Since acidity function measurements are not available for solutions of perchloric acid in 10% dioxane–water, we have measured the H_0 and excess acidity (X) scales for this solvent.[7,8] In very highly acidic solutions of the dithianes **4** we find evidence for the formation of substantial quantities of the corresponding α-thio carbocations, and report on their relative reactivities towards water.


(1)

$ArCH(SEt)_2$

1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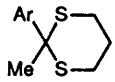
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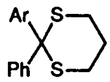
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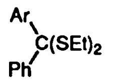

$Ar(Ph)C(SEt)_2$
5

Experimental

Materials.—Four dithianes **4** were prepared from the corresponding *p*-substituted benzophenones and 1,3-propane dithiol by the method previously described[2] for **2** and **3**. The *p*-MeO, *p*-Me, *p*-H and *p*-Cl derivatives had m.p. 94, 106, 96 and 70 °C, respectively. The diethyl thioacetals **5** (*p*-MeO, *p*-H, *p*-NO_2) were also prepared[1] from the benzophenones and ethane thiol; they are high-boiling liquids and were purified by vacuum distillation. All the *S,S*-acetals had appropriate NMR spectra, and hydrolysis in aqueous acid gave an effectively quantitative yield of the parent benzophenone. Acetal **3** (*p*-MeO) was a previous sample,[2] as was the perchloric acid and the dioxane. The H_0 scale was established using primary aromatic amines. All were recrystallised samples with m.p. agreeing with literature values. Solutions of perchloric acid in the 10% (v/v) dioxane–water solvent were made up using aq. perchloric acid with appropriate allowance for the water content of the acid.

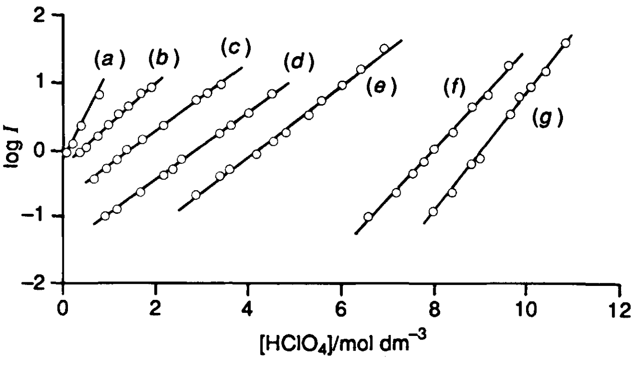


Fig. 1 Values of log *I* in 10% (v/v) dioxane–water at 25 °C. Aniline indicators: (*a*) 4-NO_2; (*b*) 4-Me-2-NO_2; (*c*) 2-NO_2; (*d*) 4-Cl-2-NO_2; (*e*) 2,5-Cl_2-4-NO_2; (*f*) 2,4-$(NO_2)_2$; (*g*) 2,6-$(NO_2)_2$.

Acidity Functions.—The H_0 measurements followed standard procedures,[7] and typical results for the ionisation ratios are in Fig. 1. Derived H_0 values (based on the pK_a values for water) are plotted in Fig. 2.

Kinetics.—The hydrolysis of the dithianes **4** was studied by our usual[1–3] spectroscopic method. The benzophenone products absorb strongly at 250–300 nm. In the range [$HClO_4$] = 4.8–8.3 mol dm^{-3}, the transient carbocation concentration existing during any run was negligible, and the formation of the benzophenone (= loss of **4**) was an accurately first-order process for at least three half-lives. The observed first-order rate constant, k_{obs}, was reproducible to within ± 10%. Our results for various acid concentrations and temperatures are in Fig. 3 and Table 1. The solvent isotope effect was studied for the *p*-

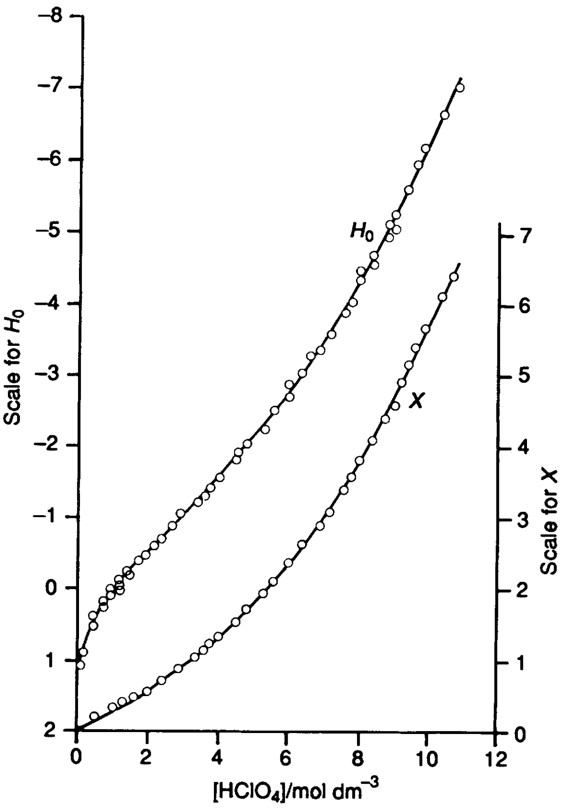


Fig. 2 H_0 and X functions at 25 °C. H_0 (referred to water) from log I values; continuous line through typical scatter; likely error ± 0.06 unit. X (referred to 10% dioxane–water) from interpolated H_0 values; likely error ± 0.05 unit.

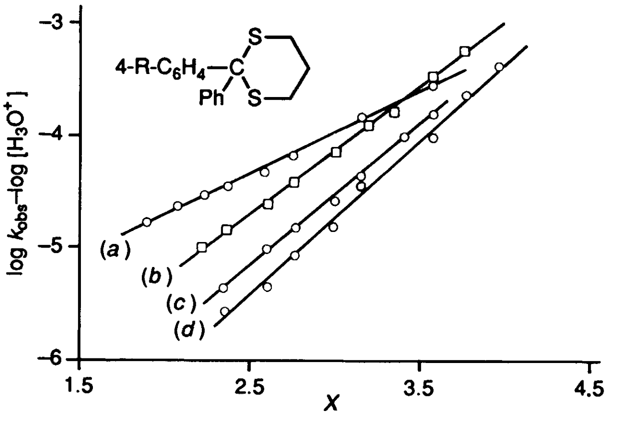


Fig. 3 Dependence of k_{obs} upon the excess acidity for hydrolysis of 2,2-diaryl-1,3-dithianes in 10% (v/v) dioxane–water containing perchloric acid at 25 °C. (a) MeO; (b) Me; (c) H; (d) Cl.

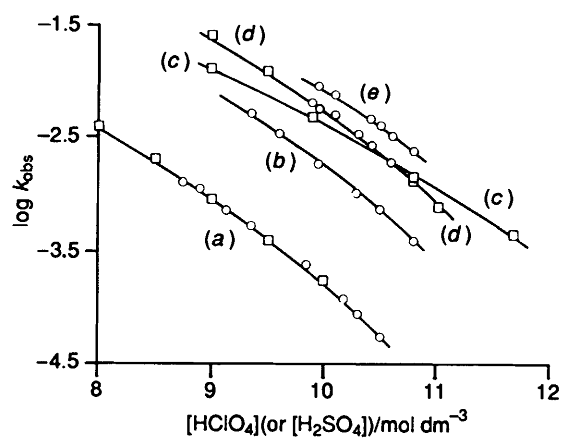


Fig. 4 Hydrolysis of α-thio carbocations at 25 °C. Solvent = 10% (v/v) dioxane–water containing perchloric acid unless stated otherwise. ○: cation from **4**, (a) 4-MeO; (b) 4-Me; (d) 4-H; (e) 4-Cl. □: corresponding cation from **5** (4-MeO or 4-H) in aq. acid (see text). (c) cation from **5** (4-MeO) in aq. sulfuric acid.

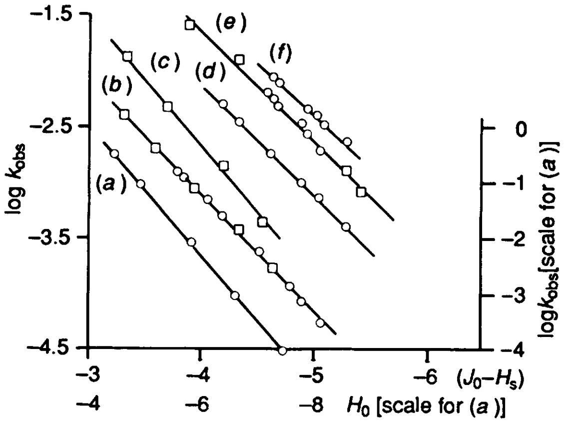


Fig. 5 Tests of eqn. (11) at 25 °C. (a) 4-MeOC$_6$H$_4$C$^+$(OEt)$_2$ in aq. sulfuric acid.[9] (b, d, e and f) ○: cations from **4** (4-MeO, 4-Me, 4-H and 4-Cl), respectively, in 10% dioxane–water containing perchloric acid. (b and e) □: cations from **5** (4-MeO and 4-H) in aq. perchloric acid. (c) cation from **5** (4-MeO) in aq. sulfuric acid.

methoxy derivative (Table 1). For any given *S,S*-acetal **4** at acidities somewhat stronger than those corresponding to Fig. 3, kinetic behaviour characteristic of two consecutive reactions begins to appear, and also evidence of new long-wavelength absorption in the region 370–450 nm. We attribute these effects[9] to the formation of significant quantities of the corresponding α-thio carbocations; at sufficiently high acidities all the acetals **4** could be rapidly and quantitatively converted into the carbocation. In solutions of appropriate acidity these ions react at convenient rates with the water in the medium to give the benzophenone. These are well-behaved first-order reactions with excellent isosbestic points. We studied them over a range of acidities for acetals **4**, and also for some other *S,S*-acetals. Compound **4** (*p*-MeO) was also examined in aq. sulfuric acid [containing 1% (v/v) dioxane]. In the concentrated acid solutions required (Fig. 4 Table 2) the product ketone (or aldehyde) is sometimes partly or completely protonated,[7] and therefore absorbs at a different (longer) wavelength to that shown in more dilute acid, but contrary to McClelland's report[9] on a related α-thio carbocation (made not from the *S,S*-acetal, but indirectly) we found no evidence for thioketone formation at high acidities. Our results for hydrolysis of the carbocations are in Table 2 and Figs. 4 and 5. The reproducibility of k_{obs} was within ± 8%.

Results and Discussion

Acidity Functions.—Except for those for *p*-nitroaniline, the measured ionisation ratios I (= [BH$^+$]/[B]) show reasonable parallelism[7] (Fig. 1) and the H_0 values calculated from $H_0 = pK_{BH^+} - \log I$, using recent[8] pK_{BH^+} values (referred to pure water), lead to a satisfactorily self-consistent scale (Fig. 2). Comparison of these H_0 values for 10% (v/v) dioxane–water mixtures at 25 °C with the scale for perchloric acid in water shows that, in dilute acid solutions, the dioxane scale is *ca.* 0.4 units more positive (solutions less acidic) than that for water, but that the two scales slowly converge until at [HClO$_4$] ≃ 7.0 mol dm^{-3} and above they became virtually the same. When the scales for sulfuric acid in 5% dioxane–water and pure water were compared[10] a similar effect was found, except that the dioxane scale became the more negative when [H$_2$SO$_4$]$_{stoich}$ ≳ 6.0 mol dm^{-3}. The difference in the H_0 values for two solvents, as

Table 1 Derived parameters for the hydrolysis of acetals **4** in 10% (v/v) dioxane–water containing perchloric acid, and the effects of temperature and isotopic solvent

				Effect of temperature					Solvent isotope effect[c]		
Acetal **4**[a] (p-R)	$k_{H'}$[b] 10^{-8} dm³ mol⁻¹ s⁻¹	$m^*m^‡$	$m^‡$	[HClO$_4$] mol dm^{-3}	T °C	k_{obs} 10^{-4} s^{-1}	$\Delta H^‡$ kJ mol^{-1}	$\Delta S^‡$ J K^{-1} mol^{-1}	k^H_{obs} 10^{-4} s^{-1}	k^D_{obs} 10^{-4} s^{-1}	k^D_{obs}/k^H_{obs}
OMe	56	0.76	0.58	6.36	24.6	2.78	79 ± 5	−97 ± 8	0.80	0.75	0.94
					31.6	6.00					
					36.9	11.8					
					45.7	24.4					
Cl	0.13	1.39	1.08	7.44	24.6	4.09	61 ± 4	−210			
					31.6	7.22					
					36.9	11.0					
					45.7	22.8					
Me	2.8	1.15	0.87								
H	0.56	1.26	0.97								

[a] $[4]_{init} \simeq 10^{-5}$ mol dm^{-3}; T = 25 °C unless stated otherwise. [b] See discussion section. [c] $[L_3O^+]$ = 5.00 mol dm^{-3}; %D = 71.8.

Table 2 Derived parameters and the effects of temperature for the hydrolysis of α-thio carbocations in aq. perchloric acid

			Effect of temperature				
Carbocation[a] (p-R)	k_2'[b] dm³ mol⁻¹ s⁻¹	λ_{max}[c] nm	[HClO$_4$] mol dm^{-3}	T °C	k_{obs} 10^{-4} s^{-1}	$\Delta H^‡$ kJ mol^{-1}	$\Delta S^‡$ J K^{-1} mol^{-1}
From **4**[d]							
OMe	8.9	444	10.2	25.5	1.33	80 ± 5	−190 ± 10
				31.8	2.93		
				37.3	5.23		
				43.1	8.23		
Cl	354	392	10.4	17.3	19.0	77 ± 5	− 160 ± 8
				23.0	33.3		
				25.0	44.2		
				28.1	65.3		
				35.5	130		
H	224	380					
Me	70.8	404					
From **5**[e]							
OMe	8.9	435					
H	224	370					
NO$_2$	*ca.* 5000[f]	385					
From **3**[d]							
OMe	*ca.* 700[g]	438					

[a] $[\text{carbocation}]_{init} \simeq 10^{-5}$ mol dm^{-3}; T = 25 °C unless otherwise stated. [b] For k_2' and its estimation see Discussion section. [c] Max. for carbocation; [d] In 10% dioxane–water. [e] In water. [f] Calculated from k_{obs} values of 81 × 10^{-4} and 7 × 10^{-4} s^{-1} at [HClO$_4$] = 11.0 and 12.0 mol dm^{-3}, assuming the curves in Fig. 3 remain parallel. [g] Calculated from k_{obs} = 65 × 10^{-4} s^{-1} for [HClO$_4$] = 10.5 mol dm^{-3}.

$[H_3O^+]\rightarrow 0$ is a measure of ΔpK_{BH^+}, the difference in pK_{BH^+} values for an indicator in the two solvents.[7] The convergence of the two scales for the same acid in dioxane-water and pure water shows that there exists, over a wide range, a larger change in H_0 for a given increase in acid concentration in the dioxane–water mixtures than in water.

The excess acidity X can be calculated[8] (approximately) from eqn. (2) in which H is a particular acidity function (*e.g.* H_0) and

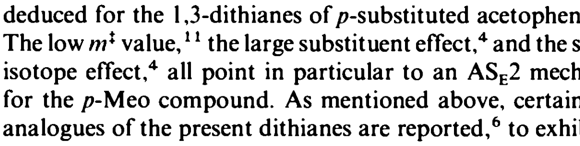
$$-H - \log[H_3O^+] = m_B^*X \qquad (2)$$

m_B^* is a parameter characteristic of the type of indicator base used to construct the scale. For primary aromatic amines used in water for the H_0 scale, $m_B^* \simeq 1.0$. Since, for any given solvent, X is defined[8] as $-\log(f_{H_3O^+}f_{B^*}/f_{B^*H^+})$, where B* is a hypothetical standard base, if the activity coefficients are referred to infinite dilution in the solvent in question, then $X\rightarrow 0$ as $[H_3O^+]\rightarrow 0$. This is the desirable situation if X is to be used in kinetic studies.[11] To obtain X referred to 10% dioxane-water from eqn. (2) it is necessary: (i) to convert our H_0 scale referred to water (Fig. 2) to the scale referred to dioxane–water by adding ΔpK_{BH^+} (0.4); and (ii) to assume that $m_B^* \simeq 1$ for primary arylamines in this solvent (probably reasonable). The resulting X values are plotted in Fig. 2. As expected from the discussion of the H_0 values, the X scale for water[8] and for 10% dioxane–water are quite similar, the values for the latter being somewhat more positive at high acid concentrations. In all calculations we assumed $[H_3O^+] = [HClO_4]_{stoich}$.

Hydrolysis of the Dithianes in the Range $[HClO_4] \simeq$ 5–8 mol dm^{-3}.—Our results are in Table 1 and Fig. 3. We find: (i) k_{obs} for all the dithianes **4** increases rapidly with increase in $[H_3O^+]$, and plots[11] of $\log k_{obs} - \log[H_3O^+]$ against X are rectilinear (Fig. 3) with slopes ($m^*m^‡$) varying from 0.76 for the p-MeO derivative to 1.39 for the *p*-Cl compound, so that, using m^* for *S*-bases[8] as 1.3, $m^\ddagger$ varies from *ca.* 0.6 to *ca.* 1.0; (ii) $\Delta S^\ddagger$ is negative, especially so for the *p*-Cl compound; (iii) the solvent isotope effect $k^{D}_{obs}/k^{H}_{obs} \gtrsim 0.94$ for the *p*-MeO derivative; and (iv) electron-releasing *p*-substituents notably increase reactivity, as shown by the second-order (catalytic) rate constants (k_{H^+}, Table 1) obtained[11] from the intercepts of the *X*-plots (Fig. 3) at $X = 0$. A Hammett plot against σ finds the *p*-MeO acetal much too reactive, whereas the plot against σ^+ finds the *p*-Cl acetal too unreactive. The plot against σ^+ is the better, and has slope $\rho^+ \simeq -2.5$.

These various facts seem most compatible with the conclusion that the detailed mechanism of hydrolysis changes somewhat on moving from **4** (*p*-MeO) to **4** (*p*-Cl), and that the mechanism for the former is an $A S_E 2$ scheme tending to an A2 scheme for the latter. This picture is consistent with that deduced for the 1,3-dithianes of *p*-substituted acetophenones.[2] The low $m^\ddagger$ value,[11] the large substituent effect,[4] and the solvent isotope effect,[4] all point in particular to an $A S_E 2$ mechanism for the *p*-Meo compound. As mentioned above, certain *O,O*-analogues of the present dithianes are reported,[6] to exhibit the $A S_E 2$ mechanism.

Hydrolysis of α-Thio Carbocations.—In sufficiently concentrated solutions of acid the dithianes **4** are rapidly, and effectively quantitatively, converted into the corresponding carbocation [eqn. (3)]. The recyclisation is evidently slower than the ring cleavage in very concentrated acid. The carbocations subsequently react irreversibly with the water in the solvent to give the benzophenone, presumably *via* the hemithioacetal[9,12] [eqns. (4) and (5)]. This hydrolysis of the carbocation becomes slower as the acidity rises (Fig. 4). What is happening under conditions of concentrated acid is that the mechanism of hydrolysis of the acetal has changed from the 'normal' situation in more dilute acid solutions in which the carbocation is formed in the slow step of a (we believe) $A S_E 2$ mechanism, and then reacts rapidly with water to give hemiacetal and parent carbonyl compound, to a situation where these latter processes are the slow phase of the overall hydrolysis. This change-over in rate-determining processes is well-established for *O,O*-acetals[9] and for orthoesters[13] in the appropriate acidity ranges, but has not been studied before for *S,S*-acetals.



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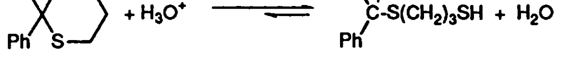

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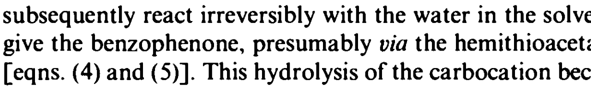


(5)

If we assume that (as seems likely from previous studies with cations derived from orthoesters[12,14,15]), at the high acidities required for the present acetals, the equilibrium (4) is rapidly set up but lies on the left hand side, the slow step becomes (5). The rate equation for loss of carbocation is then (6). The equilibrium (4) can be considered[7,12] to be controlled by $Jo(H_R)$, and for ionisation of aryl alcohols[7] (ROH) we have eqn. (7), which can be written for eqn. (4) as (8).

$$-d[\mathbf{7}]/dt = k_2[\mathbf{7}] = -d[\mathbf{6}]/dt \qquad (6)$$

$$Jo = -\mathrm{p}K_{ROH} - \log[\mathrm{R}^+]/[\mathrm{ROH}] \qquad (7)$$

therefore

$$[\mathbf{7}]/[\mathbf{6}] = \frac{\mathrm{antilog} Jo}{K_7} \qquad (8)$$

therefore

$$-d[\mathbf{6}]/dt = \frac{k_2}{K_7}(\mathrm{antilog}\ Jo)[\mathbf{6}] \qquad (9)$$

The rates of reactions analogous to (5) have been shown[12,14] to follow the H_S acidity function ($H_S = -\log a_{H_2O} \cdot f_S/f_{SH^+}$, where S is a sulfur base). We will therefore write eqn. (9) as (10), leading to eqn. (11) for k_{obs}.

$$-d[\mathbf{6}]/dt = k_2'(\mathrm{antilog}\ -H_S)(\mathrm{antilog}\ Jo)[\mathbf{6}] \qquad (10)$$

or

$$\log k_{obs} = \log k_2' + (Jo - H_S) \qquad (11)$$

Our k_{obs} for hydrolysis in 10% dioxane–water of the carbocations derived from **4** (*p*-MeO, *p*-Me, *p*-H, *p*-Cl) are in Fig. 4, together with some values for two similar ions obtained from the diethylthioacetals of benzophenones **5**. These latter ions were studied in aq. perchloric acid containing little ($\lesssim 1\%$) dioxane. As discussed above, the acidities of conc. perchloric acid in water and in 10% dioxane–water are very similar, and we find the rate constant for the *p*-MeO (and for the *p*-H) substituted carbocation to be the same (within experimental error) whether the ion is derived from the corresponding acetal **4** or **5**. This suggests that the ions carrying $-S(CH_2)_3SH$ groups have reactivites similar to those with –SEt groups. Fig. 4 shows that plots of $\log k_{obs}$ against acid molarity exhibit a mild curvature.

If our kinetic analysis is essentially correct, a plot of $\log k_{obs}$ against (Jo-H_S) should be rectilinear with a slope close to unity. Plots for the ions from the dithianes **4** and for **5** (*p*-MeO and *p*-H) are in Fig. 5. Satisfactory, effectively parallel, straight lines are found with slopes *ca.* 0.98. In the calculations we used the approximation[7] $Jo = 2H_0$ and the relation $H_S = 1.3\,H_0 + 0.3\log[H_3O^+]$ proposed by Scorrano.[16] The dominant factor is *Jo*, so that it is the changing position of the pre-equilibrium (4) with acidity that leads to the fall in k_{obs} as the acidity rises. The rate constant k_2' can be estimated for conditions corresponding to dilute acid solution by extrapolating plots such as those in Fig. 5 to $(Jo - H_S) = 0$. In all we studied eight different α-thio carbocations, all obtained from the corresponding *S,S*-acetals. The derived k_2' values are collected in Table 2, together with some activation parameters for this type of hydrolysis. A plot of k_2' against σ^+ for the diaryl cations is a good straight line of slope $\rho^+ \simeq +1.8$; *i.e.* conjugative electron-release slows the reaction down. An effect of very similar magnitude is found for oxo cations.[9] This effect probably arises partly because the ratio [**7**]/[**6**] becomes smaller when the cation is stabilised by electron-release, and it would be expected that the polar effect of a substituent on this ratio (*i.e.* on K_7) would be greater than its effect on k_2 (which will[17] become larger for electron-releasing substituents). As for changes in acidity, the pre-equilibrium (4) is the dominant influence. Although the polar effects of the substituent can account qualitatively for the observed changes in reactivity, the activation parameters show that entropic factors are also very important.

Rather few α-thio carbocations have been studied kinetically before. Those that have were mostly obtained from ketene thioacetals or from *S*-orthoesters when it is found that, compared with their *O*-analogues, they are normally formed more slowly[12,14] in reactions such as (12), and once formed, react

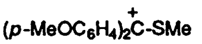
$$PhC(SEt)_3 + H_3O^+ \longrightarrow PhC^+(SEt)_2 + EtSH + H_2O \quad (12)$$

[eqn. (13)], in processes analogous to (4)–(5), much less rapidly

$$PhC^+(SEt)_2 + 2\,H_2O \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} PhC(OH)(SEt)_2 + H_3O^+ \xrightarrow[H_2O]{k_2} PhC(O)SEt + EtSH + H_3O^+ \quad (13)$$

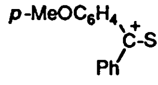
and have much larger K_{ROH} values:[15] the change to *O* from *S* greatly increases k_1 but only moderately increases k_{-1}. For both[12,14,15] α-oxo and α-thio carbocations, k_2 limits the rate of ester formation at pH $\gtrsim$ 2. Since, in all except the most acidic conditions, the cleavage of SR groups is much slower than that of OR groups,[12] k_2 is smaller for hemithio orthoesters than for the *O*-analogues. This, together with their larger K_{ROH} $(=k_{-1}/k_1)$ values, serves to make these thio carbocations much less reactive than the corresponding oxo cations in the overall hydrolysis to ester [eqn. (13)].

For acetals there appears to be only one comparison of the reactivity of an α-thio carbocation with that of its *O*-analogue in the hydrolysis to give ketone. McClelland[9] found that the ion **8** is 10^3–10^4-fold less reactive than the *O*-analogue. We have



$$(p\text{-}MeOC_6H_4)_2\overset{+}{C}\text{-}SMe$$

8



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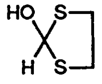
confirmed this difference in reactivity by studying **5** (*p*-OMe) in aq. sulfuric acid (Fig. 4), the medium used in McClelland's study of various oxo carbocations.[9] At a given acid molarity a carbocation will be expected to be more reactive in aq. sulfuric acid than in aq. perchloric acid because of the lower level of acidity in the former,[7] and k_{obs} should have a different dependence on molarity. This can be seen for **9**, the ion from **5** (*p*-OMe), in Fig. 4. In sulfuric acid **9** has a reactivity *ca.* five-fold larger than that of **8** (as assigned by McClelland's method[9]) and is indeed much less reactive than similar oxo-ions studied by McClelland. We find, however, that the dependence of k_{obs} on acidity for this carbocation, although quite similar to that found in perchloric acid solutions [the plot of log k_{obs} *vs.* $(Jo - H_S)$ in aq. sulfuric acid has a slope of *ca.* 1.15, Fig. 5], is not the same as that reported for the oxo-ions[9] (as implied by McClelland for **8**), but is less steep. Some difference in behaviour would be expected on the basis of eqns. (4) and (5), since for the α-oxo carbocations the rate of reaction (5) would be expected to parallel H_0 more closely than H_S. In agreement with this expectation,* McClelland's results[9] give satisfactory plots of log k_{obs} *vs.* $(Jo - H_0) \simeq H_0$, with slopes *ca.* 1.15 (Fig. 5). Because k_{obs} falls less rapidly for the α-thio ions as the acidity is increased, their normally lower reactivity compared with their *O*-analogues might be reversed in sufficiently acidic solutions where[16] H_S greatly exceeds H_0.

Our mechanism (4)–(5) for the hydrolysis of the thio carbocations is the same as Okuyama's[12,14] for orthoesters, except that he treats **7** as a steady state intermediate. That may be preferable, but our simplification to a pre-equilibrium system is evidently satisfactory for the present systems. McClelland's simplification[9] appears to be less satisfactory (especially for α-thio carbocations): he assumes that the forward step of eqn. (4) is the slow process. It is difficult on that basis to explain why, even in very dilute acid solutions, the rate of hydrolysis to ketone falls as $[H_3O^+]$ rises, since the activity of water is roughly constant in dilute solutions; virtually the whole of the effect on k_{obs} has to be attributed to changes in activity coefficients.[9] A kinetically important reverse step in equilibrium (4) seems to us needed to explain the deceleration.

Although our overall mechanism (4)–(5) is the same as Okuyama's, we disagree with his assignment[14] of the detailed mechanism of step (5). For at least two hemithio orthoesters, **10**



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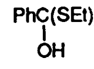

$$PhC(SEt)_2(OH)$$

11

and **11**, Okuyama finds that the rate of step (5) reflects H_S, and that a plot of log k_{obs} for this step (log k_2) against H_S has a slope of unity. He deduces[14] from this result that this catalysed reaction has an A1 mechanism. However, the slopes of plots against individual acidity functions can be misleading, as the excess acidity[11] (and other[18]) treatments show. We have recently identified[1–3] a number of A1, $A_{S_E}2$ and (perhaps) A2 mechanisms in *S*,*S*-acetal hydrolysis. A plot of log k_{obs} against H_S for such systems displaying the A1 mechanism usually gives rise to a straight line, but with slope > 1 (often much greater). Our results show that slopes of *ca.* 1 are more characteristic of $A_{S_E}2$ or A2 mechanisms. We believe therefore that the mechanism of reaction (5) is more similar to the still ill-defined (but not A1) mechanism found[18,19] for *O*,*O*-hemiacetals, and which perhaps includes a slow proton transfer from H_3O^+ to the leaving OR group, accompanied by removal by water of a proton from the OH group. Such a mechanism for hemithioacetals should have a solvent isotope effect $k^D_{obs}/k^H_{obs} < 1$ whereas (as our studies[1,20] with *S*,*S*-acetals show) an A1 scheme will have an isotope effect $\gtrsim 1.3$. Okuyama[14] suggests his observed isotope effect for acid catalysis of step (5) is *ca.* 1, but examination of his actual results shows it to be < 1.

References

1 M. Ali and D. P. N. Satchell, *J. Chem. Soc., Perkin Trans. 2*, 1991, 575.
2 M. Ali and D. P. N. Satchell, *J. Chem. Soc., Perkin Trans. 2*, 1992, 219.
3 M. Ali and D. P. N. Satchell, *J. Chem. Res.* (*S*), 1993, 114.
4 E. H. Cordes and H. G. Bull, *Chem. Rev.*, 1974, **74**, 581.
5 D. P. N. Satchell and R. S. Satchell, *Chem. Soc. Rev.*, 1990, **19**, 55.
6 R. H. DeWolfe, K. M. Ivanetich and N. F. Perry, *J. Org. Chem.*, 1969, **34**, 848.
7 C. H. Rochester, *Acidity Functions*, Academic Press, London, 1970.
8 R. A. Cox and K. Yates, *J. Am. Chem. Soc.*, 1978, **100**, 3861.
9 R. A. McClelland and M. Ahmad, *J. Am. Chem. Soc.*, 1978, **100**, 7031.
10 D. S. Noyce and M. J. Jorgenson, *J. Am. Chem. Soc.*, 1962, **84**, 4312; 1961, **83**, 2525.
11 R. A. Cox and K. Yates, *Can. J. Chem.*, 1979, **57**, 2944.
12 T. Okuyama, M. Kitano and T. Fueno, *J. Org. Chem.*, 1987, **52**, 2657.
13 M. Ahmad, R. G. Bergstrom, M. J. Cashen, Y. Chiang, A. J. Kresge, R. A. McClelland and M. F. Powell, *J. Am. Chem. Soc.*, 1979, **101**, 2669.
14 T. Okuyama, *J. Am. Chem. Soc.*, 1984, **106**, 7134.
15 T. Okuyama, W. Fugiwara and T. Fueno, *J. Am. Chem. Soc.*, 1984, **106**, 657 and earlier papers.

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* There is also the possibility that for oxo-ions the pre-equilibrium is not set up, and the overall slow step is just the forward step of the equilibrium (4). A different acidity dependence would then also seem likely.

16 P. Bonvicini, A. Levi, V. Lucchini, V. Modena and G. Scorrano, *J. Am. Chem. Soc.*, 1973, **95**, 5960 and earlier papers.
17 T. J. Przytas and T. H. Fife, *J. Am. Chem. Soc.*, 1981, **103**, 4884.
18 R. A. McClelland and L. J. Santry, *Acc. Chem. Res.*, 1983, **16**, 394.
19 B. Capon, M. I. Dosunmu and M. de N. de Sanchez, *Adv. Phys. Org. Chem.*, 1985, **21**, 37.
20 M. Ali and D. P. N. Satchell, unpublished results.

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