Tetrahedron. Vol. 30, pp. 3891 to 3896. Pergamon Press 1974. Printed in Great Britain

SULPHUR-OXYGEN VERSUS CARBON-OXYGEN BOND FISSION IN THE SOLVOLYSIS OF BENZYL SULPHENATES[a,1]

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(*Received in the UK* 8 *May* 1974; *Accepted for publication* 10 *June* 1974)

Abstract—In contrast to p-anisyl trichloromethanesulphenate 1, which readily undergoes ethanolysis at room temperature with carbon-oxygen bond fission, the ethanolysis of the corresponding 2-nitrobenzenesulphenate 2 proceeds at a similar rate only at 100°, and involves sulphur-oxygen bond cleavage. While the solvolysis of 1 showed first-order kinetics, the solvolysis of 2 was second-order (first-order with respect to ester and to added base). The solvolysis rate of 2 decreases on going from 100% to 80% ethanol and by using pyridine instead of acetate as base, consistent with an S_N2 type mechanism involving nucleophilic displacement at sulphur by the base or lyate ion. The rate of solvolysis of 1 is greatly enhanced in polar solvents and correlates satisfactorily with the ionization of p-methoxyneophyl tosylate. An ionization mechanism to some ion pair species is suggested for the solvolysis of 1.

In principle, esters of sulphonic, sulphinic and sulphenic acids can undergo solvolysis by either carbon-oxygen or sulfur-oxygen bond fission, depending on structure and reaction conditions. While this duality in behaviour has been extensively studied in the case of sulphonates[2] and sulphinates,[3] only sulphur-oxygen bond scission has been reported so far for the solvolysis of sulphenates.[4,5,7,8] Hogg *et al*[4] have recently studied the alkaline hydrolysis of various alkyl arenesulphenates in aqueous ethanol and aqueous dioxan solutions, to the corresponding disulphide and the salt of the corresponding sulphinic acid. The reactions were second-order, first-order in ester and first-order in hydroxide ion. Consideration of the relative rates of hydrolysis for the alkyl 2-nitrobenzenesulphenates and the nature of the products obtained has lead these authors to suggest that the reaction involves a nucleophilic attack by hydroxide ion at the sulphur atom. It was also observed that the values of log $k_2^?$ for the alkaline hydrolysis of several ethyl 4-substituted-2-nitrobenzenesulphenates do not give a linear Hammett plot, but both electron-releasing and electron-withdrawing substituents increase the rate of reaction relative to that of the unsubstituted compound. This type of behaviour has been interpreted as indicating different degrees of bond formation and fission in the transition state. The question of the timing of bond formation and breaking in nucleophilic substitution at sulphenate sulphur has been the subject of an interesting study by Senatore, Ciuffarin and Fava.[5] These authors have measured the effect of the basicity of entering and leaving groups on the reaction of hydroxide and *p*-substituted phenoxide ions with *p*-substituted triphenylmethanesulphenates, in 45% aqueous dioxan. The kinetic data plotted in a Brønsted fashion against the pKa of the conjugate acid of the nucleophile and the leaving group, respectively, gave good linear relations, characterized by $\beta = 0{\cdot}25$ and $\beta = 0{\cdot}97$. These results establish that for the particular substitution under investigation, bond breaking is far more advanced than bond formation. Therefore, the authors conclude that this finding can only be consistent with a one-step process (i.e. a synchronous S_N2 displacement at sulphur) and not with a two-step addition-elimination (labeled[6] S_AN) mechanism, involving a pentacovalent sulphur intermediate along the reaction path. However, in a subsequent report Ciuffarin *et al*[7] have shown by a similar Brønsted relationship that for the nucleophilic substitution at sulphur of p-nitrophenyl triphenylmethanesulphenate, by a variety of amines in the same solvent, a large degree of bond formation in the transition state occurs. Consequently, these authors conclude that contrary to the case with oxygen nucleophiles, substitution with nitrogen nucleophiles proceeds by an S_AN mechanism.

Extensive kinetic studies of the solvolysis of alkyl and aryl trichloromethanesulphenates under various reaction conditions have been reported by Horak.[8] The results obtained for the reaction of the alkyl esters[8b] in methanol ether mixtures with sodium methoxide, have been interpreted as involving a nucleophilic substitution of a chlorine atom from the trichloromethyl group in the first and rate determining step. The reaction product has been considered to be the orthoester of carbonic acid. On the other hand, the solvolysis of the aryl esters was suggested to take place by an initial fast nucleophilic substitution on the sulphur atom, resulting in the formation of methyl trichloromethanesulphenate,

*Dedicated to the memory of the late Professor David Darwish, of the University of Alberta, Edmonton, Alberta, Canada.

which subsequently and slowly undergoes nucleophilic substitution of a chlorine atom as described above. The solvolysis of the aryl esters has also been studied under acid catalysis.[8d] In the presence of hydrogen chloride, solvolysis is accompanied by a cleavage reaction caused by hydrogen chloride, which complicates the kinetics. Examination of the two reactions separately was made possible by using 80% methanol-water for measurements of the solvolysis rates, and 80% ether, methanol for measurements of the cleavage rates. This study revealed that the solvolysis is monomolecular and is initiated by an S_N1 type substitution of a chlorine atom of the trichloromethyl group. The rate of this reaction is unaffected by the type of substitution of the benzene ring of the ester, but is highly sensitive to the polarity of the medium. On the other hand, the cleavage reaction is initiated by attack of the chloride ion on the conjugated form of the ester, and results in the formation of Cl_3CSCl and the corresponding phenol. This process is accelerated by electron-withdrawing substituents in the aryl group, and a satisfactory correlation between log k and pK_a of the corresponding phenol was obtained.

The observation so far of only sulphur-oxygen bond fission in the solvolysis of sulphenates, may not be surprising in view of the greater electrophilicity of the sulphur atom in the sulphenate relative to that in the other two types of esters,[9] as well as the poor leaving group ability of the sulphenate anion and its lack of stability, in general.[10] Prompted by our success in observing carbon-oxygen bond fission by an ionization mechanism for the rearrangement of benzyl trichloromethanesulphenates to sulphoxides and chlorides under non-solvolytic conditions,[11] we examined the possible operation of such a mechanism during the solvolysis of these and related benzyl sulphenates.

RESULTS AND DISCUSSION

Solvolysis of Benzyl Trichloromethanesulphenates. This investigation was initiated by an examination of p-ainsyl (p-methoxybenzyl) trichloromethanesulphenate **1**, which was prepared by the usual procedure,[11,12] reaction of the corresponding alcohol with Cl_3CSCl. This ester was found to undergo facile ethanolysis on standing at room temperature for one day in buffered anhydrous ethanol, with the formation of p-anisyl ethyl ether and dichlorosulphine, obtained by spontaneous decomposition of the trichloromethanesulphenic acid.[13]

This result indicates that ethanolysis of **1** involves carbon-oxygen bond fission. This appears to be the first observation of solvolysis by carbon-oxygen bond cleavage of a sulphenate ester. In order to determine further details about the mechanism of solvolysis, a kinetic study of the reaction under various conditions has been performed. The rates of solvolysis of **1** at 0°, were conveniently measured by the decrease in intensity of the methylene NMR signal at τ 4·78, and are presented in Table 1. The reaction showed first-order kinetics.

Inspection of the data in Table 1 indicates that the rate of solvolysis of p-anisyl trichloromethanesulphenate is greatly enhanced by increasing the ionizing power of the solvent. For example the rate increases by a factor of ten in going from 100% to 80% methanol-water. A graph of log k for solvolysis of **1** against log k for ionization of p-methoxyneophyl tosylate[14] for the four solvent systems mentioned in Table 1 gives a straight line with a slope of 1·33. These data may be used as supporting evidence for an ionization mechanism for the reaction of **1**. In line with this mechanism is also the observation that substitution of potassium acetate by 2,6-lutidine as the added base in either anhydrous methanol or 60% ethanol-water had no influence on the rate of solvolysis (Table 1). No organic azide could be detected on addition of sodium azide to the reaction mixture of **1** in anhydrous ethanol at room temperature. This result tends to exclude ionization to dissociated ions as the sole or predominant route of reaction. The possibility of an initial rearrangement of **1** to

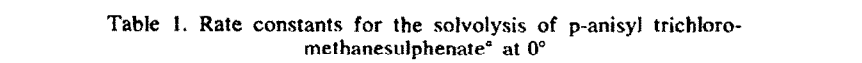

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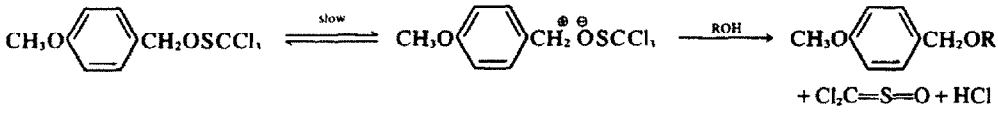
Table 1. Rate constants for the solvolysis of p-anisyl trichloromethanesulphenate[a] at 0°

Solvent	Added base	[Base], M	10^5k, sec^{-1}
MeOH	KOAc	0·1998	2·27 ± 0·23
MeOH	2,6-Lutidine	0·2000	2·25 ± 0·13
80% EtOH-H_2O	KOAc	0·2035	7·33 ± 0·19
80% MeOH-H_2O	KOAc	0·2127	23·6 ± 1·1
60% EtOH-H_2O	KOAc	0·2093	30·3 ± 1·7
60% EtOH-H_2O	2,6-Lutidine	0·2093	29·5 ± 1·1

[a] [Ester] = 0·05M



the corresponding chloride, as observed in aprotic polar solvents,[11] was ruled out, since the rate of solvolysis of p-anisyl chloride (e.g. in methanol at 0°, $k = 1{\cdot}51 \times 10^{-5}$ sec^{-1}) was slower than that of **1**, under the same conditions. In the light of the evidence presented we feel that the solvolysis of **1** proceeds by an ionization mechanism to the stage of some ion-pair species.

The observation of the unique carbon-oxygen bond fission by ionization, as well as the relatively high reactivity reported above for the solvolysis of **1** is undoubtedly a result of a higher degree of acid strength of the trichloromethanesulphenic acid as compared to the arenesulphenic acids, with consequent better leaving group ability of the corresponding anion. It is worthwhile to point out that the reactivity of **1** is much higher than that of the corresponding benzenesulphinate (e.g. in 80% ethanol-water at 75°, $k = 4{\cdot}77 \times 10^{-4}$ sec^{-1}),[3f] and as mentioned above also exceeds that of the corresponding chloride. However, it should be stressed that the stability of the intermediate carbonium ion is of crucial importance. It was thus found that benzhydryl and furfuryl trichloromethanesulphenates undergo ethanolysis at room temperature with complete carbon-oxygen bond cleavage and at a rate similar to that of **1**, as expected from the study of related systems[15] which indicated comparable stabilities for p-anisyl, benzhydryl and furfuryl cations. In contrast, the ethanolysis of benzyl, p-chloro- and p-methylbenzyl trichloromethanesulphenates, under the same conditions, proceeds with sulphur-oxygen bond fission as indicated by the formation of ethyl trichloromethanesulphenate, as the only detectable product in each case. Furthermore, the reactivity of these esters is drastically decreased (e.g. at 40° and [KOAc] ~ 0·10M, $k = 12{\cdot}6 \pm 0{\cdot}5 \times 10^{-5}$ and $7{\cdot}68 \pm 0{\cdot}28 \times 10^{-5}$ sec^{-1}, for the benzyl and p-chlorobenzyl sulphenates, respectively). This behaviour is analogous to that observed with regard to the ability of rearrangement to sulphoxide for the variously substituted benzyl sulphenates.[11] It is also reminiscent of the behaviour reported for benzylic arenesulphinates[3f] and illustrates again the great rate enhancement produced by a p-methoxy group in the benzyl system.[3d,f,16]

Finally, it is interesting to note again that although the solvolysis of trichloromethanesulphenates has been studied by Horak,[8] the ionization mechanism reported above for the reaction of **1** has not been observed in his studies. This may be due to the use of strong acid or base catalysis and/or the choice of esters unable to develop sufficiently stable carbonium ions.

Solvolysis of Benzyl Nitrobenzenesulphenates. Following the observation that the mechanism of solvolysis of benzyl trichloromethanesulphenates displays a remarkable sensitivity to substitution of the benzyl group and can thus be shifted from an S_N1-type carbon-oxygen bond fission to an S_N2-type sulphur-oxygen bond cleavage, it became of interest to investigate the influence of the sulphenyl group on the reaction. For this purpose we have prepared and examined the reactivity of p-anisyl 2-nitrobenzenesulphenate **2**. We have found that in sharp contrast to **1**, the ethanolysis of **2** in the presence of potassium acetate proceeded at a similar rate only at 100°, under the same conditions. Furthermore, in this case the products of the reaction are ethyl 2-nitrobenzenesulphenate and p-anisyl alcohol.

This result clearly indicates that the ethanolysis of **2** involves sulphur-oxygen bond fission. The rates of solvolysis of this ester were measured by the decrease in intensity of the methylene NMR signal at τ 5·21 and are presented in Table 2.

Although good first-order rate constants were obtained for the solvolysis of **2**, they changed with the concentration of potassium acetate in a linear manner and as shown in Table 2, the reactions are, in fact, second-order (first-order with respect to ester and first-order with respect to the added base). Inspection of the data in Table 2 also shows that the rate of solvolysis of **2** decreases by a factor of 3·5 on going from 100% to 80% ethanol, and by a factor of 5 by using pyridine instead of acetate as base. These results are similar to those obtained by Darwish and Noreyko[3e] for the base catalyzed solvolysis of p-methoxyneophyl arenesulphinates, which also proceeds by sulphur-oxygen bond fission under comparable conditions. The data presented above for the solvolysis of p-anisyl 2-nitrobenzenesulphenate are consistent with an S_N2 type mechanism involving nucleophilic displacement at sulphur by the base or lyate ion to yield an intermediate or final product, respectively. In the case of acetate ion, the intermediate would be a mixed anhydride, which is subsequently and rapidly converted to ethyl 2-

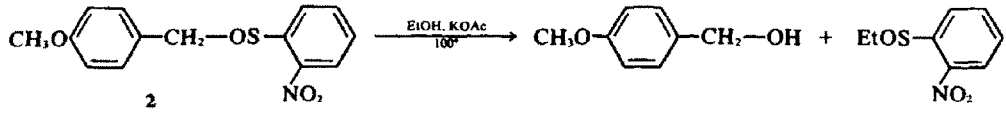


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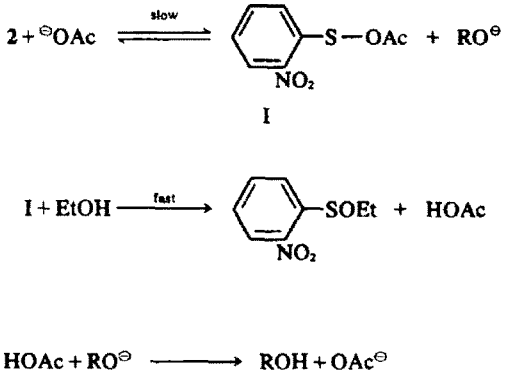
Table 2. Summary of solvolysis rate constants of p-anisyl 2-nitrobenzenesulphenate[a] at 100°

Solvent	Added base	[Base], M	10^5k $10^3k_i/[Base]$ sec^{-1} $1mole^{-1}$ sec^{-1}	
EtOH	KOAc	0·0499	6·7 ± 0·2	1·34
EtOH	KOAc	0·0834	11·8 ± 0·6	1·41
EtOH	KOAc	0·1139	15·4 ± 0·4	1·35
EtOH	KOAc	0·1273	16·7 ± 1·3	1·31
EtOH	Pyridine	0·0562	1·3 ± o·1	0·23
80% EtOH-H_2O	KOAc	0·0553	1·8 ± 0·1	0·33

[a] [Ester] = 0·0275M.



nitrobenezenesulphenate, by reaction with the solvent.

This interpretation essentially parallels that suggested for the solvolysis of p-methoxyneophyl arenesulphinates[3e] as well as that advanced for the alkaline hydrolysis of alkyl 2-nitrobenzenesulphenates[4] and other bivalent sulphur systems.[17]

In view of the somewhat greater stability of the benzyhydryl carbonium ion as compared with the p-anisyl cation,[11] it was of interest to examine the solvolysis of benzydryl 2-nitrobenzenesulphenate. Reflux of an ethanol solution of this ester in the presence of potassium acetate afforded ethyl 2-nitrobenzenesulphenate and the corresponding alcohol as the only solvolysis products. Finally, the ethanolysis of p-anisyl 2,4-dinitrobenzenesulphenate under similar conditions, also involved sulphur-oxygen bond fission as indicated by formation of the corresponding ethyl ester. These results indicate that relatively moderate changes in the nature of the expected ions, are unable to affect the normal course of reaction, and further substantiate the uniqueness exhibited in the reaction of the corresponding trichloromethanesulphenates.

EXPERIMENTAL

Melting points and boiling points are uncorrected. Melting points were taken on a Thomas Hoover melting point apparatus. Infrared spectra were recorded on Perkin Elmer Grating Infrared Spectrometer Model 457. NMR spectra were recorded on Varian HA 100 NMR Spectrometer, and mass spectra on Perkin Elmer Hitachi RMU6 Mass Spectrometer. Microanalyses were performed by Alfred Bernhardt, Microanalytisches Laboratorium, Engelskirchen, West Germany.

Solvents and Reagents. Ethanol was dried by treatment with magnesium ethoxide, as described by Fieser,[18a] Methanol was dried by a similar method.[18b] X% ethanol-water means a solution prepared by mixing X volumes of ethanol with (100-X) volumes of distilled water at 25°. The same pipette was used for measuring all volumes. Eastman grade 2,6-lutidine was purified by refluxing with, and distillation from, barium oxide (bp 140–142°). Pyridine was purified by the same method (bp 115–116°). Commercially available alcohols (Merck, Fluka, Aldrich), 2,4-dinitrobenzenesulphenyl, 2-nitrobenzenesulphenyl and trichloromethanesulphenyl chlorides were used.

Preparation of the sulphenates.

p-Anisyl, benzyl, benzhydryl and furfuryl trichloromethanesulphenates. These esters were prepared from the appropriate alcohol and Cl_3CSCl, in the presence of pyridine as described previously,[11] except that cooling of the reaction mixture was at 0°, instead at −70°.

p-*Chlorobenzyl trichloromethanesulphenate*, was prepared from p-chlorobenzyl alcohol and Cl_3CSCl as described above. Some unreacted alcohol was removed by filtration after its precipitation from a pentane solution of the product, at 10°. The ester was also crystallized from pentane, but at a lower temp. (− 12°). Mp 25° (yield 60%), infrared absorption ($CHCl_3$) showed characteristic[11] bands at 950 and 925 cm^{-1}. The NMR spectrum ($CDCl_3$) showed two singlets τ 2·70 (4H) and 4·74 (2H). Calcd. for $C_8H_6Cl_4OS$: C, 32·90; H, 2·07; Cl, 48·57; S, 10·98. Found: C, 33·00; H, 2·18; Cl, 48·25; S, 10·74%.

p-*Methylbenzyl trichloromethanesulphenate*, was prepared from p-methylbenzyl alcohol and Cl_3CSCl, as described for the p-chloro analogue. Mp 26° (68% yield), characteristic IR bands at 950 and 920 cm^{-1}, and NMR absorption ($CDCl_3$) at τ 2·81 (4H, d, J = 4 Hz), 7·76 (2H, s), 7·68 (3H, s). Calcd. for $C_9H_9OSCl_3$: C, 39·8; H, 3·34; Cl, 39·16; S, 11·81. Found: C, 39·98; H, 3·49; Cl 39·04; S, 12·49%.

Ethyl trichloromethanesulphenate, was prepared by reaction of ethanol with Cl_3CSCl, as described above. The product was obtained as a yellowish liquid showing characteristic IR absorption ($CHCl_3$) at 900 cm^{-1}, and NMR absorption ($CDCl_3$) at τ 5·60 (2H, q, J = 8 Hz) and 8·64 (3H, t, J = 6 Hz).

p-*Anisyl 2-nitrobenzenesulphenate* 2. A solution of

3·8 g (0·02 mole) of 2-nitrobenesulphenyl chloride in 100 ml. of anhydrous ether was added gradually, with stirring, during one hour to a mixture of 6·0 g (0·04 mole) of p-anisyl alcohol and 3·5 g (0·04 mole) of dry pyridine, dissolved in 25 ml of ether and cooled in ice-water bath. After additional stirring for 1 h at the same temperature, and addition of 100 ml of ether, the ether solution was washed consecutively 3 times with 100 ml portions of water, 1% HCl, 5% $NaHCO_3$ and water again. After drying over anhydrous magnesium sulphate, filtration, and evaporation of the solvent, the product crystallized as yellow needles (from ether) on standing in the Frigidaire. Mp 76° (98% yield), characteristic IR bands at 940 and 915 cm^{-1}, and NMR peaks ($CDCl_3$) at τ 1·72–3·17 (8H, m), 5·21 (2H, s), 6·22 (3H, s). Calcd. for $C_{14}H_{13}NO_4S$: C, 57·71; H, 4·49; N, 4·80; O, 21·96; S, 11·00. Found: C, 57·56; H, 4·52; N, 4·91; O, 22·16; S, 10·96%.

Benzhydryl 2-nitrobenzenesulphenate. A solution of 2·5 g (0·013 mole) of 2-nitrobenesulphenyl chloride in 150 ml of anhydrous ether was added gradually (1 h) with stirring to a mixture of 4·0 g (0·022 mole) of benzhydrol and 1·75 g (0·02 mole) of pyridine, dissolved in 25 ml of ether, and cooled in an ice-water bath. The reaction mixture was left for an additional half hour with cooling and stirring, and the precipitated pyridinium chloride was then removed by filtration. Its removal by washing with water decomposed the ester to disulphide. After evaporation of the solvent at a water aspirator, the unreacted alcohol was removed from the solid residue by washing with pentane and methanol. The yellow-coloured ester was crystallized from ethanol-benzene, mp 99°, characteristic IR absorption ($CHCl_3$) at 950 and 910 cm^{-1}, and NMR signals ($CDCl_3$) at τ 1·75–2·90 (14H, m) and 4·40 (1H, s).

Ethyl 2-nitrobenzenesulphenate, was prepared from ethanol and 2-nitrobenezenesulphenyl chloride as described for **2**. Mp 30° (lit[19], 26°), NMR absorption signals ($CDCl_3$) at τ 1·7–2·8 (4H, m), 6·04 (2H, q, J = 6 Hz), 8·60 (3H, t, J = 7 Hz).

p-Anisyl 2,4-dinitrobenzenesulphenate. A mixture of 4·0 g (0·017 mole) of 2,4-dinitrobenzenesulphenyl chloride, 2·5 g (0·031 mole) of pyridine and 7·55 g (0·055 mole) of p-anisyl alcohol was dissolved in 150 ml of dry methylene chloride and heated at the reflux temperature with stirring for one hour. After washing with 100 ml of water, twice with 100 ml of 1%HCl and again five times with 100 ml of water, the solution was dried over $MgSO_4$, and the solvent evaporated. The ester crystallized from ethanol-benzene as yellow needles, mp 88° (yield 79%). The IR spectrum showed bands at 920 and 940 cm^{-1} and the NMR spectrum ($CDCl_3$) showed signals at τ 0·94 (1H, d, J = 2 Hz), 1·61 (1H, dd, Jo = 8 Hz, Jm = 2 Hz), 2·13 (1H, d, J = 8 Hz), 2·70 (2H, d, J = 9 Hz), 3·12 (2H, d, J = 9 Hz), 5·15 (2H, s) 6·20 (3H, s). Calcd. for $C_{14}H_{12}N_2O_6S$: C, 50·00; H 3·60; N, 8·33; S, 9·52. Found: C, 49·72; H, 3·71; N, 8·03; S, 9·41%.

Solvolysis of sulphenates.

Ethanolysis of p-anisyl trichloromethanesulphenate **1**. A 1·5 g quantity (0·005 mole) of **1** and 2·08 g (0·02 mole) of KOAc were dissolved in 50 ml of anhydrous ethanol. The solution was kept at room temperature for 66 h with magnetic stirring. After addition of 50 ml of pentane and washing with four portions of 50 ml of water, the pentane solution was dried over anhydrous magnesium sulphate, and the solvent evaporated at the water aspirator. A weighed quantity of mesitylene, serving as standard, was added to the residue and the NMR spectrum recorded. The weight of the p-anisyl ethyl ether formed (0·65 g, 75% yield) was calculated from the ratio of the integrated peak areas of the product (τ 5·62) and of mesitylene (τ 7·86). The product showed IR absorption bands ($CHCl_3$) at 1610, 1465, 1500, 1240, 1170 and 1085 cm^{-1}, and NMR absorption ($CDCl_3$) at τ 3·00 (4H, AA'BB' quartet), 5·62 (2H, s), 6·30 (3H, s), 6·54 (2H, q, J = 7 Hz), 8·80 (3H, t, J = 7 Hz).

Ethanolysis of benzyl, p-chloro-, and p-methylbenzyl trichloromethanesulphates. Each one of these esters was dissolved in ethanol (~ 0·05 M) in the presence of potassium acetate (~ 0·1 M). After two days at room temperature the product was extracted with pentane and washed several times with water. After drying over $MgSO_4$ and removal of the solvent, the IR and NMR spectra were recorded. In all three cases, these were identical to those of ethyl trichloromethanesulphenate (see above).

Ethanolysis of p-anisyl 2-nitrobenzenesulphenate **2**. In each one of two ampoules were placed 1·0 g of **2** and 1·13 g of potassium acetate, dissolved in 30 ml of anhydrous ethanol. The ampoules were sealed and immersed in a constant temperature oil bath at 100°, for 66 h. The contents of one ampoule were then extracted with 75 ml of pentane, washed with four portions of 25 ml of water and dried. After evaporation of the solvent, the NMR spectrum of the residue (0·64 g, 94% yield) was recorded. This spectrum was identical with that of ethyl 2-nitrobenzenesulphenate (see above). The ethanol from the second ampoule was evaporated under reduced pressure, and chloroform was added to the residue. After filtration of the potassium acetate, the chloroform was removed and the NMR spectrum of the residue was taken. It showed the presence of p-anisyl alcohol and ethyl 2-nitrobenzenesulphenate in a 1 : 1 ratio.

Preparation and Ethanolysis of p-ainisyl chloride. Essentially, the procedure for the preparation of t-butyl chloride[20] was adopted. A 6·9 g quantity (0·05 mole) of p-anisyl alcohol and 12·5 ml of conc. HCl (0·15 mole) were placed in a 100 ml separatory funnel and enough calcium chloride was added to saturate the solution. After shaking for several minutes, two phases separated. The lower layer was removed and the upper layer was filtered through anhydrous calcium chloride and sodium bicarbonate. The product was distilled under reduced pressure, bp 115°/15 mm Hg, IR absorption (neat) at 1615, 1515, 1305, 1250, 1175, 1030 and 830 cm^{-1}, and NMR peaks ($CDCl_3$) at τ 2·99 (4H, AA'BB' quartet), 5·52 (2H, s) and 6·29 (3H, s).

A 0·25 g quantity of p-anisyl chloride and 0·71 g of potassium acetate were dissolved in 50 ml of anhydrous ethanol, and the solution stirred at room temperature for 24 h. The product was extracted with pentane, washed, and identified as p-anisyl ethyl ether by spectral means. The infrared spectrum showed bands (neat) at 1615, 1510, 1465, 1245, 1170 and 1035 cm^{-1}. The NMR spectrum ($CDCl_3$) displayed signals at τ 3·00 (4H, AA'BB' quartet), 5·63 (2H, s), 6·31 (3H, s), 6·54 (2H, q, J = 7 Hz) and 8·82 (3H, t, J = 7 Hz).

Kinetic measurements. Essentially the same procedure was used for all the kinetic runs on the sulphenate esters. This is illustrated below by the procedure used for ester **1**, indicating the modifications for the other esters, at the end.

Appropriate quantities of ester **1**, base and mesitylene, used as standard for following ester disappearance in the NMR spectrum, were weighed into a volumetric flask and

the appropriate solvent was added to the mark. The flask was immersed in an ice-water bath, and 5 ml. aliquots were removed at different time intervals and immediately delivered into an 100 ml separatory funnel containing 25 ml of pentane and 10 ml of distilled water. After shaking the stoppered funnel, the water layer was discraded. The pentane layer was washed again three times with 10 ml of water, dried over anhydrous magnesium sulphate, and the solvent evaporated under reduced pressure. The NMR spectrum of the residue, in $CDCl_3$ using TMS as internal standard, was recorded. The rate constants were calculated from the first-order kinetic expression, $k = (2{\cdot}303/t) \log (a/a-x)$, where a represents the ratio of the signal area of the benzylic methylene protons of the ester, to the peak area of the methyl protons of mesitylene at τ 7·84, at $t = 0$, while $(a - x)$ is the same ratio after t seconds. Plots of $\log (a - x)$ *vs* time gave good straight lines for each run. Errors were calculated by means of the least square method. All calculations and plots were obtained by means of an IBM 360/50 computer, using the APL language.

For all the other esters, the sealed ampoule technique was used, and heating was by constant-temperature oil baths. In the case of ester **2**, the samples were extracted with 30 ml of ether and 10 ml of chloroform, and after drying as usual, the drying agent was rinsed by another 10 ml of chloroform. Pseudo first-order rate constants were calculated as described for **1**.

For the solvolysis of p-anisyl chloride, the titrimetric method was used. Samples were titrated with a solution of sodium methoxide in methanol, using phenolphthalein as indicator. First-order rate constants were calculated from the expression, $k = (1/t)[(\ln(T_\infty - T_0)/(T_\infty - T_t)]$, where t and T are time and ml of titre, respectively.

REFERENCES

[1]For a preliminary account of part of this work see S. Braverman and D. Reisman, *Tetrahedron Letters* 3563 (1973)

[2]e. g. R. Otto, *Chem. Ber.* **19**, 1832 (1886); F. Ullman and G. Nadai, *Ibid.*, **41**, 1870 (1908); J. Ferns and A. Lapworth, *J. Chem. Soc.* **101**, 273 (1912); J. Kenyon, H. Phillips and F. M. H. Taylor, *Ibid.* 173 (1933); J. Kenyon, H. Phillips and V. P. Pittman, *Ibid.* 1072 (1935); M. S. Morgan and L. H. Cretcher, *J. Am. Chem. Soc.* **70**, 375 (1948); E. T. Borrows, J. C. Clayton, B. A. Hems and A. G. Long, *J. Chem. Soc.* S190 (1949); C. A. Bunton and Y. F. Frei, *Ibid.* 1872 (1951); C. A. Bunton and V. A. Welch, *Ibid.* 3240 (1956); J. F. Bunnett and J. Y. Bassett, *J. Am. Chem. Soc.* **81**, 2104 (1959)

[3a]J. Kenyon, H. Phillips and G. R. Shutt, *J. Chem. Soc.* 1663 (1935); [b]H. F. Herbrandson and C. M. Cusano, *J. Am. Chem. Soc.* **83**, 2104 (1961); [c]C. A. Bunton and B. N. Hendy, *J. Chem. Soc.* 2562 (1962); 627 (1963); [d]D. Darwish and R. A. McLaren, *Tetrahedron Letters* 1231 (1962); [e]D. Darwish and J. Noreyko, *Can. J. Chem.* **43**, 1366 (1965); [f]S. Braverman and S. Steiner, *Israel J. Chem.* **5**, 267 (1967); [g]S. Braverman and C. Simons, *Esters of Sulfinic and Sulfenic Acids* in *Mechanisms of Reactions of Sulfur Compounds*, Ed. N. Kharasch, vol. 2, Intra-Science Research Foundation, Santa-Monica, 1968, p. 101

[4]C. Brown and D. R. Hogg, *Chem. Comm.* 38 (1967); D. R. Hogg and P. W. Vipond, *J. Chem. Soc.* (*B*) 1242 (1970)

[5]L. Senatore, E. Ciuffarin and A. Fava, *J. Am. Chem. Soc.* **92**, 3035 (1970)

[6]E. M. Kosower, *Introduction to Physical Organic Chemistry*, Wiley, New York, N.Y., 1968, p. 65

[7]E. Ciuffarin, L. Senatore and M. Isola, *J. Chem. Soc.* (*B*) 2187 (1971); see also L. Senatore, E. Ciuffarin and L. Sagramora, *Ibid.* 2191 (1971)

[8a]J. Horák, *Coll. Czech. Chem. Comm.* **28**, 2637 (1963); [b]J. Horák, *Ibid.* **31**, 3189 (1966) [c]J. Horák, *Ibid.* **32**, 868 (1967); [d]J. Horák and K. Krajkarova, *Ibid.* **32**, 2134 (1967)

[9]J. L. Kice, *Int. J. Sulfur Chem.* (*C*) **6**, 3 (1971)

[10]E. Kühle, *Synthesis* 566 (1971), and refs cited therein

[11]S. Braverman and B. Sredni, 40th Meeting of the Israel Chemical Society, Haifa, October 20–22 (1970); *Suppl. Proc. Israel J. Chem.* **8**. 30p (1970); B. Sredni, M.Sc. Thesis, Bar-Ilan University, 1972; S. Braverman and B. Sredni, *Tetrahedron*, **30**, 2379 (1974)

[12]G. Sosnovsky, *J. Chem. Soc.* 3139 (1956)

[13]J. Silhanek and M. Zbirovsky, *Chem. Comm.* 878 (1969)

[14]S. G. Smith, A. H. Fainberg, and S. Winstein, *J. Am. Chem. Soc.* **83**, 618 (1961)

[15]A. Fava, A. Iliceto, A. Ceccon and P. Koch, *J. Am. Chem. Soc.* **87**, 1045 (1965); A. Fava, U. Tonellato, and L. Congin *Tetrahedron Letters* 1657 (1965); L. A. Spurlock and R. G. Fayter, *J. Org. Chem.* **34**, 4035 (1969); D. S. Noyce and G. V. Kaiser, *Ibid.* **34**, 1008 (1969); S. Braverman and B. Goldrath, *Int. J. Sulfur Chem.* (*A*), **8**, 55 (1973); S. Braverman and T. Globerman, *Tetrahedron Letters* 3023 (1973)

[16]G. S. Hammond, C. E. Reeder, F. T. Fang and J. K. Kochi, *J. Am. Chem. Soc.* **80**, 568 (1958)

[17]O. Foss, *Organic Sulfur Compounds*, vol. 1, ch. 9, Ed. N. Kharasch, Pergamon Press, Oxford, 1961; E. Ciuffarin and A. Fava, *Progress in Physical Organic Chemistry* Vol. 6, Eds. A. Streitwieser and R. W. Taft, Interscience Publishers, New York, N.Y., 1968, p. 81

[18]L. F. Fieser, *Experiments in Organic Chemistry*, 3rd Edition, D. C. Heath and Co., Boston, 1957. [a]p. 286 [b]p. 289

[19]T. Zincke and F. Farr, *Annalen* **391**, 55 (1912)

[20]L. F. Fieser, *Experiments in Organic Chemistry*, 3rd Edition, D. C. Heath and Co., Boston, 1957, p. 307