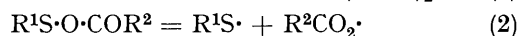
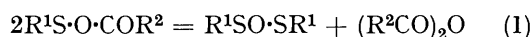


## Thermal Decomposition of Sulphenyl Carboxylates

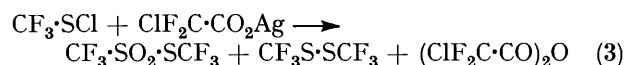
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Thermal decomposition of arenesulphenyl carboxylates in an inert medium gives the carboxylic acid anhydride, the acid, and products derived from the aryl arene *S*-sulphinate. A mechanism involving formation of an intermediate thiosulphonium salt,  $\text{ArS}^+(\text{SAr})\text{O}\cdot\text{COR}\text{RCO}_2^-$ , is proposed. Decomposition of 2,4-dinitrobenzenesulphenyl acetate in benzene gives 2,4-dinitrophenyl phenyl sulphide in good yield.

SULPHENYL carboxylates,  $\text{R}^1\text{S}\cdot\text{O}\cdot\text{COR}^2$ , which are mixed anhydrides of sulphenic and carboxylic acids, decompose comparatively readily. It was suggested<sup>1</sup> that the two most likely modes of thermolysis were disproportionation to the carboxylic acid anhydride and *S*-thiosulphinate, equation (1), or homolysis of the sulphur-oxygen bond, equation (2). Since the disul-



phide and acetic acid were the only isolable products from the thermolysis of anthraquinone-1-sulphenyl acetate, the latter alternative was preferred.<sup>1</sup> In contrast the attempted preparation of trifluoromethanesulphenyl chlorodifluoroacetate,  $\text{CF}_3\text{SO}\cdot\text{COCF}_2\text{Cl}$ , gave<sup>2</sup> a mixture of carboxylic acid anhydride, disulphide, and *S*-thiosulphonate, reaction (3). The formation of these products is readily explained by formation of the sulphenyl carboxylate, decomposition by equation (1), and disproportionation<sup>3</sup> of the *S*-thiosulphinate to disulphide and *S*-thiosulphonate. Photolysis of the



isolable trifluoromethanesulphenyl trifluoroacetate gave similar products but thermolysis afforded carbon dioxide and bis(trifluoromethyl) sulphide.<sup>2</sup> In view of these

observations a more detailed study of the thermolysis of some simple sulphenyl carboxylates seemed desirable.

Benzenesulphenyl benzoate has not been isolated owing to its instability at room temperature.<sup>1</sup> The i.r. spectra of the partially decomposed material have three main bands in the carbonyl region (1700, 1740, and 1790  $\text{cm}^{-1}$ ) which vary in their relative intensities with the sample and with time. These bands were attributed to benzoic acid, benzenesulphenyl benzoate, and benzoic anhydride respectively. The second anhydride band<sup>4</sup> at 1725  $\text{cm}^{-1}$  is presumably masked by the other bands. The allocation of the band at 1740  $\text{cm}^{-1}$  to the sulphenyl benzoate agrees with the suggestion<sup>5</sup> that the carbonyl stretching frequency in  $\text{RCO}\cdot\text{OX}$  is dependent on the electronegativity of X. Benzoic anhydride could not be isolated from the reaction mixture, but its presence was confirmed by converting it into benzanilide using conditions under which benzoic acid does not react. Diphenyl disulphide and benzoic acid were isolated and spectral evidence obtained for the presence of phenyl *S*-thiosulphinate in the reaction mixture and phenyl *S*-thiosulphonate amongst the final products.

Sulphenyl acetates are generally less stable than the benzoates<sup>1,6</sup> and spectral evidence for the formation of benzenesulphenyl and toluene-*p*-sulphenyl acetate could not be obtained. Reaction of benzenesulphenyl chloride in carbon tetrachloride with anhydrous sodium acetate

<sup>1</sup> R. E. Putnam and W. H. Sharkey, *J. Amer. Chem. Soc.*, 1957, **79**, 6526.

<sup>2</sup> A. Haas and D. Y. Oh, *Chem. Ber.*, 1969, **102**, 77.

<sup>3</sup> P. Koch, E. Ciuffarin, and A. Fava, *J. Amer. Chem. Soc.*, 1970, **92**, 5971.

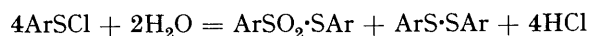
<sup>4</sup> L. J. Bellamy, 'The Infrared Spectra of Complex Molecules,' 2nd edn., Methuen, London, 1958, p. 127.

<sup>5</sup> J. P. Freeman, *J. Amer. Chem. Soc.*, 1958, **80**, 5954.

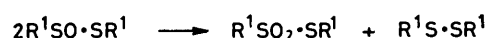
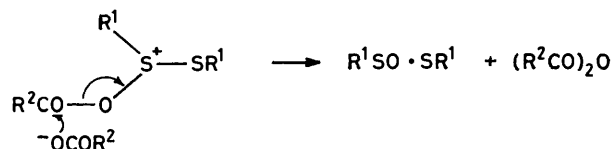
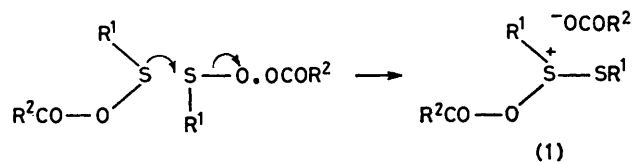
<sup>6</sup> A. Brydon, G. G. Cameron, and D. R. Hogg, *Internat. J. Sulfur Chem. A*, 1972, **2**, 289.

gave instead a mixture of acetic anhydride, acetic acid, diphenyl disulphide, and phenyl *S*-thiosulphonate. I.r. evidence was again obtained for an intermediate *S*-thiosulphinatone. Toluene-*p*-sulphenyl chloride gave similar products.

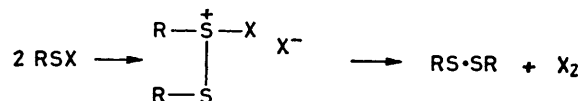
The proportion of acetic anhydride in the volatile products appears to depend upon the amount of residual water in the sodium acetate and little or no anhydride is obtained unless the sodium acetate has been freshly fused. Consequently the carboxylic acid is considered to be formed by reaction of sodium acetate with hydrogen chloride, formed in the rapid hydrolysis of the sulphenyl halide.



These results are best explained by the initial formation of the appropriate sulphenyl carboxylate, which then decomposes to give the anhydride and the *S*-thiosulphinatone as in equation (1). Since electron-withdrawal at sulphur increases the stability of sulphenyl carboxylates,<sup>1,6</sup> a mechanism involving substitution by the carboxylic acid anion at the carbonyl group of the sulphenyl carboxylate seems unlikely. We therefore suggest that the disproportionation of sulphenyl carboxylates proceeds by a bimolecular process similar to those proposed for the ionisation of sulphenyl halides in liquid sulphur dioxide<sup>7</sup> and for the reaction of formic acid with *p*-chlorobenzenesulphenyl chloride.<sup>8</sup> Stabilis-



ation of sulphenyl carboxylates by electron-withdrawing substituents attached to the sulphur is consequently attributed to their effect in reducing the nucleophilicity



of the sulphur and in destabilising the thiosulphonium salt (I), both effects reducing the rate of the first step.

<sup>7</sup> G. Capozzi, V. Lucchini, G. Modena, and F. Rivetti, *J.C.S. Perkin II*, 1975, 361, 900.

<sup>8</sup> G. H. Schmid and V. M. Csizmadia, *Internat. J. Sulfur Chem.*, 1973, **8**, 433.

<sup>9</sup> P. S. Magee in 'Sulfur in Organic and Inorganic Chemistry, Volume 1,' ed. A. Senning, M. Dekker, New York, 1971, p. 261.

<sup>10</sup> J. P. Danehy in 'Sulfur in Organic and Inorganic Chemistry, Volume 1,' ed. A. Senning, M. Dekker, New York, 1971, p. 327.

Electron-withdrawing substituents similarly increase the thermal stability of sulphenyl halides,<sup>9</sup> suggesting that thermolysis of these compounds follows a similar mechanism, which must be the reverse of that for the halogenation of disulphides.

On this basis, the decreased stability of sulphenyl bromides<sup>9</sup> and iodides,<sup>10</sup> compared with the corresponding chlorides, may be explained by the greater leaving-group ability of their anions and the increased susceptibility of bromine and iodine atoms to nucleophilic substitution compared with chlorine.

In contrast to other sulphenyl acetates, 2,4-dinitrobenzenesulphenyl acetate is stable at room temperature and has been fully characterized.<sup>11</sup> When heated in carbon tetrachloride it decomposes to give products which are entirely analogous to those previously described. Rather surprisingly in view of the original method of preparation,<sup>11</sup> it decomposes smoothly in boiling benzene to give 2,4-dinitrophenyl phenyl sulphide and acetic acid in excellent yield, together with a small amount of an insoluble brown solid. These products are also obtained on photolysis.<sup>12</sup> This change in the products is tentatively attributed to the decreased selectivity of the thiosulphonium ion intermediate, which in this case is supposed to react preferentially with the solvent. The corresponding sulphenate esters and sulphenyl chloride gave<sup>13</sup> similar substitutions under more vigorous conditions and these reactions were originally postulated to proceed *via* a sulphenium ion or its precursor. It is now suggested that this precursor could be a thiosulphonium salt similar to (1).

#### EXPERIMENTAL

Unless otherwise stated silica gel was used as the stationary phase in chromatography and <sup>1</sup>H n.m.r. spectra were measured in deuteriochloroform.

**Benzenesulphenyl Benzoate.**—Benzenesulphenyl chloride (1.29 g) in dry carbon tetrachloride (30 ml) was shaken with dry sodium benzoate (4.11 g) for 36 h. The mixture was filtered and the residue extracted with ether to give benzoic acid (0.48 g, 44%), m.p. 120–122 °C. The solvent was removed from the filtrate to give a red oil,  $\nu_{\text{max}}$  1790, 1740, 1700, 1320 (SO<sub>2</sub>), 1150 (SO<sub>2</sub>), and 1040 cm<sup>-1</sup> (SO), which was heated under reflux for 1.5 h with an excess of aniline (2.5 ml) in benzene (10 ml) and allowed to cool. The resulting solid was chromatographed to give benzanilide (0.32 g, 36%), m.p. 158–160 °C, and an unidentified oil. The benzene solution was extracted with dilute hydrochloric acid and water and chromatographed to give diphenyl disulphide, m.p. 58–61 °C, identical with an authentic specimen, an oily solid,  $\nu_{\text{max}}$  1150 and 1330 cm<sup>-1</sup> presumed to be *S*-phenyl benzenethiosulphonate, and a little benzanilide. The aqueous extracts gave benzoic acid. Aniline does not give benzanilide with benzoic acid under these conditions.

<sup>11</sup> A. J. Havlik and N. Kharasch, *J. Amer. Chem. Soc.*, 1956, **78**, 1207.

<sup>12</sup> D. H. R. Barton, Y. L. Chow, A. Cox, and G. W. Kirby, *J. Chem. Soc.*, 1965, 3571.

<sup>13</sup> D. R. Hogg, J. H. Smith, and P. W. Vipond, *J. Chem. Soc. (C)*, 1968, 2713; D. R. Hogg and P. W. Vipond, *ibid.*, 1970, 60.

*Benzenesulphenyl Chloride and Sodium Acetate.*—Benzenesulphenyl chloride (4.3 g, 0.03 mol) in dry carbon tetrachloride (35 ml) was shaken in the dark for 3 h with freshly fused anhydrous sodium acetate (12.3 g, 0.15 mol). The mixture was filtered to give a pale yellow filtrate which gave  $^1\text{H}$  n.m.r. signals at  $\tau$  7.86 (s) and 7.93 (s), in a 68 : 32 ratio, attributed to acetic anhydride and acetic acid respectively. The filtrate was shaken with a solution (5 ml) of *p*-hydroxybenzoic acid (1 g) in 10% sodium hydroxide solution following the method of Chattaway<sup>14</sup> to give a high yield of *p*-acetoxybenzoic acid, m.p. 183—185 °C, identical with an authentic specimen. Acetic acid was shown not to react under these conditions. Preparative t.l.c. on the filtrate gave diphenyl disulphide (0.72 g, 44%) and *S*-phenyl benzenethiosulphonate (0.21 g, 12%), m.p. 39—40 °C (lit.,<sup>15</sup> m.p. 45°),  $\nu_{\text{max}}$  1 325 and 1 140  $\text{cm}^{-1}$  ( $\text{SO}_2$ ).

*Toluene-*p*-sulphenyl Chloride and Sodium Acetate.*—Toluene-*p*-sulphenyl chloride (0.03 mol) reacted similarly in carbon tetrachloride for 2 days to give di-*p*-tolyl disulphide (22.5%); *S*-*p*-tolyl toluene-*p*-thiosulphonate (24%), m.p. 71—74 °C (lit.,<sup>16</sup> m.p. 78 °C),  $\nu_{\text{max}}$  1 325 and 1 140  $\text{cm}^{-1}$  ( $\text{SO}_2$ );  $^1\text{H}$  n.m.r. bands at  $\tau$  7.57 (s), 7.61 (s) with a total of 6 protons and 2.4—3.1 (m, 8 H); and acetic anhydride

<sup>14</sup> J. Chattaway, *J. Chem. Soc.*, 1931, 2495.

<sup>15</sup> D. Barnard, *J. Chem. Soc.*, 1957, 4673.

characterised as *p*-acetoxybenzoic acid, m.p. 185—188 °C. The same products were obtained in benzene.

*2,4-Dinitrobenzenesulphenyl Acetate.*—(a) 2,4-Dinitrobenzenesulphenyl acetate<sup>11</sup> (3.30 g),  $\nu_{\text{max}}$  1 780  $\text{cm}^{-1}$ , in benzene (100 ml) was heated under reflux in the dark for 2 h and filtered. The filtrate was shown by  $^1\text{H}$  n.m.r. to contain acetic acid. Acetic anhydride could not be detected. Removal of the solvent gave a yellow solid which was crystallised to give 2,4-dinitrophenyl phenyl sulphide (2.50 g, 71%), m.p. 119—120 °C (lit.,<sup>17</sup> m.p. 121 °C), identical with an authentic specimen. The brown residue (0.5 g) was partially soluble in water to give an acid solution and was shown by diazotisation and coupling to contain a primary amino-group. The insoluble residue contained bis-(2,4-dinitrophenyl) disulphide. (b) A similar decomposition in carbon tetrachloride (15 ml) for 1 h gave a pale yellow solution and a dark brown solid. The solution gave  $^1\text{H}$  n.m.r. signals at  $\tau$  7.78 (s,  $\text{Ac}_2\text{O}$ ) and 7.89 (s,  $\text{AcOH}$ ) in the ratio 5 : 1, and the solid gave the disulphide after extraction with acetone. G.l.c. confirmed that the carbon tetrachloride solution contained acetic acid and acetic anhydride.

[7/2022 Received, 17th November, 1977]

<sup>16</sup> H. T. Hookway, *J. Chem. Soc.*, 1950, 1932.

<sup>17</sup> L. Field and F. A. Grunwald, *J. Org. Chem.*, 1951, 16, 946.