Nucleophilic Substitution at Bivalent Sulphur. Part III.[1] Kinetics and Mechanism of the Base-catalysed Hydrolysis of Ethyl 2-Nitro-4-trifluoromethylbenzenesulphenate, the Corresponding Sulphenyl Chloride, and the Disulphide

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In the base-catalysed hydrolysis of ethyl 2-nitro-4-trifluoromethylbenzenesulphenate in 50% v/v aqueous dioxan, the reaction leading to the disappearance of ester was of the first order in ester and in hydroxide ion, while that leading to the disappearance of the intermediate sulphenate anion was of the second order in the anion. The rate of the latter reaction was inversely proportional to the concentration of hydroxide ion. The maximum concentration of sulphenate anion (80%) was much greater than with ethyl 2-nitrobenzenesulphenate and presumably reflects the decreased nucleophilicity and base strength of the anion. The mechanism proposed involves nucleophilic substitution at sulphur by hydroxide ion followed by reversible formation of the thiosulphinate from sulphenate anion and finally reaction of the thiosulphinate with hydroxide ion. Bis-2-nitro-4-trifluoromethylphenyl disulphide hydrolysed 100 times faster than the ethyl sulphenate and consequently gave a higher maximum concentration of sulphenate anion. These two hydrolyses are considered to follow similar mechanisms. 2-Nitro-4-trifluoromethylbenzenesulphenyl chloride hydrolyses very rapidly to form the disulphide and the sulphinate anion. The increased rate of reaction of the intermediates is attributed to electrophilic assistance by the sulphenyl chloride.

THE hydrolysis of diaryl disulphides and derivatives of arenesulphenic acids in alkaline solution is considered[2] to involve the formation of a sulphenic acid intermediate, ArSOH. This intermediate, or its anion, then reacts with a further molecule of reactant, or undergoes self-condensation, to give the thiosulphinate, ArSO·SAr, which may be isolated under favourable conditions [reactions (1)—(3)]. With *S*-aryl permonothioesters

$$\mathrm{ArSX} + \mathrm{OH^-} \longrightarrow \mathrm{ArSOH} + \mathrm{X^-} \qquad (1)$$

$$\mathrm{ArSOH} + \mathrm{OH^-} \rightleftharpoons \mathrm{ArSO^-} + \mathrm{H_2O} \qquad (2)$$

$$\mathrm{ArSO^-} + \mathrm{ArSX} \longrightarrow \mathrm{ArSO{\cdot}SAr} + \mathrm{X^-} \qquad (3a)$$

$$\mathrm{ArSO^-} + \mathrm{ArSOH} \longrightarrow \mathrm{ArSO{\cdot}SAr} + \mathrm{OH^-} \qquad (3b)$$

$$\mathrm{ArSO{\cdot}SAr} \longrightarrow \text{products}$$

(ArSO·CO·R) an alternative[3] initial step may be nucleophilic substitution at the acyl carbon atom to give the sulphenate anion directly.

2-Nitrobenzenesulphenyl derivatives are convenient substrates for studying these reactions as they hydrolyse to give[2a] a blue solution, the colour being attributed to the sulphenate anion. The base-catalysed hydrolysis of ethyl and t-butyl 2-nitrobenzenesulphenate was shown[2a] to be of the first order in both hydroxide ion and ester, while the reaction leading to the disappearance of the sulphenate anion was of the second order in the anion. This was held to be consistent with reaction (3b) being the major pathway for the disappearance of the sulphenate anion. We now report a similar study of the hydrolysis of ethyl 2-nitro-4-trifluoromethylbenzenesulphenate and include data on the hydrolysis of the corresponding disulphide and sulphenyl chloride. It has been suggested[4] that reaction (3a) is important with this last class of compound. The 2-nitro-4-trifluoromethylbenzenesulphenate anion should be a weaker nucleophile than the 2-nitrobenzenesulphenate anion owing to the electron-withdrawing effect of the trifluoromethyl group, while the 2-nitro-4-trifluoromethylbenzenesulphenyl system is slightly reactive[5] to nucleophiles. The former effect was expected to predominate and result in a higher relative concentration of sulphenate anion in this study and thus greater accuracy.

RESULTS AND DISCUSSION

Hydrolysis of Ethyl 2-Nitro-4-trifluoromethylbenzenesulphenate.—The hydrolysis of the ethyl sulphenate in 50% v/v aqueous dioxan at 25·0° was followed spectrophotometrically. Second-order velocity constants, k_{II}, were obtained by dividing the measured first-order velocity constants, k_{I}, by the concentration of hydroxide ion. Details are in Table 1. As with ethyl 2-nitrobenzenesulphenate,[2a] the graph of k_{I} against hydroxide ion concentration passed through or near the origin indicating that the uncatalysed reaction was slow. At higher hydroxide ion concentrations the curve went through a maximum which was previously[2a] attributed to the combination of a positive concentration effect and a negative salt effect. Extrapolation of the plot of log k_{II} against ionic strength gave a value of $1{\cdot}12 \times 10^{-2}$ l mol^{-1} s^{-1} for the velocity constant for the hydrolysis of the sulphenate at zero ionic strength. This value is somewhat higher than that obtained[5] in 50% v/v aqueous ethanol, *viz.* $6{\cdot}92 \times 10^{-3}$ l mol^{-1} s^{-1}, although the media are considered to be very similar. At these high salt concentrations, sodium hydroxide and sodium perchlorate affect the rate to a different extent due presumably to different degrees of ion association. Consequently the rate depends upon the composition of the salt mixture and at an ionic strength of 0·4 the value of k_{II} is not constant. This behaviour parallels that observed with ethyl 2-nitrobenzenesulphenate.[2a]

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[1] Part II, D. R. Hogg and P. W. Vipond, *J. Chem. Soc.* (*C*), 1970, 2142.

[2] (*a*) D. R. Hogg and P. W. Vipond, *J. Chem. Soc.* (*B*), 1970, 1242; (*b*) J. P. Danehy, *Internat. J. Sulphur Chem.* (*B*), 1971, **6**, 103 and references therein.

[3] R. E. Putman and W. H. Sharkey, *J. Amer. Chem. Soc.*, 1957, **79**, 6526.

[4] L. Di Nunno, G. Modena, and G. Scorrano, *Ricerca sci.*, 1966, **36**, 825; J. L. Kice and J. P. Cleveland. *J. Amer. Chem. Soc.*, 1970, **92**, 4757.

[5] C. Brown and D. R. Hogg, *Chem. Comm.*, 1967, 38.

Concentration of the 2-*Nitro*-4-*trifluoromethylbenzenesulphenate Anion.*—As the sulphenate ester hydrolysed, the solution became blue, the colour being attributed [2a] to the sulphenate anion. The intensity of the corresponding absorption band at 588 nm increased to a maximum and then decreased as the reaction proceeded. A typical plot of absorbance against reaction time is Figure 1. In all cases a single maximum was observed. The maximum absorbances, $A_{max.}$, of these curves are in Table 1. Gradients of the tangents to these curves at zero time were calculated and hence extinction coefficients for the 2-nitro-4-trifluoromethylbenzenesulphenate anion obtained. The mean value, $4\cdot22 \times 10^3$ l mol^{-1} cm^{-1} (s.d. $0\cdot13 \times 10^3$), which was used for all subsequent calculations, is similar to that for the 2-nitrobenzenesulphenate anion [2a] ($5\cdot26 \times 10^3$ l mol^{-1} cm^{-1}) and of the same order as that recorded for the 2-nitro-4-trifluoromethylbenzenethiolate anion ($1\cdot4 \times 10^3$ l mol^{-1} cm^{-1}) and 2-nitrobenzenethiolate anion [6] ($1\cdot6 \times 10^3$ l mol^{-1} cm^{-1}).

TABLE 1

Results for the base-catalysed hydrolysis of ethyl 2-nitro-4-trifluoromethylbenzenesulphenate in 50% (v/v) aqueous dioxan at 25·0°

[OH$^-$]/M	[NaClO$_4$]/M	10^3k_I/s^{-1}	10^3k_{II}/l mol^{-1} s^{-1}	$A_{max.}$	10^8R_d/mol l^{-1} s^{-1}	k_q/l mol^{-1} s^{-1}
0·08		0·765	9·56	0·80	3·29	0·92
0·16		1·225	7·66	0·98	7·11	1·32
0·24		1·51	6·29	1·06	6·48	1·04
0·32		1·74	5·43	1·10	7·46	1·10
0·40		1·82	4·55	1·13	6·37	0·89
0·48		1·74	3·63	1·10	7·14	1·05
0·24	0·08	1·20	5·01	0·94	7·45	1·48
0·24	0·16	1·09	4·54	0·87	7·41	1·76
0·24	0·24	1·01	4·20	0·80	7·57	2·10
0·24	0·32	0·891	3·71	0·74	7·66	2·47
0·08	0·32	0·449	5·61	0·49	5·43	4·02
0·16	0·24	0·792	4·95	0·71	6·97	2·47
0·32	0·08	1·385	4·33	1·00	7·61	1·35

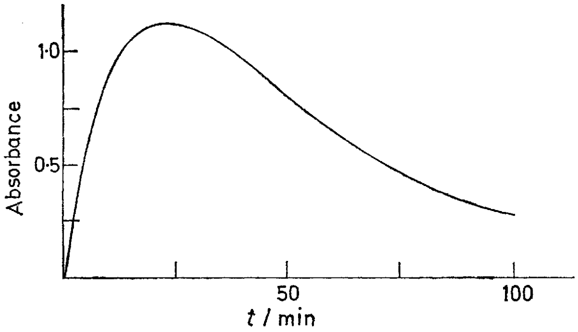

FIGURE 1 Graph of optical density at 588 nm against time

At $A_{max.}$ in a typical run, 80% of the original ester was present as the sulphenate anion, [ArSO$^-$] = $2\cdot68 \times 10^{-4}$M, and only 11·5% of the original ester had proceeded beyond this stage. In contrast the hydrolysis of ethyl 2-nitrobenzenesulphenate gave two maxima separated by a short time interval and typically at the first maximum only 17·5% of the original ester was present [7] as the sulphenate anion and more than 50% of the anion produced had reacted further. These observations are in agreement with the original supposition on the relative reactivities of the two sulphenate ions. The double maximum observed in the previous study was held to indicate more than one pathway to the sulphenate anion, the other pathway involving a later intermediate. In this study the much greater maximum concentration of sulphenate anion requires that such an alternative pathway will only be of importance at a much greater percentage reaction and this will combine with the expected lower nucleophilicity of the anion to give a more gradual decrease in the absorption at 588 nm. The plot of $A_{max.}$ against k_I was essentially linear as previously observed.[2a]

Disappearance of the 2-*Nitro*-4-*trifluoromethylbenzenesulphenate Anion.*—Rates of disappearance of the sulphenate anion, R_d, were obtained by subtracting the observed rates of formation, R_{obs}, which were calculated from the slopes of the tangents to absorbance against time curves, from the rate of formation by the hydrolysis of the ethyl sulphenate, R_F. The plots of R_d against [ArSO$^-$]^2 were essentially linear for concentrations up to the maximum, while those against [ArSO$^-$][ArSOEt] showed gross curvature. Above the maximum, when over 80% of the ester is hydrolysed, the values of R_d increase above those required for linearity. This suggests that the sulphenate anion undergoes an additional reaction. ^{19}F N.m.r. studies show [8] that the anion of 2-amino-4-trifluoromethylbenzenesulphonic acid is formed during the hydrolysis and we suggest that this additional reaction may be the rearrangement and reduction of the sulphenate ion to give the sulphonate. Possible reducing agents include the thiolate or the sulphinate ions [reactions (4)—(6)].

$$2\text{-NO}_2\text{-4-CF}_3\text{C}_6\text{H}_3\text{SO}^- + 2e + 2\text{H}^+ \longrightarrow 2\text{-NH}_2\text{-4-CF}_3\text{C}_6\text{H}_3\text{SO}_3^- \quad (4)$$

$$2\text{ArS}^- \longrightarrow \text{ArSSAr} + 2e \quad (5)$$

$$\text{ArSO}_2^- + \text{H}_2\text{O} \longrightarrow \text{ArSO}_3^- + 2\text{H}^+ + 2e \quad (6)$$

Values of R_d were also calculated at the maximum in

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[6] A. J. Parker and N. Kharasch, *J. Amer. Chem. Soc.*, 1960, **82**, 3071.

[7] D. R. Hogg and P. W. Vipond, *Internat. J. Sulphur Chem.* (*C*), 1971, **6**, 17.

[8] D. R. Hogg and J. Stewart, *J.C.S. Perkin II*, in the press.

the absorbance against time curves. These latter R_d values are in Table 1 together with the velocity constants, k_q, for the reaction leading to the disappearance of the sulphenate anion, which are obtained by dividing these R_d values by $[\mathrm{ArSO^-}]^2$. These values of k_q are in agreement with those obtained from the gradients of the plots of R_d against $[\mathrm{ArSO^-}]^2$ and are reasonably constant over a six-fold increase in hydroxide ion concentration. The reactions which contain sodium perchlorate show however, that this process is subject to a positive salt effect and hence the apparent independence of k_q and hydroxide ion concentration must arise from a fortuitous balancing of salt and concentration effects. In agreement with this conclusion the plot of $\log (k_q[\mathrm{OH^-}])$ against ionic strength (Figure 2) is linear with a slope very similar to that observed[2a] for the 2-nitrobenzenesulphenate anion and the plots of k_q against $1/[\mathrm{OH^-}]$ for reactions at the same ionic strength are linear and pass through or near the origin.

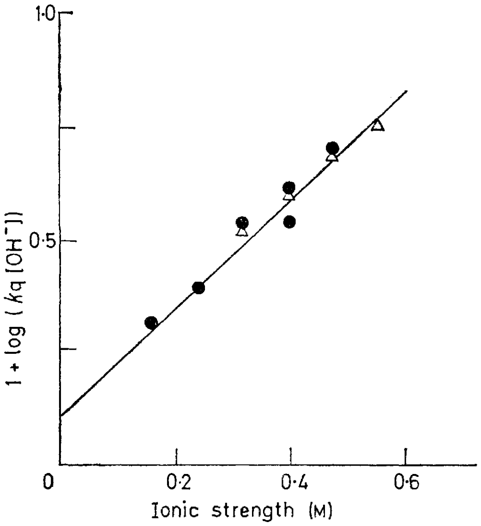
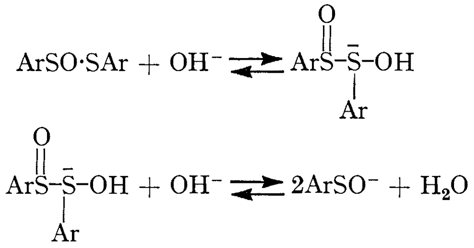


FIGURE 2 Graph of $\log (k_q[\mathrm{OH^-}])$ against ionic strength for the hydrolysis of ethyl 2-nitro-4-trifluoromethylbenzenesulphenate

These observations and the kinetics of the disappearance of the ester show that a combination of reactions (1), (2), and (3a) cannot represent a major pathway for this reaction. The results do appear to be consistent with a mechanism involving reactions (1), (2), and (3b) in which case $-d[\mathrm{ArSO^-}]/dt = k_{3b}[\mathrm{ArSO^-}][\mathrm{ArSOH}] = (k_{3b}K_w'/K_a[\mathrm{OH^-}])[\mathrm{ArSO^-}]^2$ where K_a is the acidity constant for the sulphenic acid and $k_q = k_{3b}K_w'/K_a[\mathrm{OH^-}]$. If however it is assumed that the sulphenic acid is at least 10 times as strong an acid as the corresponding thiol,[9] then k_{3b} is at least of the order of 10^{10}. In contrast reaction (3a; X = OEt), which differs only in having ethoxy instead of hydroxy as the leaving group, must have a velocity constant less than 10^{-2} as it apparently does not compete effectively with reaction (1) for the sulphenate ester. This large difference in rate between two similar reactions is not acceptable and argues against regarding the sulphenic acid as a reactant in step (3) of the mechanism.

Thiosulphonates,[10] $\mathrm{ArSO_2{\cdot}SAr}$, and disulphides react with hydroxide ion at the bivalent sulphur atom and it is to be expected that thiosulphinates would behave similarly. The formation of thiosulphinate from sulphenate anion in alkaline solution must therefore be considered to be reversible. The velocity constant for the reverse reaction should be intermediate between that for the base-catalysed hydrolysis of the disulphide and that of the thiosulphonate in keeping with the relative acidities of the leaving groups. As the value[10] for *S*-phenyl benzenethiosulphonate in 50% aqueous ethanol is of the order of 10^3 mol l^{-1} s^{-1} the reverse reaction should be relatively fast for the thiosulphinate under study.

The reaction of the thiosulphinate with hydroxide ion at the bivalent sulphur atom may follow an S_N2-type mechanism in which case the reaction is the reverse of reaction (3b), *e.g.* $\mathrm{ArSO{\cdot}SAr + OH^- \rightleftharpoons ArSO^- + ArSOH}$, or alternatively the reaction could follow an S_AN mechanism. In the latter case the intermediate could transfer a proton simultaneously with or before dissociation into sulphenate anions and hence the mechanism for the formation of thiosulphinate would differ from reaction (3b) in the timing of the proton transfer. Nucleophilic substitution at bivalent sulphur by an S_AN mechanism is considered[11] to be less favourable with negative than with neutral nucleophiles owing to electrostatic effects involving the nucleophilic atom. In this example the dipolar nature of the sulphinyl group stabilises the intermediate in a manner which is not generally possible with negative nucleophiles.



$$\mathrm{ArSO{\cdot}SAr + OH^- \rightleftharpoons Ar\overset{\overset{O}{\|}}{S}\text{-}\underset{\underset{Ar}{|}}{\bar{S}}\text{-}OH}$$
$$\mathrm{Ar\overset{\overset{O}{\|}}{S}\text{-}\underset{\underset{Ar}{|}}{\bar{S}}\text{-}OH + OH^- \rightleftharpoons 2ArSO^- + H_2O} \qquad (3c)$$

Thiolsulphinates also react with hydroxide ion at the sulphinyl sulphur atom to give[12] the sulphinic acid and the thiolate ion [reaction (7)], which, after neutralisation, are the major products of the hydrolysis of the sulphenate ester.

$$\mathrm{ArSO{\cdot}SAr + OH^- \longrightarrow ArSO_2H + ArS^-} \qquad (7)$$

The observed kinetics for the hydrolysis of the sulphenate ester and the disappearance of sulphenate anion are consistent with a mechanism involving reactions (1), (2), (3c), and (7) if (3c) is in equilibrium or if $k_7 \ll k_{3c}$. Such a mechanism is in accord with the positive salt effect observed for k_q. A similar mechanism involving (3b) as a reversible reaction leads to abnormally high values for k_{3b}.

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[9] D. R. Hogg and J. Stewart, unpublished data.

[10] S. Oae, R. Nomura, Y. Yoshikawa, and W. Tagaki, *Bull. Chem. Soc. Japan*, 1969, **42**, 2903.

[11] E. Ciuffarin and G. Guaraldi, *J. Amer. Chem. Soc.*, 1969, **91**, 1745.

[12] S. Oae, Y. Yoshikawa, and W. Tagaki, *Bull. Chem. Soc. Japan*, 1969, **42**, 2899.

Thiosulphinates undergo[13] thermal disproportionation at relatively low temperatures to give disulphides and thiosulphonates which readily hydrolyse in basic media to give the observed products. As the rate of disproportionation of *S*-phenyl benzenethiosulphinate in toluene at 80° is[12] only $1{\cdot}8 \times 10^{-5}\ \mathrm{s^{-1}}$, it is not considered to contribute effectively to the mechanism of hydrolysis.

Hydrolysis of Bis-2-nitro-4-trifluoromethylphenyl Disulphide.—The rate of disappearance of the disulphide could not be measured directly due to overlapping peaks and initial rates of hydrolysis were obtained from the rate of formation of the sulphenate anion. Details are in Table 2. The results showed considerable scatter probably due to the high rate of reaction which gave tangents with large gradients and hence substantial errors. The maximum concentration of sulphenate ion generally slightly exceeded the initial concentration of disulphide and this was attributed to oxidation of the thiolate ion to sulphenate anion by peroxide[9] or dissolved oxygen. The second-order velocity constant, $1{\cdot}2\ \mathrm{l\ mol^{-1}\ s^{-1}}$, is similar to that recorded[7] for 2,4-dinitrophenyl 2-nitrophenyl disulphide, $4{\cdot}0\ \mathrm{l\ mol^{-1}\ s^{-1}}$, measured under the same conditions. This agreement is not unreasonable as the difference in reactivity due to the differing basicities of the leaving groups will be balanced by the increase in rate produced by the additional substituent, *p*-$\mathrm{CF_3}$, in the other ring.

TABLE 2

Initial velocity constants for hydrolysis in 50% (v/v) aqueous dioxan at 25·0°

Bis-2-nitro-4-trifluoromethylphenyl disulphide ($3{\cdot}52 \times 10^{-4}$M)				
$10^3[\mathrm{OH^-}]$/M	4	8	12	
10^6 Initial rate/mol $\mathrm{l^{-1}\ s^{-1}}$	1·76	3·26	4·49	
k/l $\mathrm{mol^{-1}\ s^{-1}}$ [a]	1·24	1·16	1·06	
2-Nitro-4-trifluoromethylbenzenesulphenyl chloride ($3{\cdot}45 \times 10^{-4}$M)				
$10^3[\mathrm{OH^-}]$/M	4	8	12	16
10^6 Initial rate/mol $\mathrm{l^{-1}\ s^{-1}}$	0·67	1·14	1·61	2·42
k/l $\mathrm{mol^{-1}\ s^{-1}}$	0·49	0·41	0·39	0·44

[a] Not corrected for statistical factors.

The disulphide hydrolyses 100 times faster than the ethyl sulphenate and produces a higher maximum concentration of sulphenate anion. It therefore appears that the reactions leading to the disappearance of sulphenate anion are essentially the same in both cases. Thiolate ions react[14] rapidly with thiosulphonates even at −86°, to give disulphides and sulphinate anions, furthermore thiol–disulphide exchange with these compounds is rapid on the n.m.r. time scale.[8] The reverse of reaction (3a; X = SAr), by analogy is probably fast, and the existence of (3a) as an equilibrium in this hydrolysis cannot be discounted. Its importance may also increase with disulphides which do not have electronegative substituents.

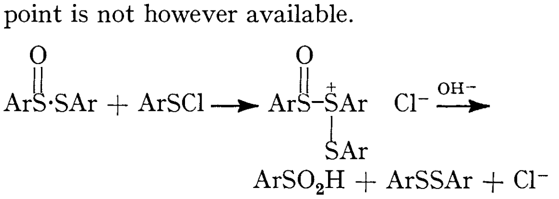
Hydrolysis of 2-Nitro-4-trifluoromethylbenzenesulphenyl Chloride.—Initial rates of hydrolysis for the sulphenyl chloride were also obtained from the initial rate of formation of sulphenate anion. The resulting velocity constants (Table 2) were approximately a third of those obtained for the disulphide. This is not in keeping with the high hydrolytic reactivity[4] of sulphenyl halides which readily hydrolyse in the presence of moisture unlike disulphides and sulphenate esters. Significantly the maximum concentration of sulphenate anion was also approximately a third of that obtained during the hydrolysis of the disulphide. The most likely explanation is that the sulphenyl chloride hydrolyses almost instantaneously [reaction (8)] to give[2] the sulphinate anion and the disulphide, whose concentration is a third of the initial concentration of the sulphenyl chloride, and that it is the rate of hydrolysis of the resulting disulphide which is being measured. These results show that it is not merely the initial step in the hydrolysis which is so much faster with the sulphenyl chloride compared with the other derivatives, but also the subsequent reactions of the intermediates. Since it seems unlikely that the mechanism of the initial step in the hydrolysis will be changed, the sulphenyl chloride must react rapidly with certain intermediates. Reaction (3a) has been suggested[4] to be important in these hydrolyses and for X = Cl the reverse reaction in basic solution is probably slow. This would lead to a mechanism in which reactions (1) and (2) were followed by (3a), (3c), (7), (9), and (10).

$$3\mathrm{ArSCl} + 4\mathrm{OH^-} \xrightarrow{\text{fast}} \mathrm{ArSSAr} + \mathrm{ArSO_2^-} + 3\mathrm{Cl^-} + 2\mathrm{H_2O} \qquad (8)$$

$$\mathrm{ArS^-} + \mathrm{ArSCl} \longrightarrow \mathrm{ArSSAr} + \mathrm{Cl^-} \qquad (9)$$

$$\mathrm{ArS^-} + \mathrm{ArSOSAr} \rightleftharpoons \mathrm{ArSSAr} + \mathrm{ArSO^-} \qquad (10)$$

Reaction (7) in this sequence is considered to be involved in determining the rate of disappearance of the sulphenate anion in the hydrolysis of the sulphenate ester and the disulphide. It therefore appears to be too slow to occupy a key position in the hydrolysis of the sulphenyl chloride. Its rate could be considerably increased by electrophilic co-operation of the sulphenyl chloride in a manner similar to that previously described[15] for other reactions involving the fission of sulphur–sulphur bonds [reaction (11)]. Direct evidence on this point is not however available.



$$\mathrm{Ar}\overset{\overset{\displaystyle\mathrm{O}}{\|}}{\mathrm{S}}\cdot\mathrm{SAr} + \mathrm{ArSCl} \longrightarrow \mathrm{Ar}\overset{\overset{\displaystyle\mathrm{O}}{\|}}{\mathrm{S}}\text{-}\underset{\underset{\displaystyle\mathrm{SAr}}{|}}{\overset{+}{\mathrm{S}}}\mathrm{Ar}\ \ \mathrm{Cl^-} \xrightarrow{\mathrm{OH^-}} \mathrm{ArSO_2H} + \mathrm{ArSSAr} + \mathrm{Cl^-} \qquad (11)$$

EXPERIMENTAL

Materials.—Dioxan was purified as previously described[16] and used within 2—3 days. *Ethyl 2-nitro-4-trifluoromethyl benzenesulphenate*, yellow crystals, had m.p. 34—36°

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[13] P. Koch, E. Cuiffarin, and A. Fava, *J. Amer. Chem. Soc.*, 1970, **92**, 5971.

[14] S. Smiles and D. T. Gibson, *J. Chem. Soc.*, 1924, **125**, 176; T. F. Parsons, J. D. Buckman, D. E. Pearson, and L. Field, *J. Org. Chem.*, 1965, **30**, 1923.

[15] J. L. Kice, *Accounts Chem. Res.*, 1968, **1**, 58.

[16] A. I. Vogel, 'Practical Organic Chemistry,' Longmans, London, 1956, p. 177.

[light petroleum (b.p. 60—80°) at −78°]; $\nu_{max.}$ 1012 cm^{-1}, τ 8·55 (3H, t), 5·90 (2H, q), 2·08 (2H, s), and 1·43 (1H, s) (Found: N, 5·5; S, 12·2. $C_9H_8F_3NO_3S$ requires N, 5·25; S, 12·0%); bis-2-nitro-4-trifluoromethylphenyl disulphide had m.p. 159—161° (lit.,[17] 161—162°); 2-nitro-4-trifluoromethylbenzenesulphenyl chloride, pale yellow solid, had m.p. 25—27°, b.p. 78—80° at 0·06 mmHg (Found: C, 33·0; H, 1·5. Calc. for $C_7H_3ClF_3NO_2S$: C, 32·7; H, 1·2%). They were all prepared by known methods.

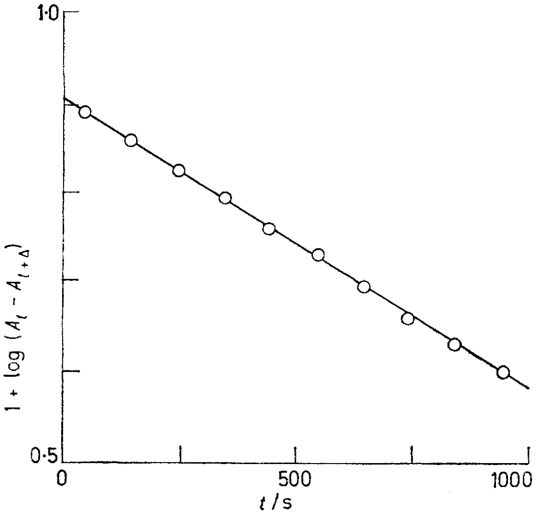

FIGURE 3 Graph of log($A_t - A_{t+\Delta}$) against time for the hydrolysis of ethyl 2-nitro-4-trifluoromethylbenzenesulphenate in 50% v/v aqueous dioxan at 25·0°: [NaOH] = 0·08M $\Delta = 3600$ s

Rate Measurements.—Measurements were carried out as previously described.[2a] The disappearance of the ethyl sulphenate was monitored at 395 nm and the appearance and disappearance of the sulphenate ion at 588 nm. The initial concentration of ethyl sulphenate in the reaction mixtures was 3·38 × 10^{-4}M. First-order velocity constants, k_I, were most conveniently obtained from the plot of log ($A_t - A_{t+\Delta}$) against time, where A_t is the absorbance at time t and $A_{t+\Delta}$ that at time t + 3600 s. A typical plot, linear to over 50% reaction, is given as Figure 3.

The equations for the graphs of absorbance at 588 nm against time were obtained using a least-squares polynomial program on the I.C.L. system 4/50 computer and hence the gradients of the tangents at zero time, m_0, were calculated. The extinction coefficient, ε, for the sulphenate anion was calculated from $m_0/\varepsilon = k_I[\text{ArSOEt}]_0$. R_d at time t was obtained from the expression $R_d = R_F - R_{obs} = k_I[\text{ArSOEt}]_t = m_t/\varepsilon_{mean}$ and at $A_{max.}$ from $R_d = R_F = k_I[\text{ArSOEt}]_{t\max.}$.

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[17] A. I. Kiprianov and L. M. Yagapolskii, *Zhur. obshchei Khim.*, 1952, **22**, 2209.