Displacements at Divalent Group VI Elements

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Reactions, spectra and syntheses of aromatic divalent sulphur, selenium and tellurium compounds are described. Displacing tendencies at sulphur and selenium do not correlate with hydrogen or carbon basicity, and decrease in a series of bases

$\text{C}_6\text{H}_5\text{Se}^- > \text{C}_6\text{H}_5\text{S}^- > \text{CN}^- > \text{OH}^- > \text{SO}_3^{2-} > p\text{-NO}_2\text{C}_6\text{H}_4\text{Se}^- > \text{S}_2\text{O}_3^{2-} \approx p\text{-NO}_2\text{C}_6\text{H}_4\text{S}^- > p\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_3\text{S}^- > \text{C}_6\text{H}_5\text{O}^-$, $p\text{-NO}_2\text{C}_6\text{H}_4\text{O}^-$, in 90 % ethanol-water and $\text{C}_6\text{H}_5\text{Se}^- > \text{C}_6\text{H}_5\text{S}^- > p\text{-NO}_2\text{C}_6\text{H}_4\text{Se}^- > p\text{-NO}_2\text{C}_6\text{H}_4\text{S}^- > \text{C}_6\text{H}_5\text{O}^-$, $p\text{-NO}_2\text{C}_6\text{H}_4\text{O}^-$ in dimethylformamide. Tellurium-basicities decrease in the same order in 90 % ethanol-water *i.e.* $\text{C}_6\text{H}_5\text{Te}^- > \text{C}_6\text{H}_5\text{S}^- > \text{SO}_3^{2-}$, $\text{S}_2\text{O}_3^{2-} > p\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_3\text{S}^-$. Displacements involving multiply charged anions are strongly solvent dependent.

Methods of estimating electrophilic reactivity of divalent Group VI compounds are considered, and spectroscopic evidence for the existence of the conjugate base of *p*-nitrobenzenesulphenic acid is presented.

An investigation of displacements by bases, Y^- , at the divalent Group VI atoms, S, Se and Te (denoted collectively by M throughout this paper) has been made in order to establish whether displacements at all M atoms can be adequately described by eqn. (1) as written, for at least one combination of R, X, and Y^- . R and X are any groups satisfying the bonding requirements of divalent M.

It was of interest to compare reactivities and positions of equilibrium in (1) with similar properties of displacements at another atom such as carbon. Several questions come to mind. For example, is reaction (1) bimolecular, an $\text{S}_\text{N}1$ -like ionization involving RM^+ as intermediate, or does it have some other mechanism, perhaps non-ionic, associated with oxidation — reduction processes? If bimolecular, what are the steric requirements of (1) and is the direc-

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tion of most favourable approach by Y^- such that M, X, and Y are linear¹ in the transition state? In the forward reaction (1), what are the relative reactivities (electrophilic tendencies) of RMX if M is the only variable, and what is the effect of intramolecular interactions, between different R and M, on the electrophilic tendency of RMX? What are the relative reactivities (nucleophilic tendencies) of Y^- towards different M atoms, and if Y^- is itself RM^- , what are the nucleophilic tendencies of RM^- in (1), if M (in both RMX and RM^-) is the only variable?

M-Basicities¹ of Y^- and X^- , an equilibrium controlled property, can be estimated from the equilibria (1) and compared with carbon¹ and hydrogen basicities. It was necessary to discover if M-basicities within a series of Y^- remained comparable for all kinds of M in RMX. The effect on the M-basicity of RM^- , of different M atoms, and of intramolecular interactions, between R and M, when RM^- is the displacing base, Y^- , is also of interest¹.

Finally, the influence of the reaction medium on reactivity and the equilibria should be compared with the large changes in carbon-nucleophilic tendencies² of Y^- , and smaller changes in carbon-basicities^{1(b)}, produced by the change from protic to dipolar aprotic solvent. This paper describes some broad preliminary investigations into methods of answering these questions, and reports examples of reactions based on (1). Some observations on the U.V. absorption of organic sulphur, selenium and tellurium compounds have been made and are discussed briefly.

DISCUSSION

Displacements at sulphur, selenium and tellurium, but to a lesser degree at oxygen¹, take place according to (1) provided that R- is more electropositive than $-MX$, $-X$ is more electronegative than $RM-$, and Y^- is not a weaker M-base than X^- . Representative displacements, (2), (3), (4), in which the stoichiometry and products fit eqn. (1), have been studied here. Numerous examples exist of displacements at sulphur¹ and to a lesser extent at selenium^{7,8,28}. A few displacements at divalent tellurium (5) have been reported^{8,9}.

The reactions generally are too fast for reactivity to be measured by conventional methods, but in the few investigations of rate³⁻⁵, they have been bimolecular, and have had low activation energies (< 14 kcal/mole). Measurable rates are obtained when the reactions have abnormally large negative entropies⁶ *i.e.* low log B in the Arrhenius equation, caused by atypical solvent or salt effects.

Although rate measurements of reaction (1) were not practicable, it was hoped to answer the question of relative electrophilic tendencies of M and the effect of interactions between R and M on the reactivity of RMX, by a series of competitive reactions, (6) and (7) respectively, in a well shaken 50/50 hetero-

geneous mixture of chloroform and water, followed by spectrophotometric analysis for RMS_2O_3^- in the aqueous layer and for RMX in the chloroform layer.

(Where X is $p\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{S}^-$, RM_1^- is more electrophilic than RM_2^- in (6) and RM^- is more electrophilic than R^1M^- in (7)).

The method of competitive reactions requires that unchanged RMX should not subsequently equilibrate with RMS_2O_3^- and X^- , *i.e.* that the back reaction of (6) or (7) be very much slower than the forward reaction. This seemed likely since thiosulphate ion is a stronger M-base than p -toluenethiosulphonate ion (X^-) and because the back reactions of (6) or (7) should be slow because of the unfavourable entropy of reaction between two anions (*vide infra*). The products of (6) and (7) should be separated as soon as possible to prevent subsequent equilibration.

Reactions (6) and (7) were influenced by solvation and were not irreversible. In aqueous ethanol, (6) was displaced successively to the left by extraction with chloroform, in which RMX but not the ionic species was soluble. Equimolar amounts of sodium thiosulphate in water and of RMX in the same volume of chloroform, when shaken together for 5 min had an equilibrium constant of approximately 1 when R was phenyl or p -nitrophenyl, M was S, Se, or Te, and X was p -toluenethiosulphonate. Sodium sulphite behaved in the same way as sodium thiosulphate.

Despite these difficulties, competitive reactions (6) and (7) were carried out as outlined, and the aqueous layer was separated as soon as possible and analysed for RMS_2O_3^- by measuring the absorption at 260–350 $m\mu$. All possible pairs of the compounds in the following series, in chloroform, were treated with less than an equimolar amount of sodium thiosulphate in water. The relative concentrations of RMS_2O_3^- found for each pair of compounds suggest an order of electrophilic reactivity towards thiosulphate ion of: $p\text{-NO}_2\text{C}_6\text{H}_4\text{SeX} \approx \text{C}_6\text{H}_5\text{TeX} > p\text{-CH}_3\text{OC}_6\text{H}_4\text{TeX} > \text{C}_6\text{H}_5\text{SeX}$ and of $p\text{-NO}_2\text{C}_6\text{H}_4\text{SeX} > p\text{-NO}_2\text{C}_6\text{H}_4\text{SX}$, where X is the p -toluenethiosulphonate group.

It is not yet possible to decide if these series reflect the electrophilic tendencies of RM^- or whether the series is merely controlled by solvation differences between the various RMX and RMS_2O_3^- species, or by variable solvent effects on the rates of the back reaction of (6) and (7) when RM is changed. The results are as expected, if electron withdrawal by R increases the electrophilic reactivity of RMX , and if divalent tellurium is more electrophilic than divalent selenium, than divalent sulphur. Further discussion of the reactivity series will be postponed until other reactions, based on the competitive principle, have been investigated.

The problem of M-basicity of Y^- when Y^- is RM^- in (1), and the effect on this property of intramolecular interactions between R and M in RM^- , was considered in terms of the reactions 1–23, summarized in Table 1. The reactions were carried out in a protic (ethanol) and a dipolar aprotic (dimethyl-

formamide) solvent in order to answer the question of solvent effects on basicity of RM^- . Displacements were very fast in both solvents, so it was not possible to measure rates of reaction, and observe the effect of solvent on reactivity.

The more general question, of relative displacing tendencies at divalent sulphur, selenium and tellurium for a series of Y^- , was investigated by a study of reactions 1–68, Table 1. These reactions unless described as slow, equilibrated before measurements could be made *i.e.* < 1 min after mixing equimolar proportions of the reactants at approximately 10^{-4} M in 90 % ethanol-water. At least one, and usually two, of the reactants or products was analysed spectrophotometrically, and the concentrations at equilibrium of these species are recorded in Table 1 as moles per mole of RMX initially. Reactions were performed under nitrogen, and, except for the "slow" reactions, identical analyses were obtained 5 and 30 min after mixing, confirming that equilibration was complete, or that the reactions were extremely slow. In all reactions of Table 1 and throughout this paper, Ar is *p*-nitrophenyl, and "excess" denotes a concentration > 50 moles per mole of the other reactant. "Slow" reactions had half times > 30 sec at room temperature.

Reactions 1–23 suggest an order of S and Se-basicity, for displacement of both ArS^- and ArSe^- from both ArS - and ArSe - of $\text{C}_6\text{H}_5\text{S}^- \gg \text{ArSe}^- > \text{ArS}^- \gg \text{C}_6\text{H}_5\text{O}^-$, ArO^- ; and for displacement of $\text{C}_6\text{H}_5\text{S}^-$ or $\text{C}_6\text{H}_5\text{Se}^-$ from $\text{C}_6\text{H}_5\text{Se}$ - or $\text{C}_6\text{H}_5\text{S}$ - of $\text{C}_6\text{H}_5\text{Se}^- > \text{C}_6\text{H}_5\text{S}^- \gg \text{C}_6\text{H}_5\text{O}^-$. Thiophenoxide ion did not displace $\text{C}_6\text{H}_5\text{Te}^-$ from diphenyl ditelluride, although an interaction between diphenyl ditelluride and thiophenoxide ion altered the spectrum of a mixture of the two species. An investigation of the origin of this interaction is planned.

The bases, RM^- , used in reactions 1–23, had the same relative displacing tendencies in ethanol, dimethylformamide, dimethylsulphoxide, or acetone. This demonstrates that M-basicity, equilibrium controlled, is not changed to the extent that nucleophilic tendencies of Y^- toward carbon, kinetically controlled, is changed² in the transfer from a protic to a dipolar aprotic solvent.

Reactions 1–23 show that electron withdrawal by R in RM^- strongly reduces the displacing tendency of RM^- at divalent selenium, and confirms¹⁰ that the same principal influences S-basicity of RM^- . The M-basicities $\text{RSe}^- > \text{RS}^- \gg \text{RO}^-$ and $\text{RTe}^- > \text{RS}^- \gg \text{RO}^-$, decrease in the same direction as the polarizability of the Group VI elements, and with decreasing ability of RM^- to interact with the *d* orbitals of M in the electrophilic compound RMX . M-Basicities of RM^- decrease with increasing electronegativity of RM^- . They do not correlate with hydrogen or carbon basicity. To illustrate, RO^- is generally a stronger carbon³⁵ and hydrogen base than RS^- , but, as shown here, RS^- is a much stronger M-base than RO^- . The M-basicity, $\text{RS}^- > \text{RO}^-$ correlates with the relative strengths of the S–S and O–O bonds³⁶ just as carbon-basicity correlates with bond strength^{1(b)}. Unfortunately other bond strength data is not available.

The reactions of Table 1 show that displacing tendencies at both divalent sulphur and selenium, in 90 % ethanol, decrease in the series of bases: $\text{C}_6\text{H}_5\text{Se}^- > \text{C}_6\text{H}_5\text{S}^- > \text{CN}^- > \text{OH}^- > \text{SO}_3^{2-} > \text{ArSe}^- > \text{S}_2\text{O}_3^{2-} \approx \text{ArS}^- > \text{CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{S}^- > \text{C}_6\text{H}_5\text{O}^-$, ArO^- . Displacements at tellurium were observed when synthesizing RTeX and in the competitive experiments already described. These lead to a series of tellurium-basicity of $\text{C}_6\text{H}_5\text{Te}^- > \text{C}_6\text{H}_5\text{S}^- > \text{SO}_3^{2-}$,

Table 1. Displacements $\text{RMX} + \text{Y}^- \rightleftharpoons \text{RMY} + \text{X}^-$ in 90 % ethanol-water at 20–22°, under nitrogen. Concentrations of X^- and Y^- at equilibrium are expressed as moles per mole of RMX before reaction. Reactions are fast (see text) and are between equimolar proportions of RMX and Y^- at 10^{-4} M, unless stated otherwise. Ar is *p*-nitrophenyl, prefix *n* denotes large excess of Y^- . Reaction number followed by *s* denotes a slow reaction.

Reaction	RMX	Y^-	$\frac{[\text{Y}^-]}{[\text{RMX}]^a}$	X^-	$\frac{[\text{X}^-]}{[\text{RMY}]^b}$	M-basicity
1.	ArSSAr	ArO^-	1.0	ArS^-	0.0	$\text{ArS}^- > \text{ArO}^-$
2.	ArSSAr	$\text{C}_6\text{H}_5\text{O}^-$	1.0 *	ArS^-	0.0	$\text{ArS}^- > \text{C}_6\text{H}_5\text{O}^-$
3.	ArSSAr	ArSe^-	0.1	ArS^-	0.9	$\text{ArSe}^- > \text{ArS}^-$
4.	ArSSAr	$\text{C}_6\text{H}_5\text{S}^-$	(0.0)	ArS^-	1.0	$\text{C}_6\text{H}_5\text{S}^- > \text{ArS}^-$
5.	ArSSC ₆ H ₅	$\text{C}_6\text{H}_5\text{S}^-$	0.0 *	ArS^-	1.0	$\text{C}_6\text{H}_5\text{S}^- > \text{ArS}^-$
6.	ArSeSeAr	ArO^-	1.0	ArSe^-	0.0	$\text{ArSe}^- > \text{ArO}^-$
7.	ArSeSeAr	$\text{C}_6\text{H}_5\text{O}^-$	1.0 *	ArSe^-	0.0	$\text{ArSe}^- > \text{C}_6\text{H}_5\text{O}^-$
8.	ArSeSeAr	ArS^-	1.0	ArSe^-	0.0	$\text{ArSe}^- > \text{ArS}^-$
9.	ArSeSeAr	2 ArS^-	1.9	ArSe^-	0.1	$\text{ArSe}^- > \text{ArS}^-$
10.	ArSeSeAr	$\text{C}_6\text{H}_5\text{S}^-$	(0.0)	ArSe^-	1.0	$\text{C}_6\text{H}_5\text{S}^- > \text{ArSe}^-$
11.	ArSeSC ₆ H ₅	$\text{C}_6\text{H}_5\text{S}^-$	0.0 *	ArSe^-	1.0	$\text{C}_6\text{H}_5\text{S}^- > \text{ArSe}^-$
12.	ArSeSAr	ArO^-	1.0	ArS^-	0.0	$\text{ArS}^-, \text{ArSe}^-, > \text{ArO}^-$
13.	ArSeSAr	$\text{C}_6\text{H}_5\text{O}^-$	1.0 *	ArS^-	0.0	$\text{ArS}^-, \text{ArSe}^- > \text{C}_6\text{H}_5\text{O}^-$
14.	ArSeSAr	ArS^-	1.0	ArSe^-	0.0	$\text{ArSe}^- > \text{ArS}^-$
15.	ArSeSAr	2 ArS^-	1.9	ArSe^-	0.1	$\text{ArSe}^- > \text{ArS}^-$
16.	ArSeSAr	ArSe^-	0.2	ArS^-	0.8	$\text{ArSe}^- > \text{ArS}^-$
17.	ArSeSAr	$\text{C}_6\text{H}_5\text{S}^-$	(0.0)	ArS^- + ArSe^-	0.8 0.2	$\text{C}_6\text{H}_5\text{S}^- > \text{ArSe}^- > \text{ArS}^-$
18.	$\text{C}_6\text{H}_5\text{SSC}_6\text{H}_5$	$\text{C}_6\text{H}_5\text{O}^-$	1.0 *	$\text{C}_6\text{H}_5\text{S}^-$	0.0	$\text{C}_6\text{H}_5\text{S}^- > \text{C}_6\text{H}_5\text{O}^-$
19.	$\text{C}_6\text{H}_5\text{SSC}_6\text{H}_5$	$\text{C}_6\text{H}_5\text{S}^-$	0.5	$\text{C}_6\text{H}_5\text{S}^-$	0.5	Exchange reaction Ref. 4.
20.	$\text{C}_6\text{H}_5\text{SeSeC}_6\text{H}_5$	$\text{C}_6\text{H}_5\text{O}^-$	1.0 *	$\text{C}_6\text{H}_5\text{Se}^-$	0.0	$\text{C}_6\text{H}_5\text{Se}^- > \text{C}_6\text{H}_5\text{O}^-$
21.	$\text{C}_6\text{H}_5\text{SeSeC}_6\text{H}_5$	$\text{C}_6\text{H}_5\text{S}^-$	1.0*1.0	$\text{C}_6\text{H}_5\text{Se}^-$	0.0	$\text{C}_6\text{H}_5\text{Se}^- > \text{C}_6\text{H}_5\text{S}^-$
22.	$\text{C}_6\text{H}_5\text{SeSC}_6\text{H}_5$	$\text{C}_6\text{H}_5\text{S}^-$	1.0*1.0	$\text{C}_6\text{H}_5\text{Se}^-$	0.0	$\text{C}_6\text{H}_5\text{Se}^- > \text{C}_6\text{H}_5\text{S}^-$
23.	$\text{C}_6\text{H}_5\text{TeTeC}_6\text{H}_5$	$\text{C}_6\text{H}_5\text{O}^-$	1.0 *	$\text{C}_6\text{H}_5\text{Te}^-$	0.0	$\text{C}_6\text{H}_5\text{Te}^- > \text{C}_6\text{H}_5\text{O}^-$
24.	ArSSAr	$\text{CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{S}^-$	1.0 *	ArS^-	0.0	$\text{ArS}^- > \text{CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{S}^-$
25.	ArSeSeAr	$\text{CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{S}^-$	1.0 *	ArSe^-	0.0	$\text{ArSe}^- > \text{CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{S}^-$
26.	ArSSAr	SO_3^{2-}	(0.0)	ArS^-	1.0	$\text{SO}_3^{2-} > \text{ArS}^-$
27.	ArSeSeAr	SO_3^{2-}	(0.0)	ArSe^-	1.0	$\text{SO}_3^{2-} > \text{ArSe}^-$
28.	ArSSO ₃ ⁻	$n\text{SO}_3^{2-}$	1.0 *	ArS^-	0.0	see text
29.	ArSeSO ₃ ⁻	$n\text{SO}_3^{2-}$	1.0 *	ArSe^-	0.0	see text
30.	ArSSO ₃ ⁻	$n\text{OH}^-$	1.0 *	ArS^-	0.0	see text
31.	ArSeSO ₃ ⁻	$n\text{OH}^-$	1.0 *	ArSe^-	0.0	see text
32s.	ArSSO ₃ ⁻	$\text{C}_6\text{H}_5\text{S}^-$	(0.0)	ArS^-	1.0	$\text{C}_6\text{H}_5\text{S}^- > \text{SO}_3^{2-}$
33s.	ArSeSO ₃ ⁻	$\text{C}_6\text{H}_5\text{S}^-$	(0.0)	ArSe^-	1.0	$\text{C}_6\text{H}_5\text{S}^- > \text{SO}_3^{2-}$
34s.	ArSSO ₃ ⁻	$n\text{CN}^-$	—	ArS^-	0.2	$\text{SO}_3^{2-} > \text{CN}^-$
35s.	ArSeSO ₃ ⁻	$n\text{CN}^-$	—	ArSe^-	0.2	$\text{SO}_3^{2-} > \text{CN}^-$
36.	ArSSAr	$\text{S}_2\text{O}_3^{2-}$	(0.0)	ArS^-	1.0	$\text{S}_2\text{O}_3^{2-} > \text{ArS}^-$
37.	ArSeSeAr	$\text{S}_2\text{O}_3^{2-}$	0.7 *	ArSe^-	0.3	$\text{ArSe}^- > \text{S}_2\text{O}_3^{2-}$
38.	ArSS ₂ O ₃ ⁻	$n\text{S}_2\text{O}_3^{2-}$	1.0 *	ArS^-	0.0	see text.
39.	ArSeS ₂ O ₃ ⁻	$n\text{S}_2\text{O}_3^{2-}$	1.0 *	ArSe^-	0.0	see text.
40s.	ArSS ₂ O ₃ ⁻	$\text{C}_6\text{H}_5\text{S}^-$	0.0 *	ArS^-	1.0	$\text{C}_6\text{H}_5\text{S}^- > \text{S}_2\text{O}_3^{2-}$
41s.	ArSeS ₂ O ₃ ⁻	$\text{C}_6\text{H}_5\text{S}^-$	0.0 *	ArSe^-	1.0	$\text{C}_6\text{H}_5\text{S}^- > \text{S}_2\text{O}_3^{2-}$
42.	ArSSAr	CN^-	(0.0)	ArS^-	1.0	$\text{CN}^- > \text{ArS}^-$
43.	ArSeSeAr	CN^-	(0.0)	ArSe^-	1.0	$\text{CN}^- > \text{ArSe}^-$
44s.	ArSCN	CN^-	(0.0)	ArS^-	1.0	—
45s.	ArSeCN	CN^-	(0.0)	ArSe^-	1.0	—
46.	ArSSAr	$n\text{OH}^-$	0.0 *	ArS^-	1.0 1.0 *	$\text{OH}^- > \text{ArS}^-$
47.	ArSeSeAr	$n\text{OH}^-$	0.0 *	ArSe^-	1.5	$\text{OH}^- > \text{ArSe}^-$
48.	$\text{ArSS}_2\text{O}_2\text{C}_6\text{H}_4\text{CH}_3$	ArS^-	0.0	$\text{CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{S}^-$	(1.0)	$\text{ArS}^- > \text{CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{S}^-$

Reaction	RMX	Y ⁻	$\frac{[Y^-]}{[RMX]^a}$	X ⁻	$\frac{[X^-]}{[RMY]^b}$	M-basicity
49.	ArSS ₂ O ₂ C ₆ H ₄ CH ₃	ArSe ⁻	0.0	CH ₃ C ₆ H ₄ SO ₂ S ⁻	(1.0)	ArS ⁻ > CH ₃ C ₆ H ₄ SO ₂ S ⁻
50s.	ArSeS ₂ O ₃ ⁻	<i>n</i> CN ⁻	0.9 *	ArSe ⁻	0.1	CN ⁻ > S ₂ O ₃ ²⁻
51.	ArSeSAr	<i>n</i> OH ⁻	(0.0)	ArS ⁻	1.0	OH ⁻ > ArSe ⁻ > ArS ⁻
				+ ArSe ⁻	0.5	
52.	ArSeSAr	<i>n</i> SO ₃ ²⁻	(0.0)	ArS ⁻	0.9	SO ₃ ²⁻ > ArSe ⁻ > ArS ⁻
				+ ArSe ⁻	0.1	
53.	ArSeSAr	S ₂ O ₃ ²⁻	(0.1)	ArS ⁻	0.8	S ₂ O ₃ ²⁻ = ArSe ⁻ > ArS ⁻
				+ ArSe ⁻	0.1	
54.	ArSeSAr	CN ⁻	—	ArS ⁻	1.0	CN ⁻ > ArSe ⁻ > ArS ⁻
55s.	ArSeSAr	2 CN ⁻	—	ArS ⁻	1.0	CN ⁻ > ArSe ⁻ > ArS ⁻
				+ ArSe ⁻	1.0	
56.	S ₄ O ₆ ²⁻	ArS ⁻	1.0	S ₂ O ₃ ²⁻	(0.0)	S ₂ O ₃ ²⁻ > ArS ⁻
57s.	4 S ₄ O ₆ ²⁻	ArS ⁻	0.9	S ₂ O ₃ ²⁻	0.1 *	S ₂ O ₃ ²⁻ > ArS ⁻
58s.	S ₄ O ₆ ²⁻	ArSe ⁻	0.1	S ₂ O ₃ ²⁻	0.9 *	ArSe ⁻ > S ₂ O ₃ ²⁻

ArS⁻ or ArSe⁻ was not displaced from ArSS₂O₂C₆H₄CH₃ or ArSeS₂C₆H₄CH₃ by an equimolar proportion of C₆H₅S⁻, SO₃²⁻, S₂O₃²⁻ or CN⁻ or by excess OH⁻. Excess SO₃²⁻ or S₂O₃²⁻ did not displace ArS⁻ or ArSe⁻ (cf. 28, 29, 38, 39), but excess CN⁻ and C₆H₅S⁻ displaced ArS⁻ or ArSe⁻ (cf. 44, 45, 5, and 11).

Displacements in 20 % ethanol-water.

59.	ArSSAr	SO ₃ ²⁻	(0.0)	ArS ⁻	1.0	SO ₃ ²⁻ > ArS ⁻
60.	ArSeSeAr	SO ₃ ²⁻	(0.34)	ArSe ⁻	0.66	SO ₃ ²⁻ ≈ ArSe ⁻
61.	ArSeSeAr	2 SO ₃ ²⁻	(0.26)	ArSe ⁻	0.74	SO ₃ ²⁻ ≈ ArSe ⁻
62.	ArSS ₂ O ₃ ⁻	<i>n</i> SO ₃ ²⁻	1.0 *	ArS ⁻	0.0	see text.
63.	ArSeS ₂ O ₃ ⁻	<i>n</i> SO ₃ ²⁻	1.0 *	ArSe ⁻	0.0	see text.
64.	ArSSAr	S ₂ O ₃ ²⁻	(0.1)	ArS ⁻	0.9	S ₂ O ₃ ²⁻ > ArS ⁻
64s.	S ₄ O ₆ ²⁻	ArS ⁻	0.2	S ₂ O ₃ ²⁻	0.8 *	ArS ⁻ > S ₂ O ₃ ²⁻
66.	ArSeSeAr	S ₂ O ₃ ²⁻	0.92	ArSe ⁻	0.08	ArSe ⁻ > S ₂ O ₃ ²⁻
67.	ArSeSeAr	10 S ₂ O ₃ ²⁻	0.90	ArSe ⁻	0.10	ArSe ⁻ > S ₂ O ₃ ²⁻
68s.	S ₄ O ₆ ²⁻	ArSe ⁻	0.0	S ₂ O ₃ ²⁻	1.0 *	ArSe ⁻ > S ₂ O ₃ ²⁻

^a Concentrations marked with an asterisk are for RMX, others for Y⁻.

^b Concentrations marked with an asterisk are for RMY, others for X⁻. Concentrations in parenthesis were not measured, but can be assumed from the stoichiometry of reaction.

S₂O₃²⁻ > *p*-CH₃C₆H₄SO₂S⁻ in aqueous ethanol, and is the same as sulphur or selenium-basicity.

Other features of reactions 1—68 deserve comment. Sulphite and thiosulphate ion reactions, 26—29, 36—39, 59—64, 66, and 67, were strongly solvent dependent. For example, the reaction between thiosulphate ion and ArSeSeAr had an equilibrium constant of 0.2 in 90 % ethanol-water, but of only 0.008 in 20 % ethanol-water; and sulphite ion is a stronger M-base than ArSe⁻ in 90 % ethanol-water, but is of equivalent strength to ArSe⁻ in 20 % ethanol-water. This is because the back reaction in each case was between two anions and such reactions tend to be much faster, relative to reaction between an anion and a dipolar molecule, in solvents of high dielectric constant than in solvents of low dielectric constant³⁶. Reactions of tetrathionate ion (56—58, 65, 68) were also strongly solvent dependent, because they involve a reaction between two anions. Thus ArS⁻ slowly displaced S₂O₃²⁻ from S₄O₆²⁻ more

rapidly in 20 % ethanol-water than in 90 % ethanol-water. All displacements involving reaction between two anions (30–35, 38–41, 49, 57 and 58) were "slow" and became faster as the water content (*i.e.* dielectric constant) of the solvent increased. By analogy with the studies made by Bartlett and Davis⁶, and Fava and Pajaro³, we conclude that these reactions have large negative entropies of activation (*i.e.* low $\log B$).

The entropy effect for reactions between anions may reverse the M-basicity of Y^- . Thus thiosulphate ion readily displaced ArS^- from both $ArS\cdot$ ⁽³⁶⁾ and $ArSe\cdot$ ⁽⁵²⁾, but not from $-SSO_3^{3-}$ ⁽³⁸⁾ even under highly favourable conditions of solvent and thiosulphate concentration. Displacements from $-SO_3^-$ did not take place (28–35) except by the indirect routes shown in eqns. (8) and (9), because the sulphur of $-SO_3^-$ does not have a vacant d orbital available for occupation in the transition state for displacement, *i.e.* it is not electrophilic.

In the indirect two step displacements like (8) and (9) the base apparently approaches the anion containing electrophilic sulphur or selenium from a direction which is furthest from the negative charge, and least sterically hindered, to form a linear transition state⁴.

Apparent displacements of ArS^- from both $-SO_3^-$ and $-S_2O_3^-$ (32–35, 40, 41 and 49) only take place with bases (*e.g.* $C_6H_5S^-$) which are much stronger than SO_3^{2-} or $S_2O_3^{2-}$, respectively, but not with those bases which are merely stronger than ArS^- . This suggests that the reaction path is as in (8) and (9).

Cyanide ion rapidly displaced one mole of ArS^- from $ArSSAr$ and one mole of $ArSe^-$ from $ArSeSeAr$ (*cf.* 42 and 43), but excess cyanide ion only *slowly* displaced a further mole of ArS^- or $ArSe^-$, presumably from $ArSCN$ and $ArSeCN$ respectively. These reactions are a novel example of displacement from unsaturated carbon as shown in eqn. (10), and as such would be slower than displacement from sulphur. ArS^- was displaced faster than $ArSe^-$ from $-CN$.

The cyanogen formed in (10) would be hydrolysed under the reaction conditions, but no analysis of hydrolysis products was made.

$ArSe^-$ behaved as the electrophilic, and ArS^- as the displaced portion of $ArSeSAr$ in reactions 15–17, 50–55, in agreement with the M-base strength $ArSe^- > ArS^-$. The opposite mode of displacement was apparent at equilibrium however, because a little $ArSe^-$ was detected. A 50/50 mixture of $ArSSAr$ and $ArSeSeAr$ behaved in the same way as $ArSeSAr$ in reactions 15–17, 50–55, as expected, because any $ArSe^-$ displaced from the mixture subsequently displaced ArS^- from $ArSSAr$.

Fig. 1. Evidence for ArSO^- . Absorption spectra in 80 % ethanol-water of the reactions:

- (1) $\text{ArSS}_2\text{O}_2\text{C}_6\text{H}_4\text{CH}_3 + 2 \text{OH}^- \rightarrow \text{ArSO}^- + \text{CH}_3\text{C}_6\text{H}_4\text{S}_2\text{O}_2^- + \text{H}_2\text{O}$
 - (2) $\text{ArSSAr} + 2 \text{OH}^- \rightarrow \text{ArSO}^- + \text{ArS}^- + \text{H}_2\text{O}$
 - (3) $\frac{1}{2} \text{ArSSAr} + \text{C}_6\text{H}_5\text{S}^- \rightarrow \text{ArS}^- + \frac{1}{2} (\text{C}_6\text{H}_5\text{S})_2$
- (where 1 mole proportion is 10^{-4} M).

Reactions 28 and 29, suggested that ArSeSAr and the mixture, $\text{ArSeSeAr} + \text{ArSSAr}$, might behave differently towards sulphite ion, as in eqns (11) and (12), respectively. The fact that the compound and mixture give the same products, must be due to secondary, rapid reactions of the mixture, (cf. eqns. (13) and (14)). Equilibrium (13) lies well to the left as shown by reactions 27 and 51 of Table 1, but apparently sufficient sulphite ion is displaced to enable (14) to proceed to completion.

Sulphenic acids in displacements at sulphur. Reaction 46, and that between hydroxide ion and $\text{ArSS}_2\text{O}_2\text{C}_6\text{H}_4\text{CH}_3$ provide evidence for the existence of sulphenic acids¹¹ as intermediates for displacements by hydroxide ion at divalent sulphur. The spectra for some reactions of hydroxide ion are in Fig. 1. It is apparent that the same species (shown not to be ArSO_2^-), absorbing at longer wavelengths than does ArS^- , has been formed in the same concentration from reactions of hydroxide ion with *p*-nitrobenzenesulphenyl *p*-toluenethiosulphonate (ArSX) and with the same concentration of di-*p*-nitrophenyl disulphide (ArSSAr), respectively.

The position of λ_{max} observed for ArS^- (420 $\text{m}\mu$), ArSH (316 $\text{m}\mu$) ArSSAr (314 $\text{m}\mu$), $\text{ArSS}_2\text{O}_2\text{C}_6\text{H}_4\text{CH}_3$ -*p* (290 $\text{m}\mu$), and ArSSO_3^- (350 $\text{m}\mu$) suggests that

Fig. 2. Absorption spectra of diphenyl disulphide, diphenyl diselenide, benzeneselenenyl thiophenoxide, diphenyl ditelluride, benzenetellurenyl thiophenoxide, and sodium thiophenoxide at 10^{-3} M in 96 % ethanol.

electron withdrawing groups attached to ArS^- cause shifts of ArS absorption to shorter wave lengths, and electron donating groups, or negative charges, cause shifts to longer wave lengths. If this is so, the species with λ_{max} 475 $\text{m}\mu$ in Fig. 1 must have a group attached to ArS^- which is very strongly electron donating; ArSO^- seems most likely.

In completely aqueous solution, ArSO^- decomposed rapidly. No satisfactory evidence for the existence of ArSeO^- could be obtained. When $\text{ArSeS}_2\text{O}_2\text{C}_6\text{H}_4\text{CH}_3$ was treated with excess hydroxide ion in ethanol, 1/2 mole proportion of ArSe^- was slowly formed, together with a species absorbing below 400 $\text{m}\mu$. ArSeSeAr gave one mole proportion of ArSe^- rapidly and a further 0.5 mole slowly, when treated with excess hydroxide ion in ethanol. These observations could be explained by eqn. (15).

Spectra of aromatic sulphur, selenium, and tellurium compounds. Spectra of aromatic disulphides^{12,13}, diselenides^{14,15} and related compounds^{12,16} have been reported and discussed in detail. Our results for ditellurides extend the series, and give a set of results measured under identical conditions. No unexpected results were obtained, and, since the intention was to develop a spectrophotometric method of analysing the reactions without disturbing established equilibria, it is sufficient to record the spectra (Fig. 2 and Table 2) and make the following general comments.

Table 2. Absorptions of sulphur, selenium, and tellurium compounds in 90 % ethanol unless stated otherwise. Values in parenthesis denote poorly defined $\lambda_{\max}$ or inflection point.

Compound	$\lambda_{\max}$ (m μ)	log ϵ	$\lambda_{\max}$ (m μ)	log ϵ	$\lambda_{\min}$ (m μ)	log ϵ	λ^a (m μ)	log ϵ^a
$(p\text{-NO}_2\text{C}_6\text{H}_4\text{S})_2$	314	4.31	(228)	4.15	255	3.83	> 420	< 2
$(p\text{-NO}_2\text{C}_6\text{H}_4\text{Se})_2$	325	4.22	(232)	4.11	265	3.88	> 442	< 2
$p\text{-NO}_2\text{C}_6\text{H}_4\text{Se}-\text{SC}_6\text{H}_4\text{NO}_2\text{-}p$	316	4.25	—	—	260	3.87	> 420	< 2
$p\text{-NO}_2\text{C}_6\text{H}_4\text{O}^-^e$	406	4.23	433 ^d	4.35 ^d	—	—	420	3.89
$p\text{-NO}_2\text{C}_6\text{H}_4\text{S}^-^e$	420	4.09	504 ^d	4.22 ^d	—	—	490	3.58
							442	4.07
$p\text{-NO}_2\text{C}_6\text{H}_4\text{Se}^-^e$	442	4.03	532 ^d	4.20 ^d	—	—	490	3.78
							420	3.99
$p\text{-NO}_2\text{C}_6\text{H}_4\text{OH}^f$	314	4.20	—	—	254	—	—	—
$p\text{-NO}_2\text{C}_6\text{H}_4\text{SH}^f$	316	4.01	—	—	—	—	—	—
$p\text{-NO}_2\text{C}_6\text{H}_4\text{SeH}^f$	326	3.92	—	—	—	—	—	—
$(\text{C}_6\text{H}_5\text{S})_2$	239	4.23	(300)	2.95	(270)	3.32	— ^b	—
$(\text{C}_6\text{H}_5\text{Se})_2$	240	4.22	330	2.99	(298)	2.85	— ^b	—
$(\text{C}_6\text{H}_5\text{Te})_2$	247	4.25	393	2.93	330	2.54	— ^b	—
$\text{C}_6\text{H}_5\text{TeSC}_6\text{H}_5$	240	4.24	393	2.63	—	—	— ^b	—
$\text{C}_6\text{H}_5\text{SeSC}_6\text{H}_5$	240	4.23	(325)	2.84	—	—	— ^b	—
$\text{C}_6\text{H}_5\text{S}^-^e$	269	4.16	—	—	—	—	— ^c	—
$p\text{-NO}_2-\text{C}_6\text{H}_4\text{SO}^-^e$	475	3.90	—	—	—	—	—	—

^a Reactions were analysed for $p\text{-NO}_2\text{C}_6\text{H}_4\text{S}^-$ and $p\text{-NO}_2\text{C}_6\text{H}_4\text{Se}^-$ at 420, 442, and 490 m μ . Absorption by the substrates in this region therefore does not interfere with the analysis.

^b Reactions of these compounds with thiophenoxide ion were analysed between 320—400 m μ , their absorption in this region is shown in Fig. 1.

^c Absorption was very weak above 310 m μ , cf. Fig. 1.

^d Measured in dimethylformamide.

^e Measured in a solution buffered to pH > 7 by bicarbonate.

^f In ethanol of pH < 2.

^g In 80 % ethanol-water.

There was a shift of the first, and a smaller shift of the second, $\lambda_{\max}$ of RMX (where R is an aromatic nucleus, M is O, S, Se, or Te, and X is a group, or negative charge, satisfying the divalent requirements of M) to longer wave lengths as M changed from the smaller to the larger elements of Group VI. If X did not absorb, or if its absorption was known and allowed for, the absorption curves were of almost the same height and shape for the same R group but different M, except that the first and second $\lambda_{\max}$ were most separated in tellurium compounds, but overlapped in sulphur compounds.

The absorption associated with RM⁻ was not shifted or changed by X in a variety of compounds, RMX. However when X was strongly electron withdrawing (e.g. RSO₂S⁻) a shift to shorter wavelengths took place, and when X was strongly electron donating (e.g. X the negative charge on M as in ArM⁻) a shift to longer wavelengths was observed. Shifts to shorter wavelengths corresponded to a small decrease in intensity, shifts to longer wavelengths were associated with a small increase in intensity.

There was a large solvent shift (27—90 m μ) to longer wave lengths in the absorption of ArM⁻ (Ar = *p*-nitrophenyl) when changing from the protic

solvent ethanol to the dipolar aprotic solvent dimethylformamide (*cf.* Table 2). Assuming that a shift to longer wavelengths means that the transition energy of the process

was less, the solvent effect agrees with Miller and Parker's postulate¹⁷ that polarizable quinonoid anions are much more solvated in dimethylformamide than in ethanol. As expected¹⁷ the shift was greater when M was more polarizable (*e.g.* Se *vs* O).

Solutions of disulphides, diselenides, and ditellurides obeyed Beer's Law and did not, as has been suggested by some workers¹⁸, dissociate into radicals, R.M., at room temperature.

The spectra of Fig. 2 agree with absorption maxima or shoulders between 260–280 $m\mu$ found for divalent sulphur compounds, between 300–330 $m\mu$ for divalent selenium compounds, and between 380–400 $m\mu$ for divalent tellurium compounds such as diaryl and aryl alkyl, but not dialkyl sulphides^{12,19,20} and selenides;^{12,16,21,22} diaryl and dialkyl disulphides^{12,13,23} diselenides^{12,15,23} and ditellurides^{18,23}, elemental sulphur⁶, and aromatic thiols^{12,20}. We conclude that divalent sulphur absorbs at 260–280 $m\mu$, divalent selenium at 300–330 $m\mu$, and divalent tellurium at 380–400 $m\mu$, provided that at least one weak electron donor (*e.g.* an aromatic nucleus or a conjugated system, or divalent S, Se, or Te), but not a strongly electron perturbing group, is bonded to these elements.

It is felt that the shifts to longer wavelengths of the first absorption of ArM^- when M has increasing atomic weight, depend on electron donation by M^- to Ar (to form $\text{Ar}^- = \text{M}$) and that the larger elements of Group VI interact with an electron deficient aromatic nucleus (Ar) either in the ground state and/or the excited state, more readily than do the smaller elements of Group VI. The dependence of absorptions on interactions in the excited state makes meaningless any correlation of absorption shifts with M-basicity of ArM^- , because the latter property depends on ground state interactions only.

Analysis of sulphur, selenium and tellurium chromophores. When Z is $\text{C}_6\text{H}_5\text{S}$, $\text{C}_6\text{H}_5\text{Se}$ or $\text{C}_6\text{H}_5\text{Te}$, and Y is ArS , ArSe , or ArTe , the absorptions between 300–450 $m\mu$ of the compounds, Z–Y, Z–Z, and Y–Y were proportional to the concentrations of the chromophores Z and Y, and were the sum of the absorptions of the appropriate Z and Y for *all combinations* of Z and Y studied. As was shown earlier with the appropriate disulphides¹⁰, Z does not affect the absorption due to Y when they are bound together. It is clear that the spectra of any Z–Y gives the concentration of Z and Y in Z–Y, provided that the spectra of standards, Z–Z and Y–Y have been measured.

An alternative means of analysis of Z–Z, Z–Y, or Y–Y is to displace Z^- or Y^- with a stronger M-base, measure the absorption and compare with that of a standard solution of Z^- or Y^- . This procedure is best suited to compounds in which Z or Y is a nitro substituted benzenesulphenyl or selenenyl group.

EXPERIMENTAL

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Benzeneselenenyl thiophenoxide, m.p. 58° ^{27c}, pale yellow needles from dilute methanol.

Benzeneselenenyl p-toluenethiosulphonate, m.p. 126–127°, yellow crystals from methanol. Compound V above. (Found: Se 22.9. Calc. for $C_{13}H_{12}SeS_2O_2$: Se 23.0).

Benzenetellurenyl p-toluenethiosulphonate, m.p. 138°, orange needles from methanol. Compound III above. (Found: Te 32.4. Calc. for $C_{13}H_{12}TeS_2O_2$: Te 32.5).

p-Methoxybenzenetellurenyl p-toluenethiosulphonate, m.p. 123–124°, orange-red needles from methanol. (Found: Te 30.2. Calc. for $C_{14}H_{14}TeS_2O_2$: Te 30.2).

Di-p-nitrophenyl disulphide, m.p. 180° ^{27g}, pale yellow needles from acetic acid.

Di-p-nitrophenyl diselenide, m.p. 179° ^{27h}, deep yellow crystals from acetic acid.

Method D gives greatly improved yields (80 %) of diselenide compared with other methods ^{27h}.

p-Nitrobenzeneselenenyl p-nitrothiophenoxide, m.p. 179–180°, yellow crystals from acetic acid.

Step M, based on that of Nakasaki ³⁰, was performed in refluxing acetic acid containing a trace of pyridine, under nitrogen for 8 h. (Found: Se 22.8. Calc. for $C_{12}H_8N_2O_4SeS$: Se 22.2).

As has been observed with other disulphides, diselenides and their mixed compounds ³¹, mixed melting points of many disulphides and diselenides were not depressed, *e.g.* — $ArSSAr + ArSeSeAr$ had m.p. 179°; $ArSeSAr + ArSeSeAr$ had m.p. 179–180°; $ArSeSAr + ArSSAr$ had m.p. 179–180°; $ArSSAr$ had m.p. 180°; and $ArSeSeAr$ had m.p. 179°.

It was therefore necessary to use other criteria to show that $ArSeSAr$ was not a mixture of $ArSeSeAr$ and $ArSSAr$. A paper chromatogram of a 50/50 mixture of $ArSeSeAr$ and $ArSSAr$ in a dimethylformamide-ligroin-ethanol solvent mixture, on paper saturated with dimethylformamide showed two red bands when sprayed with alcoholic alkali, but $ArSeSAr$ showed only one band. Spectrophotometric measurements confirm the identity of $ArSeSAr$ (*vide infra*).

p-Nitrobenzenesulphenyl p-toluenethiosulphonate, m.p. 134–135°, colourless crystals from methanol. Analysed spectrophotometrically (*vide infra*).

In this case only one mole of *p*-toluenethiosulphonate per mole of $ArSCl$ was used in step G.

p-Nitrobenzeneselenenyl p-toluenethiosulphonate m.p. 124°, yellow crystals from methanol. (Found: Se 20.3. Calc. for $C_{13}H_{11}NO_4S_2Se$: Se 20.2).

Tellurium tetrachloride ^{27m}, potassium selenocyanate ³³, potassium *p*-toluenethiosulphonate ³⁴, potassium tetrathionate ³⁴, and *p*-nitrothiophenoxide ²⁷ⁿ were prepared as described in the literature. Other reagents were commercial products, purified where necessary by standard methods.

Analysis by ultra violet absorption measurements. Benzenetellurenyl thiophenoxide and benzeneselenenyl thiophenoxide, separately in 90 % ethanol at 10^{-3} M, had absorptions between 300–400 $m\mu$ which were identical with those of a 50/50 10^{-3} M mixture of diphenyl ditelluride and diphenyl disulphide and with that of diphenyl diselenide and diphenyl disulphide, respectively. The spectra of the artificial mixtures were changed by recrystallisation from methanol, but those of the compounds were not. *p*-Nitrobenzeneselenenyl *p*-nitrothiophenoxide at 10^{-4} M in 90 % ethanol had an absorption between 260–420 $m\mu$ which was identical with a 50/50 mixture at 10^{-4} M of ArSeSeAr and ArSSAr. Between 220–240 $m\mu$ the absorption of ArSeSeAr is noticeably less than that of the mixture. No point of inflection was observed for ArSeSeAr in this region, but ArSSAr, ArSeSeAr, and mixtures of the two have points of inflection at 228 $m\mu$ and 232 $m\mu$, respectively, which have been attributed to the S–S ¹³ and Se–Se ¹⁵ bonds. Apparently the Se–S bond does not absorb noticeably in this region.

The following compounds at 10^{-4} M in 90 % ethanol, when treated with an excess of sodium thiophenoxide under nitrogen, had absorptions between 410–480 $m\mu$ corresponding exactly to quantitative displacement of ArS[–] and ArSe[–]: Di-*p*-nitrophenyl disulphide, *p*-nitrobenzenesulphenyl *p*-toluenethiosulphonate, *p*-nitrobenzeneselenenyl *p*-toluenethiosulphonate, and *p*-nitrobenzeneselenenyl *p*-nitrothiophenoxide. This confirms their identity.

Spectrophotometric measurements were made on a Beckmann DU spectrophotometer at 20–22°. Solutions of mercaptides and tellurium compounds, if required for longer than 10 min after preparation, were flushed with nitrogen and kept under nitrogen to prevent oxidation. All solutions obeyed Beer's Law between 10^{-3} – 10^{-4} M.

Reactions with bases. The spectra of standard solutions of substrates, of bases, and of expected products in the solvents used were examined between 230–550 $m\mu$. Absorptions were strictly additive when expected products were mixed with either of the reactants, except for those reactions involving unstable equilibria. Beer's Law was obeyed between 10^{-3} – 10^{-6} M.

Known concentrations of substrate and base were mixed at 20–22°, and the absorption of the mixture was measured within 5 min of mixing in a region selected so that at least one of the reactants and or products could be readily distinguished. Solutions in ethanol were buffered with excess sodium bicarbonate (provided that the reactants, as shown in a separate experiment, did not react in some other way with bicarbonate) to ensure a pH > 7 when mercaptides, selenides, or other strong bases were involved. Reactions were carried out under nitrogen in oxygen free solvents, although this precaution is rarely necessary if measurements are made without delay.

p-Nitrobenzenesulphenyl *p*-toluenethiosulphonate and the selenenyl analogue in chloroform were treated separately with an equal volume of an equimolar amount of sodium sulphite in water. The two layers were shaken vigorously together for 5 min and separated. The aqueous layer contained 0.5 mole proportion of ArSSO₃[–] or ArSeSO₃[–] and the chloroform layer, 0.5 mole proportion of ArSS₂O₂C₆H₄CH₃ or ArSeS₂O₂C₆H₄CH₃. Analysis was by the spectrophotometric method. In the same way it was shown that the reaction between sodium thiosulphate in water and ArSS₂O₂C₆H₄CH₃ or ArSeS₂O₂C₆H₄CH₃ in chloroform also had an equilibrium constant of 1.

The procedure for competitive reactions of RMX with sodium thiosulphate has been outlined in the discussion. The reactants were shaken together for thirty seconds, and the aqueous and chloroform layers were then separated and analysed spectrophotometrically.

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