Chemistry of Sulphenates in Acidic Media

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Methyl toluene-*p*-sulphenate is hydrolysed rapidly in moist solvents (dioxan, benzene, chloroform, or nitrobenzene) yielding methyl toluene-*p*-sulphinate, di-*p*-tolyl disulphide, and methanol. The reaction is acid catalysed. At higher concentration of water (>1%) the products are: *p*-tolyl toluene-*p*-thiolsulphonate, di-*p*-tolyl disulphide, and methanol. A mechanism is suggested where thiolsulphinate, which is usually suggested as the intermediate in the hydrolysis of sulphenyl derivatives, combines with unchanged sulphenate ester to yield an intermediate sulphonium salt. The sulphonium salt then rapidly reacts with either methanol or water to yield the products. Some implications for the chemistry of sulphenic acids are also discussed.

THE importance of the chemistry of sulphenic acids is widely recognized.[1,2] However, due to their high lability they cannot be isolated except in a few special cases, so that knowledge of their chemistry has been obtained in an indirect manner. Sulphenic acids are thought to be extremely powerful nucleophiles towards sulphenyl sulphur and it was suggested that part of their nucleophilic reactivity could be due to the fact that they are possible α-effect nucleophiles.[1] Sulphenic acids have been generated in a variety of reactions from a variety of substrates, mostly sulphenyl derivatives. Sulphenates are perhaps less studied among the sulphenyl derivatives even though they are the closest homologues of sulphenic acids and might possess the closest chemical behaviour, *e.g.* they should be α-effect nucleophiles. A few papers deal with the alkaline hydrolysis of sulphenyl esters[3] and nothing is known of the chemistry of sulphenates in acidic media except for the reaction products of the HCl catalysed reaction of trimethylsilyl 2-nitrobenzenesulphenate in water–ethanol.[2]

The present work is a first approach to the chemistry of methyl toluene-*p*-sulphenate in acidic media.

RESULTS AND DISCUSSION

Methyl toluene-*p*-sulphenate (1) is stable in solution (dioxan, benzene, chloroform, or nitrobenzene) even in the presence of strong acids such as sulphuric or trifluoromethanesulphonic acid. This is true, however, only if the solvents are absolutely dry. In moist solvents (dioxan, benzene, chloroform, or nitrobenzene) (1) reacts rapidly yielding methanol, disulphide, and sulphinate according to equation (1).

$$\underset{(1)}{3\mathrm{ArS{-}OMe}} + \mathrm{H_2O} \xrightarrow{\mathrm{H^+}} \mathrm{ArSO{-}OMe} + \mathrm{ArSSAr} + 2\mathrm{MeOH} \quad (1)$$

$$\mathrm{Ar} = p\text{-tolyl}$$

When CF_3SO_3H is used as catalyst the reaction stops when all water present in the solvent is used up but can be brought to completion by further additions of *small* quantities of water. When sulphuric acid is the catalyst, traces of water are sufficient for the reaction to proceed to completion because water is rapidly regenerated in the esterification process between methanol and sulphuric acid [equation (2)].[4,†] Since on the other hand

$$\mathrm{MeOH} + \mathrm{H_2SO_4} \longrightarrow \mathrm{HSO_3{-}OMe} + \mathrm{H_2O} \quad (2)$$

this reaction consumes sulphuric acid, it stops when all the sulphuric acid is used up and can be brought to completion by further addition of sulphuric acid.

In solvents such as chloroform, benzene, or nitrobenzene where only traces of water can be dissolved the only possible reaction for the trifluoromethanesulphonic acid catalysed hydrolysis of (1) is that shown in equation (1). In dioxan on the other hand a different spectrum of products can be observed when the concentration of water is >1% [equation (3)]. Thiolsulphonate is formed instead of sulphinate. Traces of thiolsulphinate can also be observed.

$$4\mathrm{ArS{-}OMe} + 2\mathrm{H_2O} \xrightarrow{\mathrm{H^+}} \mathrm{ArSO_2{-}SAr} + \mathrm{ArSSAr} + 4\mathrm{MeOH} \quad (3)$$

The diversity of reaction products which is brought about upon changing the concentration of water from a deficit to an excess relative to the concentration of sulphenate (0.2M),[‡] is even more surprising if one considers that addition of water to the reaction mixture, *after* the formation of sulphinate ester [equation (1)] is completed, has almost no effect.[§]

These results indicate that water not only changes the reaction products but the reaction mechanism as well.

Two reactions have to be considered in an initial approach to the mechanism: the acid catalysed hydrolysis of the sulphenate to yield sulphenic acid and methanol [equation (4)] followed by rapid formation of thiolsulphinate [equation (5)].[7] An indication of the

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[†] Batts[4] reports the rates of esterification in dioxan. We found that esterification is also quite fast in near anhydrous benzene, chloroform, and nitrobenzene.

[‡] When methanol is added to the mixture the products are those of reaction (1) even in the presence of an excess of water. Clearly methanol and water compete for the same intermediate (see later).

[§] In aqueous, acidic media sulphinates are slowly hydrolysed to sulphinic acid.[5,6]

[1] (*a*) J. L. Kice and J. P. Cleveland, *J. Amer. Chem. Soc.*, 1973, **95**, 104, and references therein; (*b*) J. O. Edwards and R. G. Pearson, *ibid.*, 1962, **84**, 16.

[2] F. A. Davis and A. J. Friedman, *J. Org. Chem.*, 1976, **41**, 897 and references therein.

[3] D. R. Hogg and J. Stewart, *J.C.S. Perkin II*, 1974, 1040, and previous papers in the series.

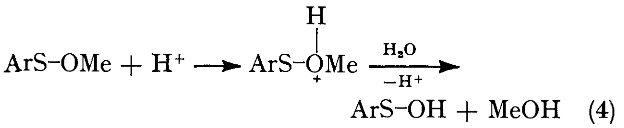
[4] B. D. Batts, *J. Chem. Soc.* (*B*), 1966, 547.

[5] C. A. Bunton and B. N. Hendy, *J. Chem. Soc.*, 1962, 2563.

[6] M. Kobayashi, R. Nishi, and H. Minato, *Bull. Chem. Soc. Japan*, 1974, **47**, 888.

[7] E. Vinkler and F. Klivenyi, *Acta Chim. Acad. Sci. Hung.*, 1960, **22**, 345.

latter reaction is given by the observation that traces of thiolsulphinate are always formed.



$$\mathrm{ArS{-}OMe + H^+ \longrightarrow ArS{-}\overset{H}{\underset{+}{O}}Me \xrightarrow[-H^+]{H_2O} ArS{-}OH + MeOH} \qquad (4)$$

$$\mathrm{2ArS{-}OH \longrightarrow ArS{-}SOAr + H_2O} \qquad (5)$$

The hydrolysis of sulphenyl derivatives usually yields disulphide and thiolsulphonate but can be stopped at the stage of thiolsulphinate when the experimental conditions are such that the disproportionation of thiolsulphinate or other possible reactions are relatively slow processes.[7] The disproportionation of thiolsulphinate [equation (6)] cannot account for the formation of

$$\mathrm{2ArSO{-}SAr \xrightarrow[slow]{H^+} ArSSAr + ArSO_2{-}SAr} \qquad (6)$$

thiolsulphonate in our system since it is a very slow process in the experimental conditions where equation (3) is fast. At the very low acidity of *ca.* 10^{-4}M (CF_3SO_3H), reaction (3) is over in *ca.* 10 min while reaction (6) is barely detectable after 24 h. Moreover, it does not account for the formation of sulphinic ester when only traces of water are present.

Thus, if thiolsulphinate is a reaction intermediate as suggested [equations (4) and (5)], a mechanism must be found which explains both the formation of sulphinate (with traces of water) and the formation of thiolsulphinate (at higher concentration of water) without resorting to the disproportionation reaction. A likely possibility which may account for the formation of sulphinate is a fast reaction of thiolsulphinate with the unchanged sulphenic ester [equation (7)].

$$\mathrm{Ar'SO{-}SAr' + ArS{-}OMe \xrightarrow{H^+} Ar'SO{-}OMe + Ar'SSAr} \qquad (7)$$

This was proved experimentally by mixing thiolsulphinate and sulphenate. In the absence of water they react according to equation (7) to yield sulphinate and disulphide. This reaction is very rapid and is acid catalysed. Thus, the sequence of reactions (4), (5), and (7) explains the products of reaction (1). When different aryl moieties are used for the thiolsulphinate and sulphenate [Ar′ = *p*-chlorophenyl, Ar = *p*-tolyl in equation (7)] the sulphinate comes all from the thiolsulphinate (*i.e.* there is no scrambling of aryl groups).

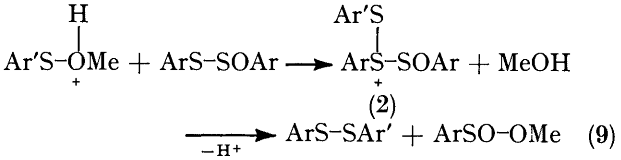
When thiolsulphinate and sulphenate are mixed in the presence of water, thiolsulphonate, disulphide, and methanol are formed according to stoicheiometry (8).

$$\mathrm{ArS{-}SOAr + 2ArS{-}OMe + H_2O \xrightarrow{H^+} ArS{-}SAr + ArS{-}SO_2Ar + 2MeOH} \qquad (8)$$

Again the reaction is fast and acid catalysed. Thus, the sequences of reactions (4), (5), and (8) explains the products at relatively high water content [equation (3)].

The above results indicate that thiolsulphinate reacts very rapidly with sulphenate in acidic media both in the absence and presence of water and that water diverts the reaction from equation (7) to (8).

The exchange of the methoxy-group between sulphenyl and sulphinyl residues [equation (9)] is quite interesting. The exchange can either occur *via* a four-centre transition state or a multistep mechanism. The four-centre transition state can be excluded because it does not explain the acid catalysis nor the effect of water on the products. Moreover, when the reaction is run in the presence of [$^2H_4$]methanol, the methoxy-group of the sulphinates is fully deuteriated.* Taking into account previously suggested intermediates[8,9] in reaction of sulphur substrates, the most likely mechanism seems that shown in equation (9).



$$\mathrm{Ar'S{-}\overset{H}{\underset{+}{O}}Me + ArS{-}SOAr \longrightarrow Ar\overset{Ar'S}{\underset{\underset{(2)}{+}}{S}}{-}SOAr + MeOH \xrightarrow[-H^+]{} ArS{-}SAr' + ArSO{-}OMe} \qquad (9)$$

The reaction sequence (9) suggests that in the absence of water the intermediate (2), formed upon reaction of thiolsulphinate with the protonated sulphenate, reacts with methanol to give sulphinate and disulphide. Methanol may also come from initial hydrolysis of the sulphenate [equation (4)]. It seems reasonable that in the presence of an excess of water the intermediate (2) reacts with water in a similar way to yield sulphinic acid [equation (10)] which in turn reacts very rapidly with

$$\mathrm{(2) + H_2O \xrightarrow[H^+]{} ArSO_2H + ArS{-}SAr} \qquad (10)$$

unchanged sulphenic ester to give thiolsulphonate [equation (11)]. Reaction (11) is in fact very fast even in the absence of any catalysing acid.

$$\mathrm{ArSO_2H + ArS{-}OMe \longrightarrow ArSO_2{-}SAr + MeOH} \qquad (11)$$

The Scheme summarizes the suggested sequence of reactions for the acid catalysed decomposition of sulphenates for the two experimental conditions, low and high water content.

The first step of the Scheme must be the slow step, so that thiolsulphinate and sulphinic acid may rapidly react with the excess of unchanged sulphenate. The two reactions have been found in fact to be over within mixing time under the same experimental conditions where the overall acid catalysed hydrolysis is a fast but measurable process. The formation of thiolsulphinate from sulphenic acid is also a fast process[1,3,7] and the intermediate thiolsulphonium salt (2) is likely to be a highly reactive species. The Scheme will be analysed

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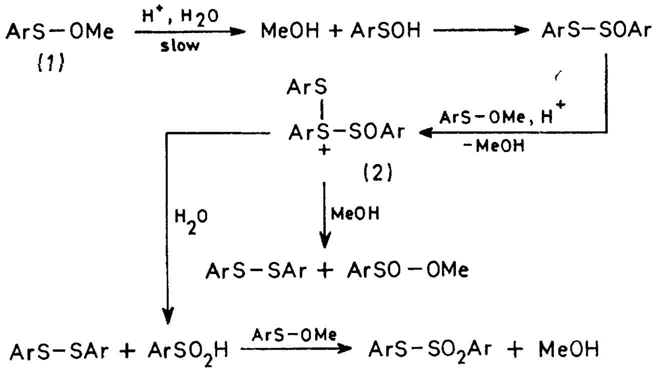
* The exchange of sulphenic ester with methanol under the same experimental conditions, but without thiolsulphinate, is a slow process. A similar exchange of sulphinate is slow both in the presence and absence of thiolsulphinate.

[8] D. R. Hogg and J. Stewart, *J.C.S. Perkin II*, 1974, 43.

[9] G. Capozzi, V. Lucchini, G. Modena, and F. Rivetti, *J.C.S. Perkin II*, 1975, 361.

kinetically. However, the proposed sequence of reactions, derived by checking the products and by taking qualitative data on the rates of reaction seems well substantiated because no small differences in rates of reaction have been taken into account.



SCHEME

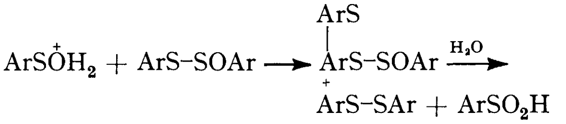
The reaction of sulphenyl halides with thiolsulphinates reported by Douglass[10] [equation (12)] is formally similar to that of protonated sulphenates with thiolsulphinates [equation (7)] and may very well go *via* the same intermediate (2) which then reacts with Cl^- to give the sulphinyl chloride. Thus, like sulphenyl halides,[10] the protonated sulphenic esters are powerful electrophilic catalysts.

$$\mathrm{MeS{-}Cl + MeS{-}SOMe \longrightarrow MeS{-}SMe + MeSOCl} \qquad (12)$$

The formation of an intermediate such as (2) can also be suggested for the acid catalysed formation of sulphinic ester in the hydrolysis of trimethylsilyl 2-nitrobenzenesulphenate in ethanol–water reported by Davis[2] instead of the suggested attack of ethanol on thiolsulphinate. In fact, the acid catalysed reaction of methanol with toluene-*p*-thiolsulphinate is a much slower process than the hydrolysis of toluene-*p*-sulphenate to yield the same products, disulphide and methyl toluene-*p*-sulphinate. One must recall that thiolsulphinate could never be isolated nor detected except in traces.

Due to the similarity of chemical structure of sulphenates and sulphenic acids, it does not seem unreasonable to compare the chemistry of the two classes of compounds. Methyl toluene-*p*-sulphenate is a relatively strong base. Titration of (1) in chloroform with trifluoroacetic acid indicate that (1) is a much stronger base then either methyl *p*-tolyl sulphoxide or methyl toluene-*p*-sulphinate.[11] (The acidity of thiolsulphinate cannot be measured because of disproportionation.) Substituting a hydrogen for a methyl group would certainly decrease the basicity but not so much as to make it unreasonable that also sulphenic acids are basic species which can be protonated by strong acids. Thus, sulphenic acids not only are, as previously suggested,[1] powerful nucleophiles for divalent sulphur, but, in protonated form, powerful electrophiles as well.

The above discussion, while not invalidating the general mechanism for the disproportionation and other acid and nucleophile catalysed substitutions studied by Kice where sulphenic acid is considered an intermediate,[1] suggests other possible kinetic paths for the reactions to proceed, thus adding additional features in the already complex mechanism and rate equations reported by Kice to explain the data. A possible reaction path which was never considered is the reaction of the protonated sulphenic acid with thiolsulphinate to yield disulphide and sulphinic acid [equation (13)].



$$\mathrm{Ar\overset{+}{S}OH_2 + ArS{-}SOAr \longrightarrow \overset{ArS}{\underset{+}{Ar S}}{-}SOAr \xrightarrow{H_2O} ArS{-}SAr + ArSO_2H} \qquad (13)$$

Equation (13) might also be included in the Scheme. However, in order to determine its importance one should know both the relative basicity of sulphenates and sulphenic acids and their relative reactivity towards thiolsulphinate, a difficult task indeed.

EXPERIMENTAL

Materials.—Methyl toluene-*p*-sulphenate was prepared by adding toluene-*p*-sulphenyl chloride[12] to an equivalent quantity of dry methanol and triethylamine in dry ether. The crude product was distilled, b.p. 58—60° at 0.25 Torr (lit.,[13] 70—72° at 0.6 Torr). *p*-Tolyl toluene-*p*-thiolsulphinate, m.p. 97°,[14] and *p*-chlorophenyl *p*-chlorobenzenethiolsulphinate, m.p. 113°,[15] have been prepared according to the procedure of Backer and Kloosterziel.[16] Methyl toluene-*p*-sulphinate, b.p. 82—83° at 0.5 Torr,[17] and methyl *p*-chlorobenzenesulphinate, b.p. 98—102° at 0.4 Torr,[18] were prepared by condensation of methanol and the corresponding sulphinyl chlorides[19] in dry ether in the presence of pyridine. *p*-Tolyl disulphide, m.p. 46°,[20] and *p*-chlorophenyl disulphide, m.p. 72—73°,[21] were prepared by oxidation of the corresponding thiols, and *p*-tolyl toluene-*p*-thiolsulphonate, m.p. 78°,[22] was prepared according to the extension of the Douglas–Farah method, as reported by Field and Parsons.[22] Toluene-*p*-sulphinic acid, m.p. 84°,[23] was prepared and purified according to the literature.[23]

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[10] I. B. Douglass and D. A. Koop, *J. Org. Chem.*, 1962, **27**, 1398.

[11] E. Ciuffarin and S. Gambarotta, unpublished data.

[12] F. Kurzev and J. R. Powell, *Org. Synth.*, 1963, Coll. vol. IV, 934.

[13] L. Sagramora, P. Koch, A. Garbesi, and A. Fava, *Chem. Comm.*, 1967, 985.

[14] (*a*) J. L. Kice, C. G. Vernier, and L. Heasley, *J. Amer. Chem. Soc.*, 1967, **89**, 3557. (*b*) F. J. Carson and F. F. Wong, *J. Org. Chem.*, 1961, **26**, 1467.

[15] G. Modena and P. E. Todesco, *Ricerca sci.*, 1960, **30**, 1788.

[16] H. J. Backer and H. Kloosterziel, *Rec. Trav. chim.*, 1954, **73**, 129.

[17] A. Wragg, J. McFadyen, and T. Stevens, *J. Chem. Soc.*, 1958, 3603.

[18] B. Bonini, S. Ghersetti, and G. Modena, *Gazzetta*, 1963, **93**, 1222.

[19] I. Douglass, B. Farah, and J. Steam, *J. Org. Chem.*, 1961, **26**, 1996.

[20] E. L. Colichman and D. L. Love, *J. Amer. Chem. Soc.*, 1953, **75**, 5737.

[21] M. B. Sparke, J. L. Cameron, and N. Kharash, *J. Amer. Chem. Soc.*, 1953, **75**, 4907.

[22] L. Field and T. F. Parsons, *J. Org. Chem.*, 1965, **30**, 657.

[23] J. L. Kice and K. W. Bowers, *J. Amer. Chem. Soc.*, 1962, **84**, 605.

100% Sulphuric acid was made by mixing 96% sulphuric acid with fuming acid until a maximum freezing point was obtained (10.4°).[24] Trifluoromethanesulphonic acid and trifluoroacetic acid were reagent grade commercial products. Dioxan and nitrobenzene were purified according to standard procedures and stored over molecular sieves (4 Å) under nitrogen.

Rate and Product Studies. Reactions (1)—(3), (6)—(8), and (11) have been followed by n.m.r. spectroscopy. Except for the catalysing acid, water, and methanol, in each case the concentration of reagents was 0.2M. The concentration of acid, water, and methanol were changed in order to observe a change in rate of reaction and products. The rates, as determined by n.m.r., were only qualitatively good. In some cases the reactions were over before the first spectrum could be run.

The identification of the products was always performed by n.m.r. and t.l.c. using authentic samples. The stoicheiometry was determined by n.m.r. integration.

In nitrobenzene, a solvent free from interference except in the aromatic region, the concentration of the products was always that required by the stoicheiometry. In dioxan good integration was not always possible because of solvent absorption, side spinning bands, and ^{13}C satellites. However, the identification of the products and the determination of their approximate concentration was always possible. In one case [equation (3)] the results were confirmed by using [$^2H_8$]dioxan. Minor products could not be detected by n.m.r. Traces of thiolsulphinate were detected by t.l.c. only.

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[24] N. F. Hall and W. F. Spengeman, *J. Amer. Chem. Soc.*, 1940, **62**, 2487.