Thermal Decomposition of t-Butyl 2-Nitrobenzenesulphenate

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t-Butyl 2-nitrobenzenesulphenate decomposes in refluxing anisole in the dark to give 2- and 4-methoxyphenyl 2-nitrophenylsulphides, isobutene and di-2-nitrophenyl disulphide. Aniline and *p*-methoxybenzenesulphonic acid were also obtained and are considered to arise from an intramolecular oxidation–reduction followed by a *trans*-sulphonation reaction. t-Butyl-alcohol was identified in the refluxing liquid. The initial step in the decomposition is suggested to be the heterolysis of the sulphur–oxygen bond, and the isobutene is considered to be formed by the dehydration of t-butyl-alcohol rather than by a cyclic process involving fission of the carbon–oxygen bond as previously proposed.

The thermal decomposition of methyl 2-nitrobenzene sulphenate in aromatic solvents gives the appropriate aryl 2-nitrophenyl sulphides as the major isolable products.[1] Evidence was adduced that these reactions and the related thermal rearrangements of the corresponding aryl sulphenate esters involved heterolytic fission of the sulphur–oxygen bond to give an ion-pair, or its precursor, *e.g.* ArS–OR $\rightleftharpoons$ ArS$^+$ $^-$OR. The t-butyl esters of arylsulphenic acids are reported[2] to give isobutene and sulphur dioxide on pyrolysis under nitrogen at 120—135°, together with a nonvolatile tarry residue which could not be purified. No evidence could be obtained for a radical mechanism and the initial breakdown was suggested[2] to occur *via* a cyclic transition state. A concerted cyclic intramolecular process is

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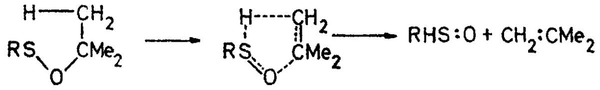

also postulated[3] for the isomerisation of allyl sulphenates to allyl sulphoxides.

The results for the decomposition of the methyl[1] and t-butyl[2] esters indicated a possible change in mechanism as the methyl group in the ester is successively alkylated. In an attempt to obtain evidence for such a change we began by studying the thermal decomposition of t-butyl 2-nitrobenzenesulphenate under similar conditions to those previously used for the methyl analogue.

The products from the thermal decomposition of t-butyl 2-nitrobenzenesulphenate in boiling anisole under nitrogen in the dark were found to vary slightly according to the experimental conditions. When a solution of the ester in anisole was slowly heated to boiling and nitrogen was passed through the solution, isobutene was evolved, and the residue contained di-2-nitrophenyl disulphide, aniline, *p*-methoxybenzenesulphonic acid, and a mixture of 2- and 4-methoxyphenyl 2-nitrophenyl sulphides in the ratio of *ca.* 1 : 4. Addition of the ester to boiling anisole led to a violent reaction and a greatly increased yield of *p*-methoxybenzenesulphonic acid. The nonvolatile products from this reaction also included 2-methyl-1-(2-nitrophenylthio)propene. A similar reaction occurred when *p*-xylene was used as the solvent. In all of these reactions considerable charring occurred.

These results agree with, but considerably extend, the previous observations[2] on this reaction. The formation of the aryl 2-nitrophenyl sulphides, which are similarly formed in the thermal decomposition of the methyl and of the aryl esters, strongly suggests that the decomposition of the t-butyl ester also proceeds through a sulphenium ion, or its precursor, and that these products are formed by an electrophilic substitution reaction involving this intermediate. Such an intermediate could arise from an initial heterolysis of the sulphur–oxygen bond as previously proposed[1] for the methyl ester or, alternatively, following the mechan-

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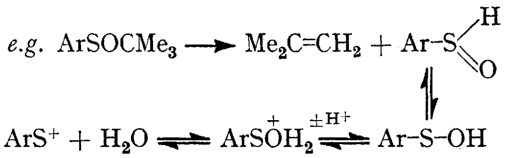
[1] D. R. Hogg, J. H. Smith, and P. W. Vipond, *J. Chem. Soc.* (*C*), 1968, 2713.

[2] R. S. Irwin and N. Kharasch, *J. Amer. Chem. Soc.*, 1960, **82**, 2502.

[3] S. Braverman and Y. Stabinsky, *Chem. Comm.*, 1967, 270; P. Bickart, F. W. Carson, J. Jacobus, E. G. Miller, and K. Mislow, *J. Amer. Chem. Soc.*, 1968, **90**, 4869.

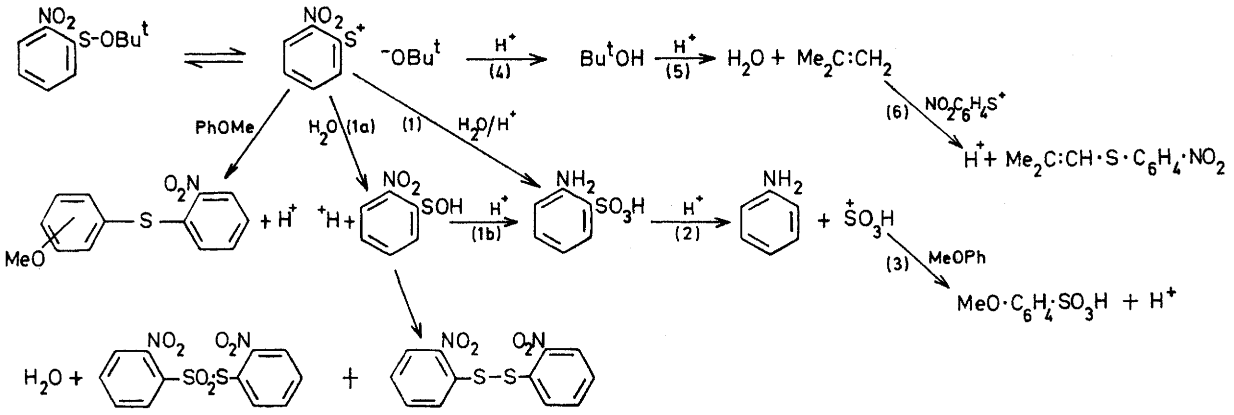
ism proposed by Kharasch,[2] from the initially formed sulphenic acid.



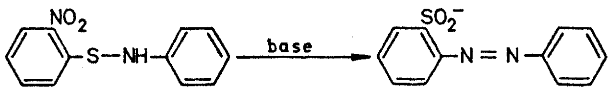
$$e.g.\ \mathrm{ArSOCMe_3} \longrightarrow \mathrm{Me_2C{=}CH_2} + \mathrm{Ar{-}S(H){=}O}$$

$$\mathrm{ArS^+} + \mathrm{H_2O} \rightleftharpoons \mathrm{Ar\overset{+}{S}OH_2} \overset{\pm H^+}{\rightleftharpoons} \mathrm{Ar{-}S{-}OH}$$

The identification of t-butyl alcohol in the distillate, when the reaction mixture was not allowed to reflux, eliminates this reaction sequence and provides strong evidence that the initial bond fission occurs predominantly between the sulphur and the oxygen atoms. The following scheme is therefore proposed for the reaction in anisole:



Oxygen transfer from an *o*-nitro-group to sulphur, as postulated in reaction (1), or the alternative (1b), is comparatively well known.[4] Zincke [5] has shown that *o*-aminobenzenesulphonic acid is formed when 2-nitrobenzenesulphenyl chloride is heated in aqueous methanol, and it has recently been shown [6] that in the base-catalysed rearrangement of 2-nitrobenzenesulphenanilide to azobenzene-2-sulphinic acid, the oxygens of the sulphinic acid group are derived from the nitro-group



As desulphonation is accelerated by electron-releasing substituents, particularly when they are in the *ortho*-position,[7] *o*-aminobenzenesulphonic acid should desulphonate comparatively readily. The formation of aniline and *p*-methoxybenzenesulphonic acid could therefore occur by a *trans*-sulphonation reaction involving anisole and *o*-aminobenzenesulphonic acid [reactions (2) and (3)]. Although *o*-aminobenzenesulphonic acid is reported [7] to be 90% desulphonated after being heated at 211° in aqueous acid for 4 hr., no reaction was observed in refluxing anisole in the presence of a trace of water. The considerable increase in the yield of sulphonic acid from the thermal decomposition when the reaction became more violent, leads us to assume that the model experiment was not sufficiently comparable with the actual experiment. By analogy with the sulphonation of toluene,[8] the *para*-isomer should be the predominant product from the sulphonation of anisole. The apparent absence of other isomers in the decomposition products may be due to experimental difficulties in separating small quantities of isomeric sulphonic acids. It has been previously reported [9] that, when alkyl substituted benzenesulphonic acids are heated at 175—180° in toluene or xylene, trans-sulphonation occurs. The postulation of a similar reaction in this study at a slightly lower temperature is considered to be reasonable in view of the expected increased reactivity of both the acid and the solvent. 4-Methoxyphenyl 2-nitrophenyl sulphide was not appreciably affected by a prolonged period in refluxing anisole and, consequently, 4-methoxybenzenesulphonic acid is not formed by the thermal decomposition of this product.

The isobutene formed in the decomposition is considered to arise from the dehydration of t-butyl alcohol in the acidic medium [reactions (4) and (5)]. Isobutene is known [10] to undergo substitution reactions with electrophilic reagents, especially in solvents of low polarity, and the formation of 2-methyl-1-(2-nitrophenylthio)-propene in the reaction under more vigorous conditions is consequently not unexpected [reaction (6)]. In methylene chloride solution at room temperature isobutene forms a normal adduct with 2,4-dinitrobenzenesulphenyl chloride and the proposed structure for this adduct is in accord with previous work.[11]

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[4] J. D. Loudon and G. Tennant, *Quart. Rev.*, 1964, **18**, 389.

[5] T. Zincke and F. Farr, *Annalen*, 1912, **391**, 57.

[6] C. Brown, *Chem. Comm.*, 1969, 100.

[7] E. E. Gilbert, 'Sulfonation and Related Reactions', Interscience, New York, 1965, p. 429.

[8] L. Vollbracht, H. Certfontain, and F. L. J. Sixma, *Rec. Trav. chim.*, 1961, **80**, 11.

[9] H. Drews, S. Meyerson, and E. K. Fields, *J. Amer. Chem. Soc.*, 1961, **83**, 3871.

[10] M. L. Poutsma, *J. Amer. Chem. Soc.*, 1965, **87**, 4285; I. V. Bodrikov, Z. S. Smolyan, and G. A. Korchagina, *Zhur. obshchei Khim.*, 1965, **35**, 933.

[11] N. Kharasch and C. M. Buess, *J. Amer. Chem. Soc.*, 1949, **71**, 2724.

Di-2-nitrophenyl disulphide could be formed in this reaction by disproportionation [12] of 2-nitrobenzenesulphenic acid which could arise from the hydrolysis of the sulphenium ion. Neither the other product in this disproportionation, 2-nitrophenyl 2-nitrobenzenethiolsulphonate, nor any compound obviously derived from it, was, however, isolated from the reaction mixture.

t-Butyl 2-nitrobenzenesulphenate decomposes much more rapidly than the methyl ester.[1] The lower rate of alkaline hydrolysis of the t-butyl ester compared with the methyl ester has been attributed [13] to the importance of steric effects in this bimolecular process. The relative rates of thermal decomposition suggest that bond fission must be virtually complete before bond formation commences at the sulphur and are consistent with the proposed mechanism. No evidence has been obtained for a change in the mechanism of the thermal decomposition of alkyl 2-nitrobenzenesulphenates with increasing α-substitution in the alkyl-group.

EXPERIMENTAL

Unless otherwise stated silica gel was used as the stationary phase in chromatography and light petroleum refers to the fraction of b.p. 60—80°. U.v. spectra were measured in ethanol solution and ^{1}H n.m.r. spectra in deuteriochloroform.

t-Butyl 2-nitrobenzenesulphenate,[14] m.p. 53·5—54·5°, and *o*-aminobenzenesulphonic acid [15] were prepared as previously described; the former was purified by chromatography with benzene–light petroleum (1 : 1) as eluant. 4-Methoxyphenyl 2-nitrophenyl sulphide, m.p. 92—94° (lit.,[16] m.p. 95°), was obtained in 50% yield by treating 2-nitrobenzenesulphenyl chloride with anisole in the presence of aluminium chloride.[17] No 2-methoxyphenyl 2-nitrophenyl sulphide was detected on examination of the reaction mixture by t.l.c. 2-Chloro-2-methylpropyl 2,4-dinitrophenyl sulphide, m.p. 83—86° (lit.,[11] m.p. 86—87°) was obtained by bubbling isobutene through a solution of 2,4-dinitrobenzenesulphenyl chloride in methylene chloride at room temperature for 2 hr. The solution was set aside for 24 hr., the solvent was removed under reduced pressure, and the product was crystallised from ethanol.

Thermal Decomposition of t-Butyl 2-Nitrobenzenesulphenate. (*a*) A solution of t-butyl 2-nitrobenzenesulphenate (3·30 g.) in anisole (50 ml.) was slowly heated to boiling and then under reflux for 2 hr., when examination of the solution by t.l.c. indicated that all the ester had reacted. Light was excluded throughout the reaction and dry nitrogen was passed through the solution. The volatile products were collected in a trap cooled to −80°.

The small quantity of colourless, volatile product was treated with a solution of 2,4-dinitrobenzenesulphenyl chloride in methylene chloride together with a few drops of pyridine. After 24 hr. the solvent was evaporated off under reduced pressure and the residue was chromatographed with benzene–light petroleum (1 : 1) as eluant to give 2-chloro-2-methylpropyl 2,4-dinitrophenyl sulphide (0·20 g., 5·6%), i.r. spectrum identical with that of an authentic specimen. No t-butyl 2,4-dinitrobenzenesulphenate could be detected in the residue.

The black anisole solution was diluted with benzene and extracted with dilute hydrochloric acid. The acid extracts were neutralised and extracted with ether. Removal of the solvent from the dried ethereal extracts yielded a pink oil which was treated with excess of 2-nitrobenzenesulphenyl chloride (0·10 g.) in methylene chloride. Preparative t.l.c., with benzene as irrigant, gave 2-nitrobenzenesulphenanilide (0·03 g., 0·8%), m.p. 93—95° (lit.,[5] m.p. 94°), i.r. spectrum identical with that of an authentic specimen. The neutralised aqueous extracts were acidified and evaporated to dryness to give a non-homogeneous red solid, the i.r. spectrum of which indicated the presence of a sulphonic acid. Examination by t.l.c. with ethanol as irrigant indicated the presence of several products, one of which had the same R_F value as *p*-methoxybenzenesulphonic acid.

The dried benzene–anisole solution was chromatographed as previously described [1] to give 2-methoxyphenyl 2-nitrophenyl sulphide (0·16 g., 4·2%), 4-methoxyphenyl 2-nitrophenyl sulphide (0·70 g., 18·5%) and di-2-nitrophenyl disulphide (0·26 g., 15%). A black residue remained at the top of the column.

(*b*) t-Butyl 2-nitrobenzenesulphenate (5·0 g.) was added to boiling anisole as rapidly as the vigorous reaction would allow and the dark solution was heated under reflux for 1 hr. The reaction mixture was chromatographed to give 2-*methyl*-1-(2-*nitrophenylthio*)*propene* (0·08 g., 6·7%), an orange oil purified by low-temperature crystallisation, $\lambda_{max.}$ 248, 278sh, and 378 nm. (log ε 4·2, 3·8, and 3·6); $\nu_{max.}$ 1619, 1592, 1568, and 742 cm.$^{-1}$; ^{1}H n.m.r. bands at τ 8·01—8·05 (3H, m), 4·05 (1H, m), 1·70—3·04 (4H, m) (Found: C, 57·6; H, 5·4; N, 6·5; $C_{10}H_{11}NO_2S$ requires C, 57·4; H, 5·3; N, 6·7%), identical with the compound obtained by treating the yellow oil from the reaction of isobutene and 2-nitrobenzenesulphenyl chloride with potassium t-butoxide in t-butyl alcohol at room temperature for 16 hr. 2- and 4-Methoxyphenyl 2-nitrophenyl sulphides and di-2-nitrophenyl disulphide were also obtained by elution with benzene–light petroleum. Elution with methanol gave, after removal of the solvent, a black solid which was dissolved in methylene chloride and extracted with water. The red aqueous extracts were evaporated to give a red oil from which *p*-methoxybenzenesulphonic acid (0·21 g., 5·1%), colourless crysyals, $\nu_{max.}$ 3400, 1190, 830 cm.$^{-1}$; ^{1}H n.m.r. bands at τ 6·15 (3H, s), 2·11—3·03 (4H, q, *J* 9 Hz), was obtained by careful addition of ethanol. This product was obtained in 11·3% yield from a similar reaction by extracting the reaction mixture with water.

(*c*) t-Butyl 2-nitrobenzenesulphenate (3·10 g.) dissolved in anisole (15 ml.) was slowly heated to the boiling point in the dark and the pale yellow distillate was collected in two fractions (9 ml. and 4 ml.). These fractions and the reaction mixture were examined by g.l.c. on a column containing ethylene glycol succinate (15% by weight) on g-cel. By comparison with standard solutions the first fraction was shown to contain t-butyl alcohol (>0·05 g.,

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[12] E. Vinkler and F. Klivényi, *Acta Chim. Acad. Sci. Hung.*, 1957, **11**, 15.

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

[14] C. Brown, D. R. Hogg, and D. C. McKean, submitted for publication in *Spectrochim. Acta*.

[15] E. Wertheim, *Org. Synth.*, Coll. Vol. II, 1943, 471.

[16] R. Passerini, *Boll. sci. Fac. Chim. ind. Bologna*, 1950, **8**, 122.

[17] C. M. Buess and N. Kharasch, *J. Amer. Chem. Soc.*, 1950, **72**, 3529.

5%) together with a very volatile component, presumably isobutene. Water was also present. No t-butyl alcohol was detected in the reaction mixture, and only a trace in the second fraction.

A similar decomposition of ester (3·5 g.) gave a colourless distillate (8 ml.). Treatment of the first fraction with 2-nitrobenzenesulphenyl chloride (0·5 g.) and a few drops of pyridine gave an oil which was purified by chromatography to give t-butyl 2-nitrobenzenesulphenate (0·1 g., 3%), m.p. 51—53°, i.r. spectrum identical with that of an authentic specimen. Very little decomposition occurred when the ester was heated under reflux for 1 week in ethylene dichloride solution in the presence of cyclohexene.

(*d*) Similar products were obtained when the ester was decomposed in *p*-xylene.

Attempted Thermal Decomposition of 4-*Methoxyphenyl* 2-*Nitrophenyl Sulphide*.—4-Methoxyphenyl 2-nitrophenyl sulphide (0·70 g.), dissolved in boiling anisole, was heated under reflux for 48 hr. in the dark. The solution darkened slightly but no *p*-methoxybenzenesulphonic acid could be detected. The starting material (0·59 g., 84%), m.p. 88—91°, was recovered by chromatography followed by crystallisation.

Attempted trans-*Sulphonation Reaction with* o-*Aminobenzenesulphonic Acid*. A stream of nitrogen was passed through a solution of *o*-aminobenzenesulphonic acid (1·00 g.) in refluxing anisole (20 ml.) for 16 hr. Extraction with water gave material (0·90 g.) identical (i.r.) with the starting material. No *p*-methoxybenzenesulphonic acid could be detected by t.l.c. Similar results were obtained when water was added to the initial solution.

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