

Spiro- λ^4 -sulfanes with a N-S^{IV}-O axial bond system. A kinetic study on the mechanism of hydrolysis

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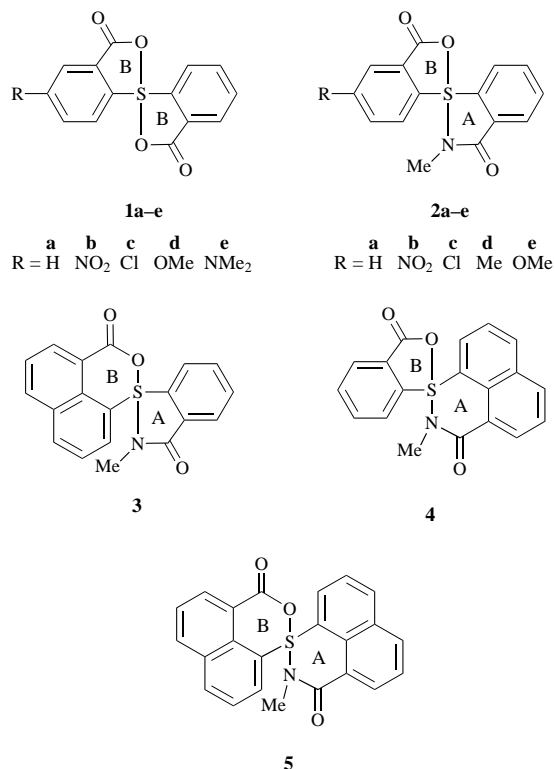
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Kinetics of the hydrolysis of diaryl(acylamino)(acyloxy)spiro- λ^4 -sulfanes (**2a–e**, **3–5**) leading to sulfoxides have been studied under pseudo-first-order conditions in dioxane–water mixtures or aqueous buffer solutions. A sulfonium-carboxylate-type dipolar structure of the starting spiro- λ^4 -sulfanes is supported by IR spectroscopic data. Solvent polarity and ionic strength have no significant influence on the rate of hydrolysis of compounds **2a** and **3**. Electron-withdrawing *para*-substituents promote the reaction in both neutral (ρ 1.43) and acidic media (ρ_{cat} 0.90). Hydrolysis is moderately accelerated by strong acids owing to the protonation of the negatively polarized acyloxy group of the substrate. In 50:50 (v/v) dioxane–H₂O(D₂O) the primary deuterium isotope effect is $k_{\text{H}_2\text{O}}/k_{\text{D}_2\text{O}}$ 3.68. Spiro- λ^4 -sulfanes **2a–e** and **3** with a five-membered N-containing ring are much more reactive than the six-membered analogues **4** and **5**. A mechanism involving the rate-determining nucleophilic attack of water on the positively polarized sulfur atom is proposed which is accompanied by a simultaneous O–H and S–N bond cleavage. Spiro- λ^4 -sulfanes **4** and **5** with six-membered N-containing spiro-rings, which are slightly reactive towards water, undergo a fast parallel reaction with OH[–] ions even in neutral solutions. The different reactivities of (acylamino)(acyloxy)spiro- λ^4 -sulfanes and their diacyloxy analogues are discussed and interpreted.

Introduction

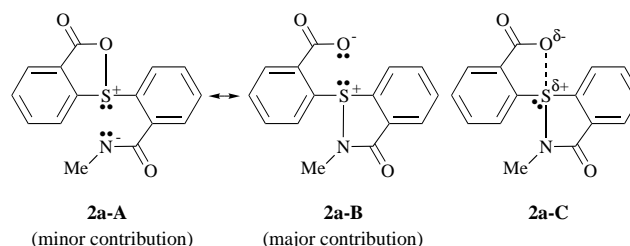
In a previous paper¹ we reported on kinetic investigations of the hydrolysis of diaryl(diacyloxy)spiro- λ^4 -sulfanes (e.g. **1a–e**,



also known as diaryldiacyloxyspirosulfuranes) with two equivalent S^{IV}-O(acyl) hypervalent bonds in the axial position. For this reaction, which leads to bis(carboxyaryl)-sulfoxides with the opening of both spiro-rings B, we found that (i) the hydrolysis is considerably assisted by strongly ionizing reaction media, (ii) electron-releasing substituents on the aromatic ring increase, whereas electron-withdrawing ones decrease the

reactivity (ρ –0.52); (iii) the reaction is more or less strongly catalysed by acids, depending on the substituent (for the catalytic constants ρ_{cat} –1.55); (iv) in neutral media the reaction shows a secondary deuterium solvent isotope effect ($k_{\text{H}_2\text{O}}/k_{\text{D}_2\text{O}}$ 1.66) which is superimposed on the isotope effect of a protonation pre-equilibrium in acidic media, and therefore an inverse isotope effect is observed (the ratio of catalytic constants was 0.56); (v) diaryl(diacyloxy)spiro- λ^4 -sulfanes containing two five-membered spiro-rings B are significantly more stable towards hydrolysis than the analogues with six-membered ring (the so-called five-membered ring effect has been observed). On the basis of these findings a multi-step mechanism has been proposed, according to which the spiro- λ^4 -sulfane in solution first undergoes an equilibrium process like valence isomerization to give a reactive monocyclic sulfonium-carboxylate zwitterion (in acidic media protonation leads to a carboxy-substituted monocyclic sulfonium cation); the sulfonium species, attacked in the subsequent step by a water molecule, is converted finally into sulfoxide by fast proton-transfer steps. An equilibrium involving ring-opening and recyclization for spiro- λ^4 -sulfanes has been proved earlier by isotope labelling² as well as by NMR measurements.³ Both the substituent effect and the ring-size effect observed have been correlated with the stability of the spiro-rings B, i.e. with the readiness of the formation of a reactive sulfonium-carboxylate intermediate.

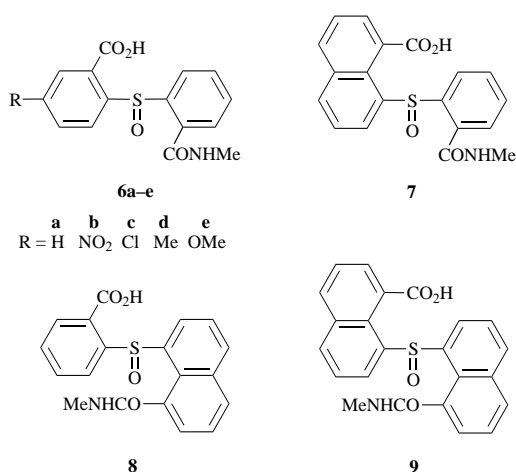
The synthesis and X-ray structure determination of diaryl(acylamino)(acyloxy)spiro- λ^4 -sulfanes **2a** and **3–5** with



axial N(acyl)-S^{IV}-O(acyl) bond system has been reported in an earlier paper.⁴ Whereas the diaryl(diacyloxy)spiro- λ^4 -sulfane **1a**

exhibits an almost perfect trigonal-bipyramidal (TBP) arrangement and medium length axial hypervalent S–O bonds (1.84 Å) about the central sulfur atom,⁵ the diaryl(acylamino)(acyloxy) analogues show a similar TBP geometry but with a practically covalent S–N bond (1.71–1.73 Å) in spiro-ring A and with an unusually long and polarized S–O hypervalent bond (2.13–2.25 Å) in spiro-ring B. For **2a** the ‘disproportion’ of axial hypervalent bonds may be described by a major contribution of the limiting structure **2a-B**. The ‘condensed’ formula **2a-C** reflects the view that the unusually long and weak hypervalent S–O bond in **2a** may also be regarded as an effective S⋯O close contact (*cf.* refs. 6 and 7). Owing to this interaction the TBP geometry with the linearity of the axial N–S⋯O part is conserved in the actual conformation, and the charges on the sulfonium–sulfur and acyloxy–oxygen atoms are somewhat reduced.

In this paper, we report on the mechanism of hydrolysis of diaryl(acylamino)(acyloxy)spiro- λ^4 -sulfanes **2–5** leading to the corresponding sulfoxides **6–9**, using data obtained from detailed kinetic studies. The synthesis of compounds **2b–e** is also described.

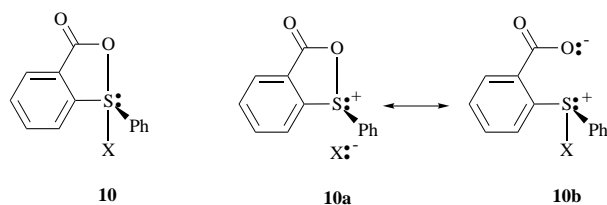


The differences in reactivity of acylamino-acyloxy compounds **2–5** relative to the analogous diacyloxy derivatives of type **1** will be attributed primarily to the ‘disproportion’ of bond strengths in the highly polarized axial N–S^{IV}–O array, which is also reflected in the infrared spectra of compounds **2–5**.

Results and discussion

IR spectra of λ^4 -sulfanes **2–5**

In an earlier paper, Livant and Martin⁸ reported that the carbonyl frequencies of acyloxy- λ^4 -sulfanes of type **10** are very sensitive to the nature of the axial ligand X and thus indicative of the charge distribution along the highly polarizable O–S^{IV}–X axial bond system in λ^4 -sulfanes. Depending on whether the structure **10a** or **10b** makes a higher contribution, the carbonyl



frequencies will range from $\sim 1830 \text{ cm}^{-1}$ (a value even higher than usual for γ -lactones because of the electron-withdrawing effect of the sulfonium centre) to $\sim 1600 \text{ cm}^{-1}$ or even less (a value characteristic of a carboxylate group).

The $\nu_{\text{C=O}}$ frequencies obtained for spiro- λ^4 -sulfanes **1a**, **2a** and **3–5** in different solvents are summarized in Table 1. The (diacyloxy)spiro- λ^4 -sulfane **1a** with an axial O–S^{IV}–O array exhibits a single $\nu_{\text{C=O}}$ (acyloxy) band both in acetonitrile and in dimethyl sulfoxide (DMSO). The observed value is equally far from the two extremes reported by Livant and Martin,⁸ indicating that the two equivalent axial S^{δ+}–O^{δ-} (hypervalent) bonds in **1a** are half-polarized as is also shown by S–O bond length values (Table 1). The corresponding $\nu_{\text{C=O}}$ (acyloxy) data for (acylamino)(acyloxy)spiro- λ^4 -sulfanes **2a** and **3–5** with an axial N–S^{IV}–O array, however, point to a dramatic shift towards the zwitterionic form, which is also assisted by polar solvents (acetonitrile < dimethyl sulfoxide < 50:50 dioxane–D₂O). Extremely low $\nu_{\text{C=O}}$ (acyloxy) values were observed in the most polar dioxane–D₂O solvent for compounds **4** and **5**, which also show the longest S–O interatomic distances (*cf.* Table 1).

The $\nu_{\text{C=O}}$ (acylamino) frequencies of spiro- λ^4 -sulfanes **2–5** are comparable to (or somewhat lower than) the amide I frequencies of the corresponding lactams, pointing almost fully covalent S–N bonds, which is also reflected in short S–N bond lengths (*cf.* Table 1).

The splitting of acyloxy and/or acylamino C=O bands in some cases may be explained by an interaction with solvent molecules. For spectra recorded in dioxane–D₂O the lower frequency values may be related to hydrogen-bonded C=O groups.

Data suggest that compounds **4** and **5**, in which the N atom is incorporated in a six-membered ring A, have more pronounced ionic character than **2a** and **3** with a five-membered ring. On the other hand, ionic character is also increased if the O-containing five-membered ring B is enlarged to a six-membered one (**2a** < **3**; **4** < **5**).

From both IR and X-ray data we may conclude that the structure of the (acylamino)(acyloxy)spiro- λ^4 -sulfanes **2–5** with highly polarized S–O bonds can be well described by a high contribution of a sulfonium-carboxylate-type limiting structure (*e.g.* **2a-B**) and the polarity of the structure depends on the solvent, too. However, the role of steric factors too cannot be neglected, as is pointed out in refs. 6 and 7.

As will be shown below, structural differences observed for spiro- λ^4 -sulfanes are also reflected in their reactivity. Because the hydrolysis of (acylamino)(acyloxy)spiro- λ^4 -sulfanes with five-membered ring A (**2a–e** and **3**) and that of their analogues with six-membered rings (**4** and **5**) does not follow the same kinetics, they will be discussed separately.

Hydrolysis of spiro- λ^4 -sulfanes **2a–e** and **3**

Kinetic equations. The hydrolysis reactions of compounds **2a–e** and **3** were followed by UV-spectrophotometric methods in dioxane–water containing 10–60% v/v of water at 25 °C (for other conditions see Experimental). As water was used in great excess compared to the spiro- λ^4 -sulfanes, the hydrolysis followed pseudo-first-order kinetics according to rate eqn. (1).

$$\text{rate} = k[\text{spiro-}\lambda^4\text{-sulfane}] \quad (1)$$

The pseudo-first-order rate constants, k_{2a} for **2a** and k_3 for **3**, are listed in Table 2, indicating that **3** is more reactive toward hydrolysis in neutral media than **2a**. Rate constant k_{2a} showed a linear dependence on the molar concentration of water, eqn. (2)

$$k_{2a} = -3.47 \times 10^{-7} + 4.35 \times 10^{-7} [\text{H}_2\text{O}] \quad (2)$$

being valid for reaction mixtures containing up to 45% v/v of water. The intercept of this equation can be considered as zero within experimental error, while its slope gives the second-order rate constant (in $\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$) of the hydrolysis.

Medium effects. Spiro- λ^4 -sulfanes **2a** and **3** showed good linear relationships between $\log k$ and the empirical parameters of the solvent polarity $E_T^{9,1}$ and Y^{10} [see Table 2 and eqns. (3)–(6)].

Table 1 Selected X-ray structural data^{4,5} and IR carbonyl frequencies ($\nu_{C=O}$) of spiro- λ^4 -sulfanes **1a**, **2a** and **3–5**

Compound	Axial bond lengths/Å		Solvent	$\nu_{C=O}/\text{cm}^{-1}$	
	S–O	S–N		Acyloxy	Acylamino
1a	1.84	—	Acetonitrile	1729	—
			Dimethyl sulfoxide	1722	—
2a	2.132	1.734	Acetonitrile	1666	1706
			Dimethyl sulfoxide	1663, 1650	1702
			50:50 (v/v) Dioxane–D ₂ O	1631	1702
3	2.130	1.734	Acetonitrile	1640	1705
			Dimethyl sulfoxide	1634	1701
			50:50 (v/v) Dioxane–D ₂ O	1629, 1623	1698
4	2.247	1.710	Acetonitrile	1644	1671
			Dimethyl sulfoxide	1641	1666
			50:50 (v/v) Dioxane–D ₂ O	1623, 1611	1679, 1661
5	2.598 ^a	1.694 ^a	Acetonitrile	1627	1674
			Dimethyl sulfoxide	1625	1670
			50:50 (v/v) Dioxane–D ₂ O	1580	1692, 1676

^a Data obtained for the 1:1 molecular complex of **5** with methanol (see ref. 4).

Table 2 Pseudo-first-order rate constants k_{2a} and k_3 for the hydrolysis of spiro- λ^4 -sulfanes **2a** and **3**, respectively, in different dioxane–water mixtures at 25 °C, and parameters of the solvent polarity E_T ¹ and Y ¹⁰

H ₂ O (% v/v)	$k_{2a}/10^{-5} \text{ s}^{-1}$	$k_3/10^{-5} \text{ s}^{-1}$	$E_T/\text{kcal mol}^{-1}{}^b$	Y
10	0.283	2.055	55.4	−2.030
20	0.516	3.147	57.6	−0.833
20 ^a	0.156	—	—	—
30	0.742	3.807	59.3	0.013
40	1.003	4.914	60.6	0.715
45	1.126	—	61.2	—
50	1.320 ^c	6.574	62.1	1.361
50 ^a	0.359	—	—	—
55	1.442	—	62.9	—
60	1.607	9.006	63.5	1.945

^a Determined in dioxane–D₂O mixtures. ^b 1 cal = 4.184 J. ^c In the presence of 0.1 mol dm^{−3} LiClO₄ k_{2a} 1.175 × 10^{−5} s^{−1} was found.

$$\log k_{2a} = -10.629 + 0.0924 E_T \quad (r 0.9939) \quad (3)$$

$$\log k_{2a} = -5.143 + 0.1901 Y \quad (r 0.9984) \quad (4)$$

$$\log k_3 = -8.978 + 0.0773 E_T \quad (r 0.9958) \quad (5)$$

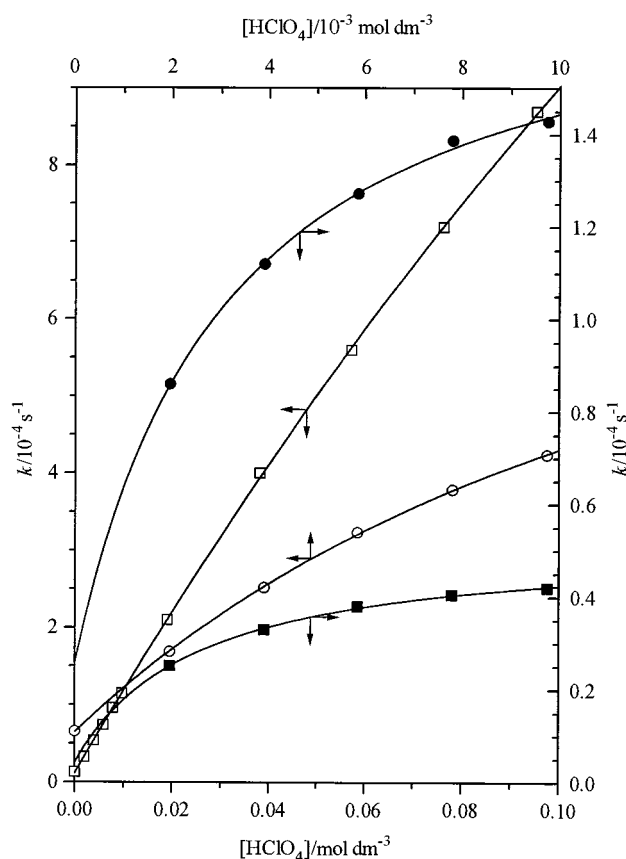
$$\log k_3 = -4.388 + 0.1555 Y \quad (r 0.9919) \quad (6)$$

The slopes of the above functions are only about a quarter of the similar values obtained earlier for diaryl(diacyloxy)spiro- λ^4 -sulfane **1a**,¹ which indicates that the hydrolysis of (acylamino)(acyloxy)spiro- λ^4 -sulfanes **2a** and **3** is less sensitive to the change in the ionizing power of the solvent. In the case of **2a** the rate enhancement caused by the increase in water concentration may be attributed to a greater nucleophile concentration rather than to an effect of solvent polarity which becomes significant only at higher (>50% v/v) water concentrations. Similarly, the rate of hydrolysis of **2a** is not enhanced by increasing the ionic strength (Table 2). Although the k_3 versus [H₂O] relationship cannot be regarded as linear, eqns. (5) and (6) are indicative of a weak solvent effect in the case of spiro- λ^4 -sulfane **3** as well.

Substituent effects. In contrast with diaryl(diacyloxy)spiro- λ^4 -sulfanes (**1a–e**),¹ the hydrolysis of diaryl(acylamino)(acyloxy)spiro- λ^4 -sulfanes (**2a–e**) is promoted by electron-withdrawing and retarded by electron-releasing substituents. Data in Table 3 fit the Hammett equation [eqn. (7)] very well (see σ values in

$$\log k_2 = \rho\sigma + \text{constant} \quad (7)$$

ref. 11) giving a reaction constant ρ 1.43 (r 0.9982) which has the opposite sign and is considerably greater in absolute value than the reaction constant found for diacyloxy analogues with ρ −0.52.

**Fig. 1** Dependence of the hydrolysis rate constants k of spiro- λ^4 -sulfanes **2a** (\square), **3** (\circ), **4** (\blacksquare) and **5** (\bullet) on the concentration of HClO₄ [in 50:50 (v/v) dioxane–water at 25 °C for **2a** and **3**; in water at 50 °C for **4–5**]. Solid lines indicate values calculated from eqn. (11).

Acid catalysis. The acid-catalysed hydrolysis of spiro- λ^4 -sulfanes **2a–e** and **3** was carried out at 25 °C in 50:50 (v/v) dioxane–water containing strong acids, *e.g.* perchloric acid (HClO₄) or toluene-*p*-sulfonic acid (TsOH) in different concentrations. As shown in Fig. 1, reactions are promoted by acid catalysis and the relative reactivities of compounds **2a** and **3** depend on the concentration of acid (at a higher acid concentration **2a** proved to be more reactive than **3**).

In the (0.2–1) × 10^{−2} mol dm^{−3} domain the measured pseudo-first-order rate constants (k) for **2a–e** are linear functions of the acid concentration [eqn. (8)]. The k_0 rate constants

$$k = k_0 + k_{\text{cat}}[\text{acid}] \quad (8)$$

Table 3 Rate constants k_2 for the hydrolysis of compounds **2a–e** in dioxane–water mixtures at 25 °C, and parameters k_0 and k_{cat} calculated from eqn. (8)

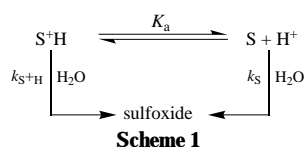
Compound	H ₂ O (% v/v)	$k_2/10^{-5} \text{ s}^{-1}$	Acid ^a	$k_0/10^{-5} \text{ s}^{-1}$	$k_{\text{cat}}/10^{-2} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	r
2a	50	1.320	HClO ₄	1.234	1.059	0.9997
2a	50		TsOH	1.205	1.048	0.9998
2a	20		HClO ₄	0.968	0.791	0.9995
2a	50 ^b		TsOH	0.385	0.596	0.9987
2a	20 ^b		TsOH	0.413	0.749	0.9991
2b	50	20.05	HClO ₄	27.10	4.510	0.9997
2c	50	2.911	HClO ₄	4.000	1.526	0.9984
2d	50	0.827	HClO ₄	0.877	0.703	0.9997
2e	50	0.663	HClO ₄	0.406	0.461	0.9959

^a Concentration range: $(0.2\text{--}1.0) \times 10^{-2} \text{ mol dm}^{-3}$. ^b Measured in dioxane–D₂O.

obtained from the linear equations can be regarded as practically identical (within experimental error) with the k_2 constants measured in neutral dioxane–water (Table 3). The susceptibility for acid catalysis of (acylamino)spiro- λ^4 -sulfanes **2a–e** is, however, far less pronounced than that of (diacyloxy)spiro- λ^4 -sulfanes **1a–e**. The catalytic constant measured for **2a** in 80:20 (v/v) dioxane–water (Table 3) is about 3000 times lower than that for its diacyloxy analogue **1a**.¹

Similarly to noncatalysed hydrolysis, the reactions carried out in acidic media were assisted by electron-withdrawing substituents but the substituent effect was weaker in this case. By substituting the catalytic constants k_{cat} (Table 3) and the appropriate σ values¹¹ into eqn. (7) a reaction constant ρ_{cat} 0.90 (r 0.9926) was obtained for the acid-catalysed reaction. The decrease in ρ values (ρ 1.43 for noncatalysed hydrolysis) may be explained by the facts that in the latter case protonation is aided by electron-releasing, while nucleophilic displacement by electron-withdrawing substituents.

By raising the concentration of acid to 0.1 mol dm⁻³, the k versus [HClO₄] plot for **2a** curves slightly downwards (Fig. 1). Compound **3** gave a similar function in the $(0.1\text{--}1) \times 10^{-2}$ mol dm⁻³ HClO₄ concentration range (Fig. 1). By assuming that the highly polarized acyloxy group in spiro- λ^4 -sulfane (S) is protonated in strong acids and the resulting carboxy-substituted sulfonium cation (S⁺H) reacts faster than the spiro- λ^4 -sulfane, a reaction pathway with two parallel steps can be written for the hydrolysis, as shown in Scheme 1.



Starting from Scheme 1, eqns. (9) and (10) can be derived,

$$k_{\text{exp}}[\text{S}]_{\text{st}} = k_{\text{S}^+\text{H}}[\text{S}^+\text{H}] + k_{\text{S}}[\text{S}] \quad (9)$$

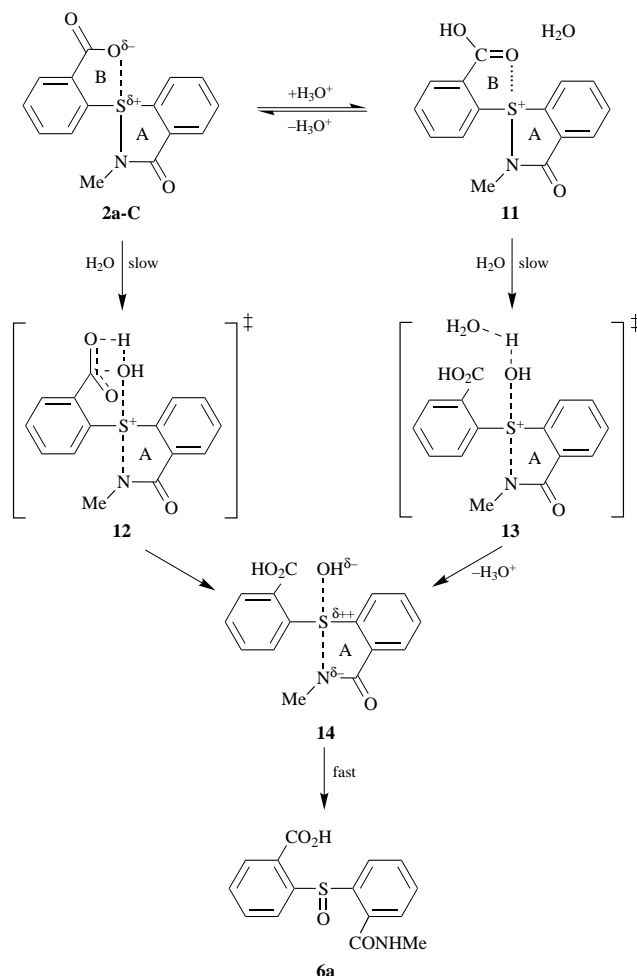
$$k_{\text{exp}}[\text{S}]_{\text{st}} = k_{\text{S}^+\text{H}} \frac{[\text{H}^+]}{[\text{H}^+] + K_{\text{a}}} [\text{S}]_{\text{st}} + k_{\text{S}} \frac{K_{\text{a}}}{[\text{H}^+] + K_{\text{a}}} [\text{S}]_{\text{st}} \quad (10)$$

where $[\text{S}]_{\text{st}} = [\text{S}] + [\text{S}^+\text{H}]$ denotes the stoichiometric concentration of spiro- λ^4 -sulfane. The experimental rate constants are described well by eqn. (11); the calculated $k_{\text{S}^+\text{H}}$, k_{S} and K_{a} constants are given in Table 4.

$$k_{\text{exp}} = \frac{k_{\text{S}^+\text{H}}[\text{H}^+] + k_{\text{S}}K_{\text{a}}}{[\text{H}^+] + K_{\text{a}}} \quad (11)$$

The rate constants k_{S} related to the hydrolysis of the nonprotonated spiro- λ^4 -sulfanes **2a** and **3** are in good agreement with the rate constants k_{2a} and k_3 obtained for these compounds in neutral 50:50 (v/v) dioxane–water (cf. Table 2). The $k_{\text{S}^+\text{H}}$ data indicate that the hydrolysis rates of protonated spiro- λ^4 -

sulfanes (*i.e.* carboxy-substituted sulfonium salts; see **11** in Scheme 2) are significantly higher than those of spiro- λ^4 -



Scheme 2

sulfanes with a polar, sulfonium-carboxylate-like structure (**2a–C**) ($k_{\text{S}^+\text{H}} > k_{\text{S}}$), and the protonated form of **2a** is more reactive than that of **3**.

Acid dissociation constants K_{a} calculated for protonated spiro- λ^4 -sulfanes from eqns. (9)–(11) are rather high. The strength of the sulfonium carboxylic acid is increased not only by the electron-withdrawing effect of the sulfonium centre but also by the through-space polar effect of the sulfonium group in the *ortho* position, especially in the case of protonated **2a**, in which a sterically favourable five-membered spiro-ring is performed.

Deuterium solvent isotope effect. The isotope effect in the noncatalysed hydrolysis of spiro- λ^4 -sulfane **2a** was studied in 50:50 and 80:20 (v/v) dioxane–H₂O(D₂O) mixtures, and $k_{\text{H}_2\text{O}}/k_{\text{D}_2\text{O}}$ values of 3.68 and 3.31 were obtained, respectively

Table 4 $k_{\text{S-H}}$, k_{S} and K_{a} constants for the hydrolysis of spiro- λ^4 -sulfanes **2a** and **3–5** in acidic media, calculated from eqn. (11)

Compound	$k_{\text{S-H}}/10^{-4} \text{ s}^{-1}$	$k_{\text{S}}/10^{-5} \text{ s}^{-1}$	$K_{\text{a}}/\text{mol dm}^{-3}$	Solvent ^a	$T/^{\circ}\text{C}$
2a	49.7	1.22	45.6	50:50 (v/v) Dioxane–water	25
3	9.94	6.51	1.5	50:50 (v/v) Dioxane–water	25
4	0.521	0.43	2.6	Water	50
5	1.82	2.62	3.1	Water	50

^a The $[\text{HClO}_4]$ range was 0–0.1 mol dm⁻³ for **2a**, 0–0.01 mol dm⁻³ for **3** and 0.02–0.1 mol dm⁻³ for **4–5**.

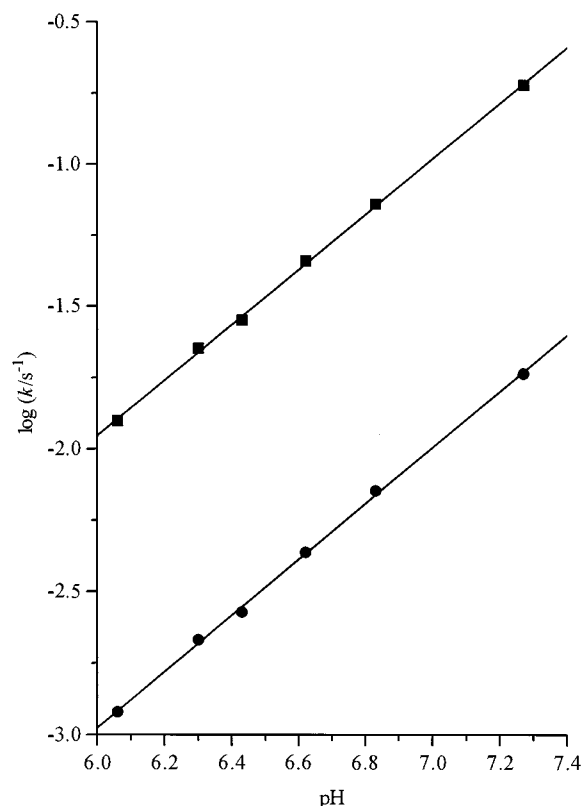


Fig. 2 pH dependence of $\log k$ for spiro- λ^4 -sulfanes **4** (■) and **5** (●) in aqueous buffer solutions at 50 °C

(*cf.* Table 2). Data indicate that the deuterium solvent isotope effect does not depend essentially on the composition of the solvent mixture. For the catalytic constants of **2a** isotope effects of $k_{\text{H}_2\text{O}}/k_{\text{D}_2\text{O}}$ 1.76 and 1.65, respectively, were found in the same solvents containing TsOH (*cf.* Table 3).

Hydrolysis of spiro- λ^4 -sulfanes **4** and **5**

The hydrolysis of compounds **4** and **5** did not follow pseudo-first-order kinetics in 50:50 (v/v) dioxane–water mixture at 25 °C throughout the whole range of measurements; the $\ln[(A - A_{\infty})/(A_0 - A_{\infty})]$ versus t plots were not linear in the initial stage of the reaction. From the second, almost linear parts of the plots the approximate values of k_4 $9.89 \times 10^{-7} \text{ s}^{-1}$ and k_5 $8.86 \times 10^{-7} \text{ s}^{-1}$ were calculated for the hydrolysis of **4** and **5**, respectively. Data indicate that compounds **4** and **5**, in which the acylamino part is incorporated in a six-membered ring A, are considerably less reactive than the **2a–e** and **3** analogues with a five-membered ring. We assumed that the curvature of the plots was caused by a shift in pH of the medium therefore the reactions were carried out in aqueous buffer solutions, too (for details see Experimental). Under these conditions the reactions became first order at pH 6–7.5. The rate increased with pH, and the $\log k$ versus pH plots [eqns. (12)–(13)] were linear

$$\log k_4 = -7.784 + 0.972 \text{ pH} \quad (r 0.9997) \quad (12)$$

$$\log k_5 = -8.863 + 0.981 \text{ pH} \quad (r 0.9996) \quad (13)$$

with a slope close to unity (Fig. 2); *e.g.* at pH 7 k_4 0.105 s^{-1} and k_5 0.0102 s^{-1} .

The above findings suggest that the role of OH^- ions as nucleophiles cannot be neglected in describing the hydrolysis of **4** and **5**. In the absence of a buffer the deviation from pseudo-first-order kinetics at the early stage of the reaction may be ascribed to the slight pH shift caused by the acid dissociation of the carboxy-substituted sulfoxide products (**8** and **9**, respectively) decreasing the concentration of OH^- ions.

As is expected, the kinetics become pseudo-first-order in solutions containing a strong acid such as HClO_4 because the concentration of OH^- ions as well as the acidity resulting from the products is not significant in this case. The character of the k versus [acid] plots obtained for compounds **4** and **5** in aqueous HClO_4 solutions at 50 °C is the same as in the case of **3** (see Fig. 1). Rate and equilibrium constants calculated from eqn. (11) are listed in Table 4. The rate constants for zero acid concentration, which were estimated from the linear portion of the $\ln[(A - A_{\infty})/(A_0 - A_{\infty})]$ versus t plots obtained in pure water at 50 °C ($1.9 \times 10^{-4} \text{ s}^{-1}$ for **4** and $5.13 \times 10^{-5} \text{ s}^{-1}$ for **5**), were not included in the calculation because they were significantly higher than expected, likely due to the participation of OH^- ions in the reaction. Comparing the rate constants we found that compound **4** is more reactive in neutral solutions (Fig. 2), whereas compound **5** shows a higher reactivity in acidic media (Fig. 1 and Table 4). We may suppose that water molecules take part as nucleophiles in the hydrolysis of compounds **4** and **5** in acidic media while in neutral solutions OH^- ions take part.

Mechanism

From X-ray, IR and kinetic data one may draw some conclusions for the hydrolysis of diaryl(acylamino)(acyloxy)spiro- λ^4 -sulfanes **2–5**; reaction pathways proposed for the noncatalytic and acid-catalysed cases are shown in Scheme 2 for compound **2a**.

(i) Spiro- λ^4 -sulfanes with a major contribution of a limiting structure such as **2a-B** exhibit long (2.13–2.25 Å)⁴ and highly polarized S–O bonds which may be classified as weak hypervalent bonds.[†] Because ring B with an acyloxy part is closed in these compounds only by a weak S–O bond (see **2a-C**), the opening of this ring, which pertains to the nucleophilic attack of water on sulfur, should occur very easily and so cannot be rate-determining. This is why the water content of the solvent influences the rate of hydrolysis only to the extent of its molar concentration, and the ionic strength of the medium has practically no effect on the reaction rate.

(ii) From the easy opening of ring B it follows that nucleophilic attack of water on the positively charged sulfonium centre should represent the rate-determining step for the non-catalysed hydrolysis (**2a-C** \rightarrow **12** \rightarrow **14**). The positive reaction constant (ρ 1.43) observed for compounds **2a–e** provides strong evidence for this view. If the ring-opening were rate-

[†] Axial S–O bonds occurring in (diaryl)spiro- λ^4 -sulfane-type compounds may be classified as follows (*cf.* ref. 6): S–O covalent single bond (1.66–1.71 Å), usual S–O hypervalent bond (1.79–1.83 Å) in symmetric structures, weak S–O hypervalent bond (1.95–2.25 Å) in unsymmetric structures and S \cdots O close contact (2.35–2.75 Å) significantly shorter than the sum of the van der Waals radii (3.25 Å).

determining, a negative reaction constant would be obtained, as was the case for (diacyloxy)spiro- λ^4 -sulfanes **1a–e** with two equivalent and strong axial O --- S^{IV} --- O hypervalent bonds ($\rho = -0.52$).¹

(iii) The significant role of steric factors for compounds **2–5** is reflected by the different order of dipolar character (**2a** \approx **3** < **4** < **5**; see Table 1) and reactivity towards non-catalysed hydrolysis in neutral, unbuffered solutions (**4** \approx **5** \ll **2a** < **3**). Spiro- λ^4 -sulfanes with five-membered ring A (**2a** and **3**) are much more reactive than the six-membered analogues (**4** and **5**). Nevertheless, the ring-size effect is in agreement with the suggested rate-determining step because other nucleophilic displacements occurring at the sulfonium centre are known to proceed several orders of magnitude more quickly in five-membered cyclic derivatives than in six-membered ones.^{12,13}

(iv) The size of the O-containing ring B also has some rate-controlling role in the noncatalysed hydrolysis of (acylamino)(acyloxy)spiro- λ^4 -sulfanes. The greater reactivity of compound **3** compared to that of **2a** may be explained by the fact that the six-membered ring B in **3** is closed by a weaker hypervalent S --- O bond than the five-membered ring in **2a**. (As shown in ref. 6 S \cdots O close contact is also less effective in a six-membered ring than in a five-membered analogue.) Thus the sulfonium centre in **3** is less shielded from nucleophilic attack than in **2a**. It is worth mentioning that (diacyloxy)spiro- λ^4 -sulfanes¹ having six-membered spiro-rings B proved also to be more reactive than those with five-membered rings.

(v) Under similar conditions of hydrolysis (acylamino)(acyloxy)spiro- λ^4 -sulfanes are less reactive than their diacyloxy analogues (*cf.* Table 2 and Table 1 in ref. 1). The decrease in reactivity may be ascribed to the acylamino part in rings A which is a poorer leaving group than the acyloxy part in rings B therefore the formation of a monocyclic λ^4 -sulfane with a polarized S --- N hypervalent bond (see **2a-C** \longrightarrow **12** \longrightarrow **14** in Scheme 2) is less favourable than the analogous process involving S --- O hypervalent bond (see **1** \longrightarrow **7** \longrightarrow **8** in Scheme 1 of ref. 1).

(vi) The deuterium solvent isotope effect measured for the hydrolysis of **2a** is compatible with a primary effect, suggesting that the nucleophilic attack of the water molecule in the rate-determining step is accompanied by O–H bond cleavage, as shown in the transition structure **12** (Scheme 2). Other water molecules or the neighbouring carboxylate group may contribute as proton acceptors. It seems very likely that ring A with an acylamino part needs a stronger nucleophile than water to undergo splitting, and such a nucleophile can be formed from the neutral water molecule by proton abstraction. This view is supported by the fact that the more reactive (diacyloxy)spiro- λ^4 -sulfanes (*e.g.* **1a**) with acyloxy-containing ring B exhibit significantly weaker deuterium solvent isotope effect; $k_{\text{H}_2\text{O}}/k_{\text{D}_2\text{O}}$ 3.31 for **2a** and 1.66¹ for **1a** in 80:20 (v/v) dioxane–water.

(vii) The values of catalytic constants k_{cat} (Table 3) show that the hydrolysis of (acylamino)(acyloxy)spiro- λ^4 -sulfanes is moderately promoted by acid catalysis. Protonation converts the starting compounds into a more reactive carboxy-substituted sulfonium ion (*e.g.* **2a-C** \longrightarrow **11**). The enhanced reactivity of the sulfonium centre in **11**-type intermediates as compared to that in **2a-C**-type structures may have two origins. (a) The *ortho*-carboxy group formed by protonation has a stronger electron-withdrawing effect than the negatively charged carboxylate group, which increases the positive polarization and so the reactivity of the sulfonium centre; (b) the carboxy group setting up S \cdots O close contact (**11**) shields the sulfonium centre against the attack of water nucleophile less successfully than the carboxylate group forming a hypervalent S --- O bond which may also increase the rate of hydrolysis. The stronger the S --- O hypervalent bond in spiro- λ^4 -sulfanes, the greater difference between the reactivity of the spiro- λ^4 -

sulfane and its protonated form that can be observed (see data for **2a** and **3** in Table 4).

Comparing k_{cat} data for compound **2a** (Table 3) and those for **1a** (Table 2 in ref. 1) one may conclude that (acylamino)(acyloxy)spiro- λ^4 -sulfanes are less sensitive to acid catalysis than the diacyloxy analogues, the difference in reactivity may be attributed to the fact that ring-opening is not a part of the rate-determining step for acylamino derivatives.

(viii) The decrease of the positive reaction constant value for the acid-catalysed hydrolysis of compounds **2a–e** may be explained by eqn. (14) showing that ρ_{cat} can be divided into two

$$\rho_{\text{cat}} = \rho_e + \rho_{\text{Nu}} \quad (14)$$

terms. The negative ρ_e elementary reaction constant reflects the fact that the protonation equilibrium is promoted by electron-releasing substituents. The positive ρ_{Nu} term is related to the nucleophilic attack at the sulfonium centre, which is assisted by electron-withdrawing groups. Because ρ_e does not overcompensate ρ_{Nu} , the overall reaction constant ρ_{cat} remains positive. It is worth mentioning that ρ_{cat} (-1.55) is negative for the acid-catalysed hydrolysis of (diacyloxy)spiro- λ^4 -sulfanes **1a–e**, indicating that the negative ρ_e term is predominant in this case.

(ix) In the acid-catalysed hydrolysis of **2a** the deuterium solvent isotope effect is only about half the value obtained for the noncatalysed reaction because the primary isotope effect due to the deprotonation of the water nucleophile (which occurs in the rate-determining step, see *e.g.* **11** \longrightarrow **13** \longrightarrow **14**) and the inverse isotope effect of the protonation pre-equilibrium (*e.g.* **2a-C** \longrightarrow **11**) are superimposed.

(x) The significant acceleration of the hydrolysis observed for the less reactive spiro- λ^4 -sulfanes **4** and **5** in nearly neutral buffered solutions [*e.g.* at pH 7 k_4 0.105 s⁻¹ *cf.* eqn. (12)] as compared with the reaction in distilled water (*e.g.* k_4 1.9 \times 10⁻⁴ s⁻¹) suggests that OH⁻ ions also take part in the reaction as nucleophiles. It is striking, however, that the order of reactivity ($k_4 > k_5$) observed in buffered solutions differs from that detected in acidic media ($k_4 < k_5$). At this moment we do not have enough information to explain this phenomenon. It seems likely, however, that reactions with OH⁻ nucleophiles do follow a reaction pathway different to those with water. In the former case *e.g.* an associative mechanism similar to that published by Martin and Balthazor¹⁴ might be taken into account.

(xi) As a result of the nucleophilic attack of H₂O or OH⁻ reactants on the central sulfur atom the S–N covalent bond in ring A is markedly weakened (see *e.g.* the transition states **12** and **13** in Scheme 2). Because the basicity of OH⁻ and Ar–CO–N(Me)⁻ species do not differ significantly, we may assume that the hypervalent S --- N and S --- O bonds are about equally as strong in the **14**-type intermediates from which the sulfoxide products (*e.g.* **6**) are formed in fast proton-transfer steps.

(xii) We found in other experiments¹⁵ that the hydrolysis of amidosulfonium salts (*e.g.* **11** without *ortho*-carboxy substituents) is not affected by acid catalysis. This suggests that the amide moiety in spiro- λ^4 -sulfanes (ring A) is not protonated in the rate-determining step of the hydrolysis but only in the subsequent fast proton-transfer steps.

Experimental

Materials

The preparation of spiro- λ^4 -sulfanes **2a**, and **3–5** has been published earlier.⁴ The synthesis of **2b–e** is described below. Melting points were determined on a Boëtius micro melting point apparatus. ¹H NMR measurements for **2b–e** were made on a Bruker WP-80SY instrument operating at 80 MHz. Toluene-*p*-sulfonic acid (TsOH) was recrystallized from concentrated HCl solution. Spectroscopic grade anhydrous dioxane used in the kinetics and IR spectroscopic studies was obtained from analytical grade dioxane (Reanal, Budapest) by an appropriate

purification method.¹⁶ Before use, traces of peroxides were removed by distillation from LiAlH₄. For the hydrolysis of **4–5** in aqueous solutions, 4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid (HEPES, Serva Feinbiochemica, analytical grade, 0.01 mol dm⁻³, pH 6.83–7.27 at 50 °C), 4-morpholinepropanesulfonic acid (MOPS, Serva Feinbiochemica, analytical grade, 0.01 mol dm⁻³, pH 6.43–6.62 at 50 °C) and 1,4-piperazinebis(ethanesulfonic acid) (PIPES, Merck, 99%, 0.01 mol dm⁻³, pH 6.08–6.30 at 50 °C) were used as buffer substances. The desired pH values were fixed by titration with NaOH, using a Beckman Φ32 pH meter with automatic temperature compensation.

Spiro-λ⁴-sulfanes 2b–e. To a saturated solution of the corresponding sulfoxide **6b–e** (0.1 g) in dry AcOH (1–4 cm³), Ac₂O (0.1 cm³) was added and the mixture was heated at 100 °C for 1 h. The solvent was evaporated, the residue was triturated with diethyl ether, filtered off and dried *in vacuo* over KOH to give 2-methyl-5'-nitrospiro[3*H*-2,1-benzoxathiole-1,1'-3*H*-1,2-benzisothiazole]-3(2*H*),3'-dione [**2b** (79 mg, 79%): mp 210–222 °C; ν_{\max} (KBr)/cm⁻¹ 1710vs, 1650vs (C=O); δ_{H} (80 MHz; [²H₆]DMSO) 7.4–8.75 (m Ar-H), 3.34 (NCH₃), 5'-chloro-2-methylspiro[3*H*-2,1-benzoxathiazole-1,1'-3*H*-1,2-benzisothiazole]-3(2*H*),3'-dione [**2c** (84 mg, 84%): mp 254–260 °C; ν_{\max} (KBr)/cm⁻¹ 1720vs, 1700vs, 1640vs (C=O); δ_{H} (80 MHz; CDCl₃) 7.0–8.6 (m Ar-H), 3.41 (NCH₃), 2,5'-dimethylspiro[3*H*-2,1-benzoxathiole-1,1'-3*H*-1,2-benzisothiazole]-3(2*H*),3'-dione [**2d** (92 mg, 92%): mp 264–267 °C; ν_{\max} (KBr)/cm⁻¹ 1692vs, 1660vs (C=O); δ_{H} (80 MHz; CDCl₃) 7.0–8.6 (m Ar-H), 3.38 (NCH₃), 2.47 (5'-CH₃)] and 5'-methoxy-2-methylspiro[3*H*-2,1-benzoxathiole-1,1'-1,2-benzisothiazole]-3(2*H*),3'-dione [**2e** (80 mg, 80%): mp 225–227 °C; ν_{\max} (KBr)/cm⁻¹ 1710vs, 1650vs (C=O); δ_{H} (80 MHz; CDCl₃) 7.0–8.6 (m Ar-H), 3.91 (5'-OCH₃), 3.38 (NCH₃), respectively.

5-Substituted 2-[2'-(*N*-methylcarbamoyl)phenylsulfinyl]benzoic acids [R = NO₂ (6b**), Cl (**6c**), Me (**6d**), MeO (**6e**)].** The corresponding sulfide **15b–e** (1.9 mmol) was dissolved in pyridine (5.7 cm³) and then water (1 cm³) and phenyltrimethylammonium tribromide (0.75 g, 2 mmol) were added to the solution. The mixture was stirred at 20 °C for 1 h and finally poured into 1 M H₂SO₄ (57 cm³). After standing at 0 °C for 1 h the precipitate formed was filtered off, washed with water and dried to give **6b** [yield 76%; mp 218–220 °C (AcOH–H₂O); ν_{\max} (KBr)/cm⁻¹ 3395s (NH), 3100–2200br (OH), 1680s, 1648vs (C=O), 970vs (S=O)], **6c** [yield 87%; mp 134–138 °C (AcOH–H₂O); ν_{\max} (KBr)/cm⁻¹ 3450s (NH), 3100–2100br (OH), 1695vs, 1642vs (C=O), 1015vs (S=O)], **6d** [yield 66%; mp 213–214 °C (AcOH–H₂O); ν_{\max} (KBr)/cm⁻¹ 3260s (NH), 3150–2300br (OH), 1680vs, 1650vs (C=O), 1030vs (S=O)] and **6e** [yield 84%; mp 125–127 °C (AcOH–H₂O); ν_{\max} (KBr)/cm⁻¹ 3400s (NH), 3100–2100br (OH), 1690s, 1655vs (C=O), 1000vs (S=O)], respectively.

5-Substituted 2-[2'-(*N*-methylcarbamoyl)phenylthio]benzoic acids [R = NO₂ (15b**), Cl (**15c**), Me (**15d**), MeO (**15e**)].** Sulfides **15b–e** were prepared from the corresponding 5-substituted thiosalicylic acid and 2-iodo-*N*-methylbenzamide as described in ref. 4 for 2-[2'-(*N*-methylcarbamoyl)phenylthio]benzoic acid (**15a**). Selected data: **15b** [yield 48%; mp 209–212 °C (EtOH); ν_{\max} (KBr)/cm⁻¹ 3370s (NH), 3200–2300br (OH), 1713s, 1625vs (C=O)], **15c** [yield 87%; mp 88–89 °C (AcOH–H₂O); ν_{\max} (KBr)/cm⁻¹ 3330s (NH), 3450–2300br (OH), 1695s, 1620vs (C=O)], **15d** [yield 46%; mp 163–169 °C (CH₂Cl₂); ν_{\max} (KBr)/cm⁻¹ 3330s (NH), 3150–2300br (OH), 1700s, 1612s (C=O)], **15e** [yield 60%; mp 173–175 °C (EtOH); ν_{\max} (KBr)/cm⁻¹ 3340s (NH), 3200–2300br (OH), 1722s, 1700s, 1613vs (C=O)]. 5-Methoxythiosalicylic acid and 5-methylthiosalicylic acid were prepared from 2-amino-5-methoxybenzoic acid¹⁷ and 2-amino-5-methylbenzoic acid (Aldrich, 97%), respectively, by analogy to 5-chlorothiosalicylic acid.¹⁸

5-Nitrothiosalicylic acid. A mixture of finely powdered 2,2'-dithiobis(5-nitrobenzoic acid)¹⁹ (155 g, 0.39 mol) and D-glucose (108 g, 0.56 mol) in 96% EtOH (500 cm³) was heated to 78–80 °C, and a solution of NaOH (85 g, 2.12 mol) in water (160

Table 5 Initial concentrations (C_0), wavelengths of measurements (λ) and absorbance values for the starting spiro-λ⁴-sulfanes **2a–e**, **3–5** (A_0) and the corresponding sulfoxide products (A_c)

Spiro-λ ⁴ -sulfane	$C_0/10^{-4}$ mol dm ⁻³	λ/nm	A_0	A_c
2a ^a	17.5	313	0.08	0.81
2b ^a	6.32	345	0.24	1.01
2c ^a	9.38	313	0.12	0.80
2d ^a	16.7	316	0.01	0.39
2e ^a	7.92	323	0.07	0.99
3 ^a	1.49	333	0.92	0.30
4 ^b	1.19	333	1.02	0.04
5 ^b	1.04	345	0.86	0.04

^a In 50:50 (v/v) dioxane–water at 25 °C. ^b In aqueous buffer (PIPES) solution of pH 6.2 at 50 °C.

cm³) was added dropwise under continuous stirring in 30 min. The mixture was stirred for an additional 15 min at the same temperature, then filtered, and the filtrate was poured onto a mixture of concentrated HCl solution (400 cm³) and ice. The precipitate formed was filtered off, washed with water and dried *in vacuo* to give 5-nitrothiosalicylic acid (104 g, 67%). Being highly sensitive to oxidation, the crude product was directly used in the synthesis of **15b**.

IR spectra

Fourier transform IR spectra of spiro-λ⁴-sulfanes **1–5** [1–5 mg cm⁻³ in 50:50 (v/v) dioxane–D₂O, acetonitrile and dimethyl sulfoxide (DMSO)] were obtained with a Bruker IFS-55 spectrometer using CaF₂ cells (0.05–0.25 mm pathlengths). In the case of spectra recorded in acetonitrile and DMSO, the contribution of the H–O–H deformation vibration (due to traces of water) to the 1600–1700 cm⁻¹ spectral region was removed by subtracting water spectra obtained in the same solvents. The 1800–1500 cm⁻¹ region of the spectra was analysed by Fourier self-deconvolution²⁰ and decomposed into individual bands by a Levenberg–Marquardt nonlinear curve-fitting procedure²¹ by using weighted sums of Lorentzian and Gaussian functions. The carbonyl frequencies are listed in Table 1.

Kinetics

Kinetic measurements were performed with a Specord 40M (Zeiss, Jena) and a Varian Cary3E UV–VIS spectrophotometer in dioxane–water (10–60% v/v water) at 25 °C (spiro-λ⁴-sulfanes **2–3**) and in aqueous buffer or HClO₄ solutions at 50 °C (spiro-λ⁴-sulfanes **4–5**), by using quartz cells of 1 cm (initial concentrations, wavelengths and absorbance values for the starting spiro-λ⁴-sulfanes and the sulfoxide products are listed in Table 5). The reactions performed in organic–aqueous solutions were started by mixing quickly aliquots of solutions of spiro-λ⁴-sulfane in dioxane with adequate quantities of water, D₂O, aqueous LiClO₄, TsOH or HClO₄ solutions, or with solutions of TsOH in D₂O, as required. The reactions performed in aqueous media were started by adding small quantities (*ca.* 1% v/v) of concentrated stock solutions of spiro-λ⁴-sulfane in DMSO to the aqueous buffer or HClO₄ solution, directly into the stirred measurement cells. The initial concentration of the spiro-λ⁴-sulfanes was (1.0–17.5) × 10⁻⁴ mol dm⁻³. The effect of the ionic strength was studied in the presence of LiClO₄ (0.1 mol dm⁻³), whereas acid catalysis was investigated by using toluene-*p*-sulfonic acid or HClO₄ (1.0 × 10⁻³–0.1 mol dm⁻³). Relative errors of the rate constants were less than ±3%.

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