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Kationoid Reactivity of Sulphur

Sulphenyl Compounds

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It was demonstrated in previous papers [1, 2] that various polythionic compounds in reactions with anionoid reagents behave as derivatives of divalent electropositive sulphur S^{++} and S_2^{++}. Thus the following compounds were found to react with piperidine to give the corresponding sulphur piperidides, as do the sulphur chlorides [3, 4] and thiocyanates [5, 6]: Sulphur di-O-methylmonothiophosphates, sulphur ethanethiosulphonates, sulphur *p*-toluenethiosulphonates, and sulphur thiosulphates (pentathionate and hexathionate).

The present paper deals with the chemistry of sulphenyl compounds, *viz.*, derivatives of alkylsulphur or arylsulphur RS^+. A rather comprehensive material concerning sulphenyl compounds is available in literature. A recent review on »The Sulfenic Acids and their Derivatives», mainly from an organic synthetic point of view, is by Kharasch, Potempa and Wehrmeister [7]. The authors, however, fail to recognize the so-called »esters of thiosulphonic acids» and »esters of thiosulphuric acid» as derivatives of sulphenic acids, as also the sulphenyl thiosulphonates of Brooker, Child and Smiles [8]. In most of the reactions with anionoid reagents the above compounds eliminate their sulphenyl group as a monovalent kation RS^+. It should be emphasized that this is the case within the majority of derivatives of sulphenic acids.

The structure of »esters of thiosulphonic acids» $RSSO_2R$ as *sulphenyl sulphinates* finds a clear proof in their reactions with cyanide ion and with mercaptide ions:

$$RSSO_2R' + CN^- = RSCN + R'SO_2^-$$
$$RSSO_2R' + R''S^- = RSSR'' + R'SO_2^-$$

Reactions of this type were demonstrated by Otto and Rössing [9], Smiles and Gibson [10], and Footner and Smiles [11]. Other examples are the reactions with

sodium derivatives of certain organic compounds [12] (*cf.* also Connor [13]), and displacement reactions [14, 15] of the type:

$$RSSO_2R' + R''SO_2^- = RSSO_2R'' + R'SO_2^-$$

The so-called »esters of thiosulphuric acid» $RSSO_3^-$ in reactions with anionoid reagents behave as *sulphenyl sulphites*, with fission in the sense (RS^+) (SO_3^{--}). Thus in reactions with cyanide ion [11, 16] and mercaptide ions [11]:

$$RSSO_3^- + CN^- = RSCN + SO_3^{--}$$
$$RSSO_3^- + R'S^- = RSSR' + SO_3^{--}$$

1-Anthraquinonesulphenyl sulphite on alkaline hydrolysis [17] yields stable 1-anthraquinonesulphenic acid:

$$RSSO_3^- + OH^- = RSOH + SO_3^{--}$$

Sulphenyl thiosulphonates were prepared by Brooker, Child and Smiles [8] by the action of the chlorides on aromatic potassium thiosulphonates:

$$RSCl + S_2O_2R^- = RSS_2O_2R + Cl^-$$

They react in two ways, *viz.*, as sulphenyl thiosulphonate, or as a mixed monosulphur mercaptide-sulphinate. Reaction products according to both modes of fission were encountered in reactions with sodium mercaptides and 2-naphtoxide. Fission exclusively as sulphenyl thiosulphonate takes place in the reactions of *o*-nitrobenzenesulphenyl *p*-toluenethiosulphonate with sulphinate ions [14]:

$$RSS_2O_2R' + R''SO_2^- = RSSO_2R'' + R'SO_2S^-$$

as also in displacement reactions demonstrated on pp. 315—321 of this paper. The pseudohalide nature of thiosulphonate ions, as well as other thio anions, has been discussed in a previous paper [18].

The present investigation was begun with the purpose of examining displacement reactions from RS^+, in order to obtain further evidence concerning base strength sequences of thio anions and anthio anions (see p. 321) found to hold in the case of displacement reactions from S^{++} and S_2^{++} [1, 2]. Some new types of sulphenyl compounds are described (chapter I). The base strength sequences and displacement reactions are considered in chapters II and III.

I. NEW TYPES OF SULPHENYL COMPOUNDS

The following new types of sulphenyl compounds are described in this chapter (Ar = 2-nitro-5-methylphenyl and, in some cases, *o*-nitrophenyl):

Sulphenyl di-O-alkylmonothiophosphates $ArSSPO(OR)_2$ (R = methyl, ethyl, *iso*-propyl).

Sulphenyl alkanethiothiosulphonates $ArSS_2O_2R$ (R = methyl, ethyl).

Solutions of sulphenyl thiosulphates $ArSS_2O_3^-$.

The only thio derivatives of RS^+ previously described are the sulphenyl thiocyanates of Lecher [19, 20] and the sulphenyl arylthiosulphonates of Brooker, Child and Smiles [8].

The sulphenyl di-O-alkylmonothiophosphates were prepared from the sulphenyl bromides and finely powdered sodium or potassium di-O-alkylmonothiophosphates (10—20 % excess) in ether or carbon disulphide suspension. The solid particles were treated with a glass rod for a few minutes, the suspension filtered, and the product isolated from the filtrate through evaporation or cooling.

The sodium and potassium di-O-alkylmonothiophosphates employed were prepared from the corresponding phosphites as described elsewhere [18].

The sulphenyl di-O-alkylmonothiophosphates form yellowish-green crystals, which are quite stable, and readily soluble in alcohols, benzene, and chloroform. The methyl compounds are slightly soluble in ether, more soluble in warm carbon disulphide. The ethyl and *iso*-propyl compounds are extensively soluble in both solvents. The compounds are insoluble in water, and are not affected by moisture. With alcoholic potassium hydroxide they slowly give a blue-violet colour, characteristic of alkaline solutions of sulphenic acids [7].

They react with secondary amines to give sulphenamides, as do sulphenyl halides and sulphenyl thiocyanates [7]:

$$RSSPO(OR)_2 + 2\ R_2NH = RSNR_2 + R_2NH_2^+ + SPO(OR)_2^-$$

Since in these reactions the amine undoubtedly is the anionoid reagent, the reactions prove the properties of the reacting compounds as derivatives of RS^+.

The sulphenyl alkanethiosulphonates were prepared from the sulphenyl bromide and sodium or potassium alkanethiosulphonates in carbon disulphide as described for the sulphenyl di-O-alkylmonothioposphates. They form stable, yellowish-green crystals, insoluble in water, practically insoluble in ether, soluble in ethanol, carbon disulphide, benzene, and chloroform.

2-Nitro-5-methylbenzenesulphenyl ethanethiosulphonate was found to react with piperidine:

$$RSS_2O_2C_2H_5 + 2\ C_5H_{10}NH = RSNC_5H_{10} + C_5H_{10}NH_2^+ + S_2O_2C_2H_5^-$$

Solutions of sulphenyl thiosulphates were obtained

(1) from 2-nitro-5-methylbenzenesulphenyl thiocyanate by reaction with thiosulphate ion:

$$RSSCN + S_2O_3^{--} = RSS_2O_3^- + SCN^-$$

(2) from sulphenamides by reaction with thiosulphuric acid:

$$RSNR_2 + S_2O_3^{--} + 2\ H^+ = RSS_2O_3^- + R_2NH_2^+$$

The reactions are rapid and quantitative, and may be employed for the iodometric analysis of sulphenyl thiocyanates and sulphenamides. The following procedures have proved their value:

(1) 0.0002 mole sulphenyl thiocyanate are dissolved by gentle heating in 2 ml ethylacetate, and 10 ml ethanol and 25 ml 0.01 *N* sodium thiosulphate are added. After standing for 5 minutes, 40 ml water, 10 ml 10 % acetic acid, and a few crystals of potassium iodide are added, and the excess of thiosulphate is back-titrated with 0.01 *N* iodine.

(2) 0.0002 mole sulphenamide are dissolved by gentle heating in 15 ml ethanol or *iso*-propanol, and 25 ml 0.01 *N* sodium thiosulphate (no turbidity should occur, or more alcohol must be added) and 5 ml 10 % acetic acid are added. After standing for 10 minutes, 40 ml water are added, and the excess of thiosulphate is backtitrated with 0.01 *N* iodine.

The sulphenyl thiosulphate $RSS_2O_3^-$ forms green solutions which seem to be quite stable. It is the structural analogon of monosulphur di-(thiosulphate) $S(S_2O_3)_2^{--}$ (pentathionate) and disulphur di-(thiosulphate) $S_2(S_2O_3)_2^{--}$ (hexathionate) [1, 2].

A method corresponding to (2) is available [2] for the iodometric analysis of sulphur piperidides, by use of the reactions (x = 1 or 2):

$$S_x(NC_5H_{10})_2 + 2\ S_2O_3^{--} + 4\ H^+ = S_x(S_2O_3)_2^{--} + 2\ C_5H_{10}NH_2^+$$

If sodium hydroxide be added to sulphenyl thiosulphate solutions, an intense blue colour is developed. The sulphenyl thiosulphate thus undergoes hydrolysis as follows:

$$RSS_2O_3^- + OH^- = RSOH + S_2O_3^{--}$$

The sulphenyl thiosulphates react rapidly with cyanide and sulphite ions:

$$RSS_2O_3^- + CN^- = RSCN + S_2O_3^{--}$$
$$RSS_2O_3^- + SO_3^{--} = RSSO_3^- + S_2O_3^{--}$$

The reactions may be employed for the iodometric analysis of sulphenyl thiosulphates (for procedures see p. 313 f.).

The reactions are polar displacements of thiosulphate ion by cyanide and sulphite ions, respectively, as are the cyanide and sulphite reactions of polythionates [1, 2].

Experimental

The melting points reported in this paper are in ° C (corr.).

Phosphorus analyses were made volumetrically by the method of Neumann (for literature references see Nylén [21]).

No compounds containing the 2-nitro-5-methylphenylsulphur group are hitherto described in literature. The sulphenyl bromide was obtained as follows:

3,4-Dinitrotoluene was converted into 2,2′-dinitro-5,5′-dimethyldiphenyldisulphide by the action of sodium disulphide. This method of preparing disulphides from aromatic dinitrohydrocarbons is due to Blanksma[22]. Displacement of the nitro group (as nitrite) by sulphide or other anionoid reagents takes place only when the nitro groups are in *ortho* or *para* positions [23]. In 3,4-dinitrotoluene (and 3,4-chlorobenzene) it is the 3-nitro group which undergoes displacement [24].

The structure of the disulphide was confirmed through convertion into 2-mercapto-6-methylbenzthiazol [25] by the method of Teppema and Sebrell [26] (see pp. 315—321).

The disulphide was treated with bromine in carbon tetrachloride to obtain the sulphenyl bromide.

2,2′-Dinitro-5,5′-dimethyldiphenyldisulphide. In ethanol at boiling temperature only poor yields were obtained. In methanol at room temperature, however, the yields are quantitative:

To 75 g 3,4-dinitrotoluene* dissolved in 500 ml methanol are added with stirring, during a period of one hour, 48 g sodium sulphide nonahydrate and 7 g sulphur dissolved in 25 ml water and 50 ml methanol. After one hour's standing the product is filtered off and washed with methanol and water. It may be recrystallized from glacial acetic acid or from benzene. Greenish-yellow crystals, m. p. 152°.

0.1447 g subst.: 0.2002 g $BaSO_4$.

$(O_2NC_7H_6S)_2$ (336,4) Calc. S 19.1 Found S 19.0

2-Nitro-5-methylbenzenesulphenyl bromide. 20 g disulphide (the crude product may be employed) in 100 ml carbon tetrachloride are heated with 5 ml bromine for 2 hours. The

* The author is indebted to Chem. Eng. Jørgine Stene Sørensen, *Institutt for Organisk Kjemi*, for a gift of 3,4-dinitrotoluene (isolated from a technical T. N. T. mother liquor).

excess bromine and the solvent are evaporated, and the product recrystallized from petroleum. Brownish-yellow crystals, m. p. 84°.

0.1347 g subst.: 0.1016 g AgBr.

$O_2NC_7H_6SBr$ (248.1) Calc. Br 32.2 Found Br 32.1

2-Nitro-5-methylbenzenesulphenamide and *piperidide* were prepared from the bromide, dissolved in ether, by the action of ammonia and piperidine, respectively. Recrystallized from methanol. Brownish-yellow crystals, m. p. 151° (amide) and 92° (piperidide).

0.1677 g subst.: 0.2130 g $BaSO_4$.

$O_2NC_7H_6SNH_2$ (184.2) Calc. S 17.4 Found S 17.5

0.1850 g subst.: 0.1705 g $BaSO_4$.

$O_2NC_7H_6SNC_5H_{10}$ (252.3) Calc. S 12.7 Found S 12.7

2-Nitro-5-methylbenzenesulphenyl di-O-methylmonothiophosphate. Coarse crystals, m. p. 93° (from carbon disulphide).

0.09344 g subst.: 0.1421 g $BaSO_4$. 0.09977 g subst.: 18.54 ml 0.4836 *N* NaOH.

$O_2NC_7H_6SSPO(OCH_3)_2$ (309.3) Calc. S 20.7 P 10.0

Found » 20.9 » 9.9

2-Nitro-5-methylbenzenesulphenyl di-O-ethylmonothiophosphate. Coarse crystals, m. p. 53° (from ether).

0.1169 g subst.: 0.1618 g $BaSO_4$. 0.1553 g subst.: 26.78 ml 0.4836 *N* NaOH.

$O_2NC_7H_6SSPO(OC_2H_5)_2$ (337.4) Calc. S 19.0 P 9.2

Found » 19.0 » 9.2

To 0.69 g dissolved in 20 ml ether were added 1 ml piperidine. The ether was evaporated off, and the crystalline residue treated with water. Yield 0.51 g (theor. 0.52 g 2-nitro-5-methylphenylsulphenpiperidide), m. p. (recrystallized from methanol) 92°, not depressed in mixture with a specimen obtained from the bromide (p. 311 f.).

*2-Nitro-5-methylbenzenesulphenyl di-O-*iso*-propylmonothiophosphate.* Coarse crystals, m. p. 44° (from ether or petroleum).

0.1398 g subst.: 0.1784 g $BaSO_4$. 0.1521 g subst.: 24.02 ml 0.4836 *N* NaOH.

$O_2NC_7H_6SSPO(OC_3H_7)_2$ (365.4) Calc. S 17.5 P 8.5

Found » 17.5 » 8.4

o-Nitrobenzenesulphenyl di-O-methylmonothiophosphate. Prepared from the bromide [27]. Prisms from carbon disulphide, m. p. 72°.

0.1083 g subst.: 0.1714 g $BaSO_4$. 0.1142 g subst.: 22.41 ml 0.4836 *N* NaOH.

$O_2NC_6H_4SSPO(OCH_3)_2$ (295.3) Calc. S 21.7 P 10.5

Found » 21.7 » 10.5

To 3 g dissolved in 20 ml methanol were added 5 ml 30 % aqueous dimethylamine. After standing for one hour the formed *o*-nitrobenzenesulphendimethylamide [27] was precipitated by means of water. Recrystallized from methanol, it had the correct melting point, *viz.*, 63°.

2-Nitro-5-methylbenzenesulphenyl methanethiosulphonate. Prisms, m. p. 98° (from carbon disulphide).

0.0527 g subst.: 0.1301 g $BaSO_4$.

$O_2NC_7H_6SS_2O_2CH_3$ (279.3) Calc. S 34.4 Found S 34.3

2-Nitro-5-methylbenzenesulphenyl ethanethiosulphonate. Small crystals, m. p. 91° (from carbon disulphide).

0.05776 g subst.: 0.1380 g $BaSO_4$.

$O_2NC_7H_6SS_2O_2C_2H_5$ (293.4) Calc. S 32.8 Found S 32.8

To 0.77 g dissolved in 25 ml chloroform were added 1 ml piperidine. After 10 minutes at room temperature the solvent and the excess of piperidine was evaporated off, and the crystalline residue treated with water. Yield 0.65 g (theor. 0.66 g 2-nitro-5-methylphenyl-sulphenpiperidide). Recrystallized from methanol, it melted at 92°, not depressed in mixture with a specimen obtained from the bromide (p. 311 f.).

2-Nitro-5-methylbenzenesulphenyl thiocyanate. Prepared from the chloride (obtained from the disulphide in carbon tetrachloride at 50—60° in presence of traces of iodine) by the method of Lecher [19]. When excess of potassium thiocyanate is employed (finely powdered, suspended in benzene) the reaction is complete after less than 5 minutes. Yellowish-green plates from benzene, m. p. 115°.

0.1027 g subst.: 0.2113 g $BaSO_4$.

$O_2NC_7H_6SSCN$ (226.3) Calc. S 28.3 Found S 28.3

Iodometric analysis of 2-nitro-5-methylbenzenesulphenyl thiocyanate (for procedure see p. 310).

Substance employed, g	Iodine consumed ml 0.01074 *N*	Substance found, g
None	22.78	
0.04439	4.54	0.04434
0.04421	4.62	0.04414
0.04503	4.22	0.04509

Iodometric analysis of sulphenamides (for procedure see p. 310). $2\text{-}O_2N\text{-}5\text{-}CH_3C_6H_3SNC_5H_{10}$ and $o\text{-}O_2NC_6H_4SN(CH_3)_2$ were dissolved in 15 ml *iso*-propanol, the more soluble $2\text{-}O_2N\text{-}5\text{-}CH_3C_6H_3SNH_2$ in 15 ml ethanol.

Compound	Substance employed, g	Iodine consumed ml 0.009993 *N*	Substance found, g
	None	23.96	
(1)	0.03683	4.00	0.03674
(1)	0.03617	4.33	0.03614
(1)	0.03704	3.92	0.03689
(2)	0.05183	3.49	0.05164
(3)	0.04946	4.36	0.04941
(4)	0.05126	3.65	0.05119
(5)	0.03872	5.12	0.03866

The employed compounds were the following:

(1) $2\text{-}O_2N\text{-}5\text{-}CH_3C_6H_3SNH_2$ from sulphenyl bromide

(2) $2\text{-}O_2N\text{-}5\text{-}CH_3C_6H_3SNC_5H_{10}$ from sulphenyl bromide

(3) —»— from sulphenyl di-O-ethylmonothiophosphate

(4) —»— from sulphenyl ethanethiosulphonate

(5) $o\text{-}O_2NC_6H_4SN(CH_3)_2$ from sulphenyl di-O-methylmonothiophosphate

Iodometric analysis of solutions of 2-nitro-5-methylbenzenesulphenyl thiosulphate.

1. 0.0008 mole 2-nitro-5-methylbenzenesulphenyl thiocyanate were dissolved by gentle heating in 10 ml ethylacetate in a 100 ml volumetric flask, and 20 ml ethanol and 10 ml 0.1 *N* sodium thiosulphate were added. After standing for 5 minutes the mixture was made up to 100 ml with water, and 3 times 25 ml were pipetted out. 40 ml water

were added to each sample. One of them (a) was titrated with 0.01 *N* iodine for excess thiosulphate (after addition of 10 ml 10 % acetic acid and a few crystals of potassium iodide). To the other two there were added (b) 5 ml 0.2 sodium sulphite, and (c) 3 ml 1 *M* potassium cyanide, respectively. After standing for 5 minutes there were added 1 ml 40 % formaldehyde, 10 ml 10 % acetic acid, and a few crystals of potassium iodide, and the solutions were titrated with 0.01 *N* iodine.

Substance employed, g	Iodine consumed ml 0.01074 *N*			Substance found calc. from (a), g
	(a)	(b)	(c)	
None	22.78			
0.1821	4.12	22.78	22.80	0.1814
0.1817	4.10	22.77	22.79	0.1816
0.1817	4.10	22.78	22.78	0.1816

2. 0.0008 mole 2-nitro-5-methylbenzenesulphenamide and piperidide were dissolved by gentle heating in 30 ml ethanol and 40 ml *iso*-propanol, respectively, in 100 ml volumetric flasks, and 10 ml 0.1 *N* sodium thiosulphate and then 10 ml 10 % acetic acid were added. After standing for 5 minutes the mixture was made up to 100 ml with water, and 4 times 20 ml were pipetted out. 40 ml water were added to each sample. One of them (a) was titrated with 0.01 *N* iodine for excess thiosulphate. To the other three were added: (b) Amide. 5 ml 0.2 *M* sodium sulphite and 5 ml 1 *N* sodium hydroxide. (c) Piperidide. 3 ml 1 *M* potassium cyanide and 5 ml 1 *N* sodium hydroxide. After standing, there were added 1 ml 40 % formaldehyde and 10 ml 10 % acetic acid (in the case of (c) also a few crystals of potassium iodide) and the solutions were titrated with 0.01 *N* iodine.

Compound	Substance employed, g	Time of standing (minutes)	Iodine consumed ml 0.009993 *N* (a)	(b)	(c)	Substance found calc. from (a), g
	None		17.88			
Amide	0.1465		2.03			0.1459
		5		17.88		
		10		17.88		
		15		17.89		
Piperidide	0.2036		1.74			0.2034
		5			17.89	
		7			17.90	
		11			17.84	

On addition of potassium cyanide to the 2-nitro-5-methylbenzenesulphenyl thiosulphate solutions the green colour rapidly faded, and crystals separated out. After the titrations the crystals were filtered off and identified as 2-nitro-5-methylphenyl thiocyanate, m. p. (recrystallized from glacial acetic acid) 135°, not depressed in mixture with a specimen obtained from the sulphenyl thiocyanate (p. 324).

II. OXIDABILITY AND BASE STRENGTH (ANIONOID REACTIVITY) OF THIO ANIONS. DISPLACEMENT REACTIONS

In previous papers [1, 2] polar (electron-sharing) displacement reactions from S^{++} and S_2^{++} were demonstrated, of the type:

$$S(SX')_2 + 2\ SX''^- = S(SX'')_2 + 2\ SX'^-$$
$$S_2(SX')_2 + 2\ SX''^- = S\ (SX'')_2 + 2\ SX'^-$$

The base strengths (anionoid reactivities) of the thio anions SX^- towards S^{++} and S_2^{++} were found to increase with decreasing redox potentials of the systems:

$$2\ SX^- \rightleftarrows (SX_2) + 2\ e$$

viz., in the order thiocyanate, di-O-methylmonothiophosphate, ethanethiosulphonate, *p*-toluenethiosulphonate, thiosulphate, and thiocarbonyl anions and mercaptides. A stronger one of these bases will displace a weaker one from its combinations with S^{++} and S_2^{++}.

Since that time the potential series has been extended.

From measurements of equilibria with iodine, the redox potentials of the systems:

$$2\ (RO)_2OPS^- \rightleftarrows ((RO)_2OPS)_2 + 2\ e$$

have been evaluated [18] for 9 different alkyl groups R.

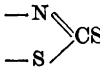
The equilibria of thiosulphonate ions with iodine [1, 2] have been found (unpublished work by the author) to obey the equation:

$$2\ RSO_2S^- + I_3^- \rightleftarrows (RSO_2S)_2 + 3\ I^-$$

with equilibrium constants (at room temperature) = 1 for ethanethiosulphonate and 50—60 for *p*-toluenethiosulphonate. The redox potentials of the systems:

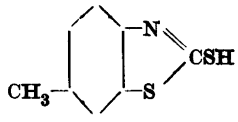
$$2\ RSO_2S^- \rightleftarrows (RSO_2S)_2 + 2\ e$$

calculated as in the case of the di-O-alkylmonothiophosphate systems [18], are —0.54 volts and —0.49 volts, respectively.

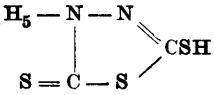
Three mercaptides containing the grouping 

have been examined (see the experimental part of this chapter), *viz.*, the anions of:

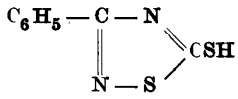
2-mercapto-6-methylbenzthiazol



2-mercapto-4-phenyl-5-thion-1-thia-3,4-diazol



2-mercapto-4-phenyl-1-thia-3,5-diazol



They are all oxidized by tetrathionate to the corresponding disulphides, as are other mercaptides [11], and xanthates [28], dithiocarbamates [29], and monothio [30] and dithio [28] carboxylates. The redox potentials of thiocarbonyl anion and mercaptide systems may be roughly estimated to ca + 0.3 volts (see, *e. g.*, the discussion by Remick [31] of the potential of the cysteine-cystine electrode).

In table I the listed values for the potentials of the thiocyanate-thiocyanogen electrode and the thiosulphate-tetrathionate electrode are those of Bjerrum and Kirschner [32] and of Zimmermann and Latimer [33], respectively.

Table 1. Redox potentials E_0 *(in volts) of systems* $2\ SX^- \rightleftarrows (SX)_2 + 2\ e$ *(at unit activity, against the hydrogen electrode).*

SX^-	E_0
SCN^-	— 0.77
$(CH_3O)_2OPS^-$	— 0.56
$C_2H_5SO_2S^-$	— 0.54
$(C_2H_5O)_2OPS^-$	— 0.53
$(n\text{-}C_3H_7O)_2OPS^-$	— 0.52
$(n\text{-}C_4H_9O)_2OPS^-$, $(iso\text{-}C_4H_9O)_2OPS^-$	— 0.51
$(iso\text{-}C_3H_7O)_2OPS^-$	— 0.50
$p\text{-}CH_3C_6H_4SO_2S^-$, $(sec\text{-}C_4H_9O)_2OPS^-$	— 0.49
$(iso\text{-}C_5H_{11}O)_2OPS^-$, $(C_2H_5(CH_3)CHCH_2O)_2OPS^-$	— 0.48
$S_2O_3^{--}$	— 0.10
RS^-, $-N\!=\!CS^-$ (−S), $ROC(S)S^-$, $R_2NC(S)S^-$, $RC(O)S^-$, $RC(S)S^-$	ca + 0.3

The base strengths (anionoid reactivities) towards RS^+ of the thio anions of table I increase with decreasing redox potentials, as will appear from the following series of displacement reactions, of the type:

$$RSSX' + SX''^- = RSSX'' + SX'^-$$

2-Nitro-5-methylbenzenesulphenyl thiocyanate reacts with di-O-ethylmonothiophosphate ion, ethanethiosulphonate ion, *p*-toluenethiosulphonate ion, and thiosulphate ion.

2-Nitro-5-methylbenzenesulphenyl di-O-methylmonothiophosphate reacts with di-O-*iso*-propylmonothiophosphate ion.

o-*Nitrobenzenesulphenyl di-O-methylmonothiophosphate* reacts with *p*-toluenethiosulphonate ion and thiosulphate ion and with the mercaptides  .

2-Nitro-5-methylbenzenesulphenyl ethanethiosulphonate reacts with *p*-toluenethiosulphonate ion and thiosulphate ion.

2-Nitro-5-methylbenzenesulphenyl di-O-ethylmonothiophosphate and *di-O*-iso-*propylmonothiophosphate* react with thiosulphate ion and ethylxanthate ion.

o-*Nitrobenzenesulphenyl* p-*toluenethiosulphonate* reacts with thiosulphate ion.

The parallelism between oxidability and base strength is logical from an electronic point of view. For the potentials the governing factor is the electron affinity of the thio sulphur atom of the concerned groups, whilst in the polar displacement reactions the driving force is the base strength of the thio sulphur atom of the anions, the reactive entity being a pair of electrons. The smaller electron affinity, the higher polarizability of the valence electrons and the greater portion of each unoccupied electron pair available for bond formation with kationoid centres.

Notice may be made to the statement of Branch and Calvin [34], on the basis of the transition state theory of reaction mechanisms, that in polar displacement reactions an increase in the number of electron shells (*i. e.*, increase in polarizability of the valence electrons) of either the reactant or the product base increases the rate.

EXPERIMENTAL

Reactions of mercaptides with tetrathionate

2-mercapto-6-methylbenzthiazol was prepared from 2,2'-dinitro-5,5'-dimethyldiphenyldisulphide (p. 311) in aqueous sodium disulphide suspension by treatment with hydrogen sulphide and carbon disulphide gas according to the method of Teppema and

Sebrell [26]. Recrystallized from glacial acetic acid, it showed the correct melting point [25], *viz.*, 181°. Its alkali salts may be titrated accurately with iodine (oxidation to disulphide):

0.4677 g 2-mercapto-6-methylbenzthiazol were dissolved in 10 ml ethanol and 5 ml 1 *N* sodium hydroxide. 200 ml water were added, and dilute acetic acid until colourless to phenolphtalein. The volume was adjusted to 250 ml, and 25 ml samples pipetted out and titrated with 0.01083 *N* iodine: 23.82 ml — 23.79 ml — 23.82 ml (theor. 23.82 ml).

Its potassium salt (I) was prepared from the mercaptan and potassium carbonate, by evaporation to dryness, and recrystallization from acetone-ether. 0.05987 g, dissolved in 25 ml water, consumed 25.16 ml 0.01083 *N* iodine (theor. 25.20 ml).

Potassium 2-mercaptido-4-phenyl-5-thion-1-thia-3.4-diazol (II) and 2-mercaptido-4-phenyl-1-thia-3.5-diazol (III) were prepared by the methods of Busch [35] and Schubart [36], respectively. Their aqueous solutions may be titrated accurately with iodine (oxidation to disulphide):

0.7183 g of (II) and 0.6339 g of (III) were each dissolved in 250 ml water, and 25 ml samples pipetted out and titrated with 0.01083 *N* iodine. (II) 25.11 ml — 25.09 ml — 25.10 ml (theor. 25.09 ml). (III) 25.14 ml — 25.18 ml — 25.17 ml (theor. 25.19 ml).

0.002 mole (0.60 g) potassium tetrathionate, dissolved in 20 ml water, were added to 0.005 mole of (I) (1.10 g), (II) (1.32 g), and (III) (1.16 g), respectively, dissolved in 20 ml water. Turbidity at once occurred. After 20 minutes' stirring the disulphides had flocculated, leaving the liquid clear, except for (II), in the case of which stirring was continued for 2 hours. The crystals were filtered off, dried, and weighed.

(I) 0.70 g (theor. 0.72 g). Colourless plates from chloroform, m. p. 202° (reported [25] 201—202°).

0.06914 g subst.: 0.1782 g $BaSO_4$. Calc. S 35.6. Found S 35.4.

(II) 0.82 g (theor. 0.90 g). Greenish-yellow plates from chloroform-ethanol, m. p. 124° (reported [35] 124—125°).

0.07129 g subst.: 0.2199 g $BaSO_4$. Calc. S 42.7. Found S 42.4.

(III) 0.75 g (theor. 0.77 g). Colourless needles from glacial acetic acid, m. p. 125° (reported [37] 121°).

0.06166 g subst.: 0.1495 g $BaSO_4$. Calc. S 33.2. Found S 33.3.

Displacement reactions

(1) To 1.13 g 2-nitro-5-methylbenzenesulphenyl thiocyanate, dissolved in 15 ml benzene, were added 1.2 g $C_2H_5SO_2SK$ (50 % excess), dissolved in 4 ml ethanol. After 5 minutes at room temperature the mixture was treated with water, the benzene layer separated, dried over anhydrous sodium sulphate, and the benzene evaported *in vacuo*. The crystalline residue was recrystallized from carbon disulphide, yield 0.94 g yellowish-green crystals, with the melting point of 2-nitro-5-methylbenzenesulphenyl ethanethiosulphonate, *viz.*, 91°, not depressed in mixture with a specimen obtained from the bromide (p. 000).

(2) To 1.13 g 2-nitro-5-methylbenzenesulphenyl thiocyanate, dissolved in 15 ml benzene, were added 1.6 g $(C_2H_5O)_2OPSK$ (50 % excess), dissolved in 4 ml ethanol. After 5 minutes was proceeded as in the case of (1). The residue was recrystallized from ether, yield 1.01 g yellowish-green crystals, with the melting point of 2-nitro-5-methylbenzenesulphenyl di-O-ethylmonothiophosphate, *viz.*, 53°, not depressed in mixture with a specimen obtained from the bromide (p. 311 f.).

(3) To 1.13 g 2-nitro-5-methylbenzenesulphenyl thiocyanate, dissolved in 20 ml ethylacetate and 20 ml ethanol, at 40—50°, were added 1.8 g p-$CH_3C_6H_4SO_2SK \cdot H_2O$ (50 % excess), dissolved in 40 ml water. On cooling, crystals began to separate. After 10 minutes they were filtered off (yield 1.65 g), and recrystallized from benzene. Yield 1.34 g yellowish-green crystals, m. p. 144°, not depressed in mixture with a specimen of 2-nitro-5-methylbenzenesulphenyl p-toluenethiosulphonate prepared from 2-nitro-5-methylbenzenesulphenyl bromide and potassium p-toluenethiosulphonate suspended in ether: Small yellowish-green crystals (from benzene), m. p. 144°.

0.08401 g subst.: 0.1650 g $BaSO_4$.

$O_2NC_7H_6SS_2O_2C_7H_7$ (355.4) Calc. S 27.1 Found S 27.0

(4) To 1.00 g 2-nitro-5-methylbenzenesulphenyl ethanethiosulphonate, dissolved in 25 ml ethanol, were added 1.7 g p-$CH_3C_6H_4SO_2SK \cdot H_2O$ (100 % excess), dissolved in 20 ml methanol, and the mixture was heated for 2 minutes. On cooling, crystals separated out. Yield 1.07 g crude product, m. p. (recrystallized from benzene, yield 0.86 g) 144°, not depressed in mixture with a specimen of 2-nitro-5-methylbenzenesulphenyl p-toluenethiosulphonate obtained from the bromide.

(5) To 1.54 g 2-nitro-5-methylbenzenesulphenyl di-O-methylmonothiophosphate, dissolved in 50 ml carbon disulphide, were added 1.65 g (iso-$C_3H_7O)_2OPSNa$ (50 % excess), dissolved in 50 ml carbon disulphide. A colourless salt at once separated out. After 5 minutes was proceeded as in the case of (1). The crystalline residue was recrystallized from petroleum, yield 1.72 g yellowish-green crystals, with the melting point of 2-nitro-5-methylbenzenesulphenyl di-O-iso-propylmonothiophosphate, *viz.*, 44°, not depressed in mixture with a specimen obtained from the bromide.

(6) To 1.55 g o-nitrobenzenesulphenyl di-O-methylmonothiophosphate, dissolved in 20 ml ethanol, were added 1.5 g p-$CH_3C_6H_4SO_2SK \cdot H_2O$ (20 % excess), dissolved in 20 ml water. A crystalline solid at once separated. Yield 1.74 g (theor. 1.73 g o-nitrobenzenesulphenyl p-toluenethiosulphonate), m. p. (recrystallized from glacial acetic acid) 141° (reported [8] 141°).

(7) 1 g 2-nitro-5-methylbenzenesulphenyl di-O-ethylmonothiophosphate, dissolved in 20 ml ether, was treated for 5 minutes with 2 g finely powdered potassium ethylxanthate. The suspension was then filtered and the ether partly evaporated off. On cooling (ice-sodium chloride), crystallization took place. Yield 0.78 g (theor. 0.82 g 2-nitro-5-methylphenyl-ethylxanthyldisulphide). Coarse green crystals, m. p. 69°, not depressed in mixture with a specimen prepared from 2-nitro 5-methylbenzenesulphenyl bromide and potassium ethylxanthate, as above: M. p. 69° (from ether).

0.1391 g subst.: 0.3379 g $BaSO_4$.

$O_2NC_7H_6SSC(S)OC_2H_5$ (289.4) Calc. S 33.2 Found S 33.4

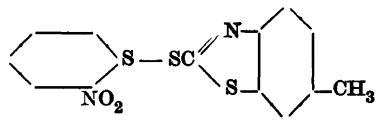
(8) 0.70 g 2-nitro-5-methylbenzenesulphenyl di-O-iso-propylmonothiophosphate, dissolved in 20 ml ether, were treated for 5 minutes with 1 g finely powdered potassium ethylxanthate. Water was added, the ethereal layer separated, dried over anhydrous sodium sulphate, and the ether partly evaporated off: Coarse green crystals, with the melting point of 2-nitro-5-methylphenyl-ethylxanthyldisulphide, *viz.*, 69°, not depressed in mixture with a specimen obtained from the bromide.

(9) To 1.5 g o-nitrobenzenesulphenyl di-O-methylmonothiophosphate, dissolved in 20 ml ethanol, were added 20 ml water containing

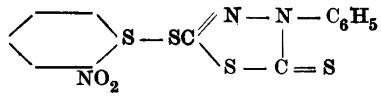
(a) 1.5 g potassium 2-mercaptido-6-methylbenzthiazol

(b) 1.5 g potassium 2-mercaptido-4-phenyl-5-thion-1-thia-3,4-diazol

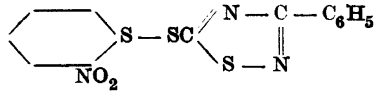
(c) 1.5 g potassium 2-mercaptido-4-phenyl-1-thia-3,5 diazol. Crystalline products at once separated out, and were further precipitated by addition of water. They were recrystallized from glacial acetic acid, from which they crystallize excellently.

(a)  Pale yellow, fatty leaves (thin plates), m. p. 147°.

0.08277 g subst.: 0.1729 g $BaSO_4$. Calc. S 28.8. Found S 28.7.

(b)  Pale yellow needles, m. p. 112°.

0.08433 g subst.: 0.2077 g $BaSO_4$. Calc. S 33.8. Found S 33.8.

(c)  Pale green, flat prisms, m. p. 121°.

0.08005 g subst.: 0.1618 g $BaSO_4$. Calc. S 27.7. Found S 27.8.

Aryl-benzthiazyldisulphides, prepared from sulphenyl chlorides and bromides, and mercaptobenzthiazols, are mentioned in patents [38], [39].

(10) 10 ml 0.1 *N* sodium thiosulphate were added to

(a) 0.283 g 2-nitro-5-methylbenzenesulphenyl ethanethiosulphonate (0.00096 mole) in 20 ml ethanol

(b) 0.287 g 2-nitro-5-methylbenzenesulphenyl di-O-ethylmonothiophosphate (0.00085 mole) in 10 ml ethanol

(c) 0.301 g 2-nitro-5-methylbencenesulphenyl di-O-*iso*-propylmonothiophosphate (0.00082 mole) in 10 ml ethanol

(d) 0.335 g *o*-nitrobenzenesulphenyl *p*-toluenethiosulphonate (0.00098 mole) in 50 ml ethanol

(e) 0.268 g *o*-nitrobenzenesulphenyl di-O-methylmonothiophosphate (0.00091 mole) in 10 ml ethanol.

The colour of the solutions rapidly changed to pure green. After 5 minutes the solutions were diluted to 100 ml. 10 ml were pipetted out, and 60 ml water, 1 g potassium iodide, and 10 ml 10 per cent acetic acid were added, and the solutions titrated with 0.01 *N* iodine for excess thiosulphate: (a) 0.6 ml (b) 1.8 ml (c) 2.1 ml (d) 0.6 ml (e) 1.0 ml. The values do not give the exact amounts of thiosulphate present, since thiosulphonate and di-O-alkylmonothiophosphate ions are attacked to a slight degree by iodine by the simultaneous oxidation of thiosulphate by iodine [3], even in the presence of much potassium iodide.

The experiments indicate that the reactions of thiosulphate ion with the above sulphenyl compounds are rapid and quantitative, as in the case of 2-nitro-5-methylbenzenesulphenyl thiocyanate.

To the remaining 90 ml were added 3 ml 1 *M* potassium cyanide. The green colour rapidly faded, and volumineous crystals separated out. After 10 minutes they were filtered off, and dried.

(a), (b), and (c): 0.14 g, 0.14 g, and 0.12 g, respectively. Pale yellow crystals (from glacial acetic acid), with the melting point of 2-nitro-5-methylphenyl thiocyanate, *viz.*, 135°.

(d) and (e): 0.12 g and 0.13 g, respectively. Pale yellow crystals (from glacial acetic acid), with the melting point of *o*-nitrophenyl thiocyanate, *viz.*, 130° [27].

III. DISPLACEMENT REACTIONS INVOLVING ANTHIO ANIONS

The term anthio anion was introduced by the author [2] as characteristic for anions capable of adding sulphur to give thio anions, *viz.*, sulphinate, sulphite, cyanide, and dialkylphosphite ions.

Displacement reactions from kationoid sulphur, involving thio anions and anthio anions as anionoid components, may be arranged into three classes (for an earlier discussion of the subject see the paper [2] mentioned above):

I. Displacements of thio anions by stronger basic thio anions.

II. Displacements of thio anions by anthio anions.

III. Displacements of anthio anions by stronger basic anthio anions.

The respective classes will be considered in detail on the following pages.

Class I. Hereto belong the reactions (displacements from RS^+) of the foregoing chapter, and the reactions [1,2] (displacements from S^{++} and S_2^{++}):

$$S(SCN)_2 + 2\ S_2O_2C_6H_4CH_3\text{-}p^- = S(S_2O_2C_6H_4CH_3\text{-}p)_2 + 2\ SCN^-$$
$$S_2(SCN)_2 + 2\ S_2O_2C_6H_4CH_3\text{-}p^- = S_2(S_2O_2C_6H_4CH_3\text{-}p)_2 + 2\ SCN^-$$
$$S(SPO(OCH_3)_2)_2 + 2\ S_2O_3^{--} = S(S_2O_3)_2^{--} + 2\ SPO(OCH_3)_2^-$$
$$S_2(SPO(OCH_3)_2)_2 + 2\ S_2O_3^{--} = S_2(S_2O_3)_2^{--} + 2\ SPO(OCH_3)_2^-$$
$$S(S_2O_3)_2^{--} + 2\ S_2COC_2H_5^- = S(S_2COC_2H_5 + 2\ S_2O_3^{--}$$
$$S_2(S_2O_3)_2^{--} + 2\ S_2COC_2H_5^- = S_2(S_2COC_2H_5)_2 + 2\ S_2O_3^{--}$$
$$S(S_2O_3)_2^{--} + 2\ S(O)CC_6H_5^- = S(S(O)CC_6H_5)_2 + 2\ S_2O_3^{--}$$
$$S_2(S_2O_3)_2^{--} + 2\ S(O)CC_6H_5^- = S_2(S(O)CC_6H_5)_2 + 2\ S_2O_3^{--}$$

Class II. If the displacing anthio anion is derived just from the thio anion which it displaces, the net reaction apparently (not actually) is a transfer of sulphur to the anthio anion, as, *e. g.*, in the reactions:

$$RSS_2O_3^- + \mathbf{SO_3^{--}} = RS\mathbf{SO_3^-} + S_2O_3^{--}$$
$$RSSCN + \mathbf{CN^-} = RS\mathbf{CN} + SCN^-$$

Examples of this class of reactions are:

(a) The reactions [2] of tetrathionate (and pentathionate and hexathionate) with cyanide (first step), sulphite, ethanesulphinate, and *p*-toluenesulphinate ions:

$$(S_2O_3)_2^{--} + CN^- = O_3SSCN^- + S_2O_3^{--}$$
$$(S_2O_3)_2^{--} + SO_3^{--} = O_3S_2SO_3^{--} + S_2O_3^{--}$$
$$(S_2O_3)_2^{--} + {}^{1}SO_2R^- = O_3S_2SO_2R^- + S_2O_3^{--}$$

(b) The reactions [14] of *o*-nitrobenzenesulphenyl *p*-toluenethiosulphonate with *p*-toluenesulphinate and *p*-bromobenzenesulphinate ions:

$$RSS_2O_2R' + SO_2R''^- = RSSO_2R'' + S_2O_2R'^-$$

(c) The reactions [40, 41], of cystine and glutatione with cyanide and sulphite ions:

$$(RS)_2 + CN^- = RSCN + SR^-$$
$$(RS)_2 + SO_3^{--} = RSSO_3^- + SR^-$$

It should be noted that mercaptides are not always displaced by anthio anions. Thus the following reactions go (R and R′ = aryl or alkyl [9, 10, 11]):

$$RSSO_3^- + SR'^- = RSSR' + SO_3^{--}$$
$$RSSO_2R + SR'^- = RSSR' + SO_2R^-$$

(d) The reactions [2, 30, 42, 43], of xanthyldisulphides and thiocarbamyldisulphides with cyanide ion (first step):

$$(ROC(S)S)_2 + CN^- = ROC(S)SCN + ROC(S)S^-$$
$$(R_2NC(S)S)_2 + CN^- = R_2NC(S)SCN + R_2NC(S)S^-$$

(e) The reactions of 2-nitro-5-methylbenzenesulphenyl thiosulphate with cyanide and sulphite ions:

$$RSS_2O_3^- + CN^- = RSCN + S_2O_3^{--}$$
$$RSS_2O_3^- + SO_3^{--} = RSSO_3^- + S_2O_3^{--}$$

(f) The following reactions, demonstrated in the experimental part of this chapter:

Of 2-nitro-5-methylbenzenesulphenyl thiocyanate and di-O-methyl-monothiophosphate with cyanide and sulphite ions:

$$RSSCN + CN^- = RSCN + SCN^-$$
$$RSSCN + SO_3^{--} = RSSO_3^- + SCN^-$$
$$RSSPO(OCH_3)_2 + CN^- = RSCN + SPO(OCH_3)_2^-$$
$$RSSPO(OCH_3)_2 + SO_3^{--} = RSSO_3^- + SPO(OCH_3)_2^-$$

Of 2-nitro-5-methylbenzenesulphenyl thiocyanate, di-O-methylmonothiophosphate, and methanethiosulphonate with sulphinate ions:

$$RSSCN + SO_2C_6H_4CH_3\text{-}p^- = RSSO_2C_6H_4CH_3\text{-}p + SCN^-$$
$$RSSPO(OCH_3)_2 + SO_2C_6H_4Br\text{-}p^- = RSSO_2C_6H_4Br\text{-}p + SPO(OCH_3)_2^-$$
$$RSS_2O_2CH_3 + SO_2C_6H_4CH_3\text{-}p^- = RSSO_2C_6H_4CH_3\text{-}p + S_2O_2CH_3^-$$

Class III. Reactions of this type are:
(a) The reactions of thiosulphate ion [44, 45] and aromatic thiosulphonate ions [46] with cyanide ion:

$$SSO_3^{--} + CN^- = SCN^- + SO_3^{--}$$
$$SSO_2R^- + CN^- = SCN^- + SO_2R^-$$

(b) The reactions [2] of ethanethiosulphonate and *p*-toluenethiosulphonate ions with sulphite ion:

$$SSO_2R^- + SO_3^{--} = SSO_3^{--} + SO_2R^-$$

p-Toluenethiosulphonate reacts more rapidly than does ethanethiosulphonate.
(c) The reactions [11] of sulphenyl suphites and sulphinates with cyanide ion:

$$RSSO_3^- + CN^- = RSCN + SO_3^{--}$$
$$RSSO_2R + CN^- = RSCN + SO_2R^-$$

(d) The reaction [2] of trithionate with cyanide ion (first step):

$$O_3S_2SO_3^{--} + CN^- = O_3SSCN^- + SO_3^{--}$$

(e) The reaction [47] of cystine disulphoxide with sulphite ion:

$$RSSO_2R + SO_3^{--} = RSSO_3^- + SO_2R^-$$

and the analogous reaction (see the experimental part of this chapter) of 2-nitro-5-methylbenzenesulphenyl *p*-toluenesulphinate with sulphite ion.
(f) The equilibria of sulphenyl sulphinates with sulphinate ions [14, 15]:

$$RSSO_2R' + SO_2R''^- \rightleftarrows RSSO_2R'' + SO_2R'^-$$

According to Gibson and Loudon [15] the equilibria are progressively displaced to the right in the order R″ = 2,5-dichlorophenyl, *o*-tolyl, *o*-nitrophenyl,

m-nitrophenyl, *p*-chlorophenyl, *p*-bromophenyl, β-naphtyl, α-naphtyl, *p*-fluorophenyl, 4-methoxy-*m*-tolyl, phenyl, *p*-acetamido, *p*-tolyl, ethyl, and *n*-pentyl.

It appears that the anthio anions may be arranged into the following sequence of increasing base strength towards kationoid sulphur: Aromatic sulphinates, aliphatic sulphinates, sulphite, and cyanide.

From the great affinity of dialkylphosphites to sulphur [18] their base strength should be expected to be of the same order of magnitude, or even greater, than that of cyanide.

It is interesting to note that the base strengths of sulphinate ions towards I^+, as expressed through the relative positions of the equilibria:

$$RSO_2^- + I_3^- \rightleftarrows RSO_2I + 2\ I^-$$

follow the same sequence [48] as that found by Gibson and Loudon [15] in the quoted case of sulphenyl sulphinate equilibria.

Experimental

(1) To 1.13 g 2-nitro-5-methylbenzenesulphenyl thiocyanate, dissolved in 10 ml ethylacetate and 20 ml ethanol, were added 100 ml 1 *M* potassium cyanide. Crystals immediately began to separate. 10 ml water were added and the crystals filtered off and dried: 0.80 g (theor. 0.97 g 2-nitro-5-methylphenyl thiocyanate). M. p. (recrystallized from glacial acetic acid) 135°. Greenish-yellow prisms.

0.1362 g subst.: 0.1649 g $BaSO_4$.

$O_2NC_7H_6SCN$ (194.2) Calc. S 16.5 Found S 16.6

(2) 0.75 g 2-nitro-5-methylbenzenesulphenyl di-O-methylmonothiophosphate, dissolved in 10 ml ethanol, 5 ml 1 *M* potassium cyanide. The reaction took place and the product was isolated as in the case of (1). Yield 0.45 g (theor. 0.47 g) crude product, m. p. (recrystallized from glacial acetic acid) 135°, not depressed in mixture with a specimen of 2-nitro-5-methylphenyl thiocyanate obtained in exp. (1).

(3) To 1.6 g 2-nitro-5-methylbenzenesulphenyl thiocyanate, dissolved in 20 ml ethylacetate and 20 ml ethanol, at 50—60°, were added 2 g p-$CH_3C_6H_4SO_2Na \cdot H_2O$, dissolved in 20 ml water. On cooling, crystallization took place. After 20 minutes, 200 ml water were added, and the product filtered off and recrystallized from methanol. Yield 1.7 g yellowish-green crystals, m. p. 104°.

0.1496 g subst.: 0.2161 g $BaSO_4$.

$O_2NC_7H_6SSO_2C_7H_7$ (323.4) Calc. S 19.8 Found S 19.8

(4) 0.70 g 2-nitro-5-methylbenzenesulphenyl methanethiosulphonate, in 20 ml ethanol, 1 g p-$CH_3C_6H_4SO_2Na \cdot 2H_2O$, in 10 ml water. On addition of water (after 10 minutes) a solid separated, which, recrystallized from methanol, had the melting point of 2-nitro-5-methylbenzenesulphenyl *p*-toluenesulphinate, *viz.*, 104°, not depressed in mixture with a specimen obtained in exp. (3).

(5) To 1.6 g *o*-nitrobenzenesulphenyl di-O-methylmonothiophosphate, in 20 ml ethanol, were added 1.5 g p-$BrC_6H_4SO_2Na \cdot 2H_2O$, in 20 ml water. Crystals rapidly separated out. 200 ml water were added, and the product filtered off, and dried: 1.9 g (theor. 2.0 g *o*-nitrobenzenesulphenyl *p*-bromobenzenesulphinate). M. p. (recrystallized from ethanol) 139° (reported [14] 137°).

0.1195 g subst.: 0.1494 g $BaSO_4$.

$O_2NC_6H_4SSO_2C_6H_4Br$ (374.2) Calc. S 17.1 Found S 17.2

(6) 10 ml 0.1 *M* sodium sulphite (in freshly boiled water containing 5 % ethanol as an antioxidant) were added to

(a) 0.181 g 2-nitro-5-methylbenzenesulphenyl thiocyanate (0.00080 mole) in 10 ml ethylacetate and 20 ml ethanol

(b) 0.247 g 2-nitro-5-methylbenzenesulphenyl di-O-methylmonothiophosphate (0.00080 mole) in 10 ml ethanol

(c) 0.266 g 2-nitro-5-methylbenzenesulphenyl *p*-toluenesulphinate (0.00082 mole) in 20 ml ethanol (at 40—50°).

After one hour the green solutions were diluted to 100 ml with freshly boiled water (they thereby remained clear), and 10 ml were pipetted out. 60 ml freshly boiled water, 1 g potassium iodide, and 5 ml 10 per cent acetic acid were added, and the solutions were titrated with 0.01 *N* iodine for excess sulphite: (a) 6.0 ml (b) 5.4 ml (c) 4.9 ml. Blind run (treated as above): 20.4 ml.

To the remaining 90 ml were added 5 ml 1 *M* potassium cyanide. After standing for 3 hours, water was added, and the formed crystals filtered off, and dried: (a) 0.12 g (b) 0.12 g (c) 0.14 g. Recrystallized from glacial acetic acid, they had the melting point of 2-nitro-5-methylphenyl thiocyanate, *viz.*, 135°, not depressed in mixture with a specimen obtained in exp. (1).

SUMMARY

Some new types of sulphenyl compounds are described, *viz.*, sulphenyl di-O-alkylmonothiophosphates, sulphenyl alkanethiosulphonates, and sulphenyl thiosulphates (in solutions).

Compounds containing the 2-nitro-5-methylphenylsuphur group are prepared for the first time.

Methods are devised for the iodometric analysis of sulphenyl thiocyanates, sulphenamides, and sulphenyl thiosulphates.

Displacement reactions are demonstrated, of the type:

$$RSSX' + SX''^- = RSSX'' + SX'^-$$

It is shown that the base strengths (anionoid reactivities) towards RS^+ of thio anions SX^- increase with decreasing redox potentials of the systems:

$$2\ SX^- \rightleftarrows (SX)_2 + 2\ e$$

as do their base strengths towards S^{++} and S_2^{++}.

The different types of displacement reactions from kationoid sulphur are discussed, and some new reactions of sulphenyl compounds are demonstrated.

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