

The Electrophilic Nature of *o*-Nitrobenzenesulfonyl and *o*-Nitrobenzeneselenenyl Halides. A Kinetic Study

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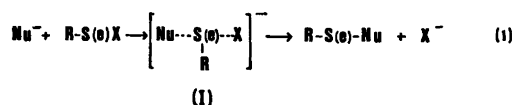
Kinetic measurements on the reaction between *o*-nitrobenzenesulfonyl chloride and 12 different nucleophiles, and some further studies involving nucleophilic substitution on *o*-nitrobenzeneselenenyl halides, have been performed in methanol using stopped-flow and conventional spectrophotometry. The kinetic plots showed the reactions to be of second order, first order in each of the reactants. The electrophilic nature of divalent sulfur and selenium has been discussed on the basis of these results and previously published kinetic data for substitutions on *o*-nitrobenzeneselenenyl halides. The proton basicity of the nucleophile was found to be of negligible importance in determining the reactivity toward S(II), confirming the statement that S(II) should be characterized as a soft electrophilic center. Regarding Se(II) as electrophilic center, the data suggest that monodentate nucleophiles form a transition state of the type: Nu---Se---X, *i.e.*, only one donor atom is bonded to the Se atom, while bidentate dithio nucleophiles appear to form a transition state where both of the donor atoms are bonded to the Se atom. A mechanism involving nucleophilic attack *trans* to the leaving group is suggested on the basis of leaving group effects and solvent effects on the rates of reaction.

During the last twenty years numerous papers dealing with kinetic studies of nucleophilic substitutions on divalent sulfur have been

published (for a review see Refs. 1–4). However, prior to 1974 no kinetic studies concerning nucleophilic substitution on divalent selenium and tellurium have been reported. Such reactions are known to be very fast. In recent studies we found that the pentathionate ions of the above-mentioned elements, *i.e.*, $S(S_2O_3)_2^{2-}$, $Se(S_2O_3)_2^{2-}$, and $Te(S_2O_3)_2^{2-}$ do react with ionic cyanide in acetonitrile at such a rate that it is possible to follow the reaction kinetically applying IR-spectroscopy.^{5,6} In a previous paper we have found that *o*-nitrobenzeneselenenyl halides, *o*-NO₂PhSeX, react with a large number of nucleophiles in methanol, and kinetic experiments have been carried out by means of the stopped-flow technique.⁷

In the present paper we wish to report the results of a kinetic study of the reaction between *o*-nitrobenzenesulfonyl chloride, *o*-NO₂PhSOCl, and various nucleophiles in methanol, and some further results from experiments concerning nucleophilic substitutions on *o*-NO₂PhSeX, X = Cl and Br. By comparing these rate constants with those obtained earlier under identical conditions for the reactions of the same nucleophiles with *o*-NO₂PhSeBr,⁷ we hope to gain some further knowledge about the electrophilic nature of S(II) and Se(II).

The bulk of information concerning nucleophilic substitution on S(II)^{3,4} and Se(II)^{5–8} points to an attack of the nucleophile *trans* to the leaving group, followed by synchronous bond formation and bond breaking, eqn. (1).



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(I) is to be considered as the transition state. In the present reactions the organic moiety is *o*-nitrophenyl, and the position *trans* to the leaving group is already occupied through an intramolecular interaction.^{9,10} In a foregoing paper we have suggested two possible reaction mechanisms.⁷

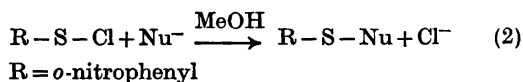
RESULTS

The stability of *o*-NO₂PhSCl in pure methanol was tested by measuring the absorbance at $\lambda_{\text{max}} = 395 \text{ nm}$ ¹¹ applying a spectrophotometer. The absorbance was found to be the same after 5 days at room temperature, which suggests that the reaction between the present sulfenyl chloride and methanol is very slow. The disappearance of the substrate due to solvolysis may then be disregarded when calculating the rate constant of the reaction between *o*-NO₂PhSCl and the various nucleophiles.

Likewise, *o*-NO₂PhSeX, (X = Cl and Br), was found to be stable against solvolysis during the kinetic runs in methanol.

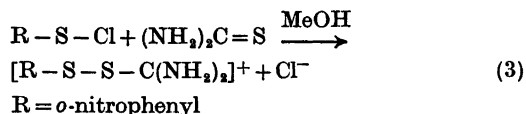
Kinetic studies on S(II). The products of the reaction between the various nucleophiles and

o-NO₂PhSCl have been synthesized, and the melting point, the recrystallization medium, and the analysis of each compound are listed in Table 1.



In most cases, except for ionic cyanide and di-*O*-ethylmonoselenophosphate, thio nucleophiles were applied. One of the nucleophiles, *i.e.*, di-*O*-ethylmonoselenophosphate, forms a yellowish-red, oily product. The other products of reaction (2) form quite stable yellowish-green solid compounds.

In the case of the neutral nucleophile, thiourea, the reaction product is a salt, eqn. (3).



In all the reactions studied, excellent second order kinetics were observed. Furthermore, the reactions were first order in each of the reactants. The rate of reaction was followed at

Table 1. Products of the reaction between various nucleophiles and *o*-nitrobenzenesulfenyl chloride.

No.	Compound (R = <i>o</i> -nitrophenyl)	M.p. °C	Recrystallized from	Found % S	Calc. % S
1	$\text{R-S-S-C} \begin{array}{c} \parallel \\ \text{S} \\ \parallel \\ \text{NC}_5\text{H}_{10}^a \end{array}$	154	chloroform	29.6	30.5
2	$\text{R-S-S-C} \begin{array}{c} \parallel \\ \text{S} \\ \parallel \\ \text{N}(\text{Me})_2 \end{array}$	157	chloroform	34.2	35.0
3	$\text{R-S-S-P} \begin{array}{c} \parallel \\ \text{S} \\ \parallel \\ \text{P}(\text{Me})_2 \end{array}$	200	chloroform	34.1	34.4
4	$\text{R-S-S-P} \begin{array}{c} \parallel \\ \text{S} \\ \parallel \\ \text{P}(\text{OEt})_2 \end{array}$	53	ether	28.2	28.3
5	R-S-S-Ph	52	ether	24.1	24.3
6	$\text{R-S-S-S}_2\text{O}_3\text{Ph}_4\text{As}$	164–166	acetonitrile/ether	14.6	14.8
7	$\text{R-S-S-SO}_2\text{-Ph}$	158–160	chloroform	29.2	29.3
8	$\text{R-S-S-SO}_2\text{-CH}_3$	85	ether	35.0	36.2
9	$\text{R-S-Se-P} \begin{array}{c} \parallel \\ \text{O} \\ \parallel \\ \text{P}(\text{OEt})_2 \end{array}$	oil	—	—	—
10	R-S-CN	116–117	benzene	18.3	17.7
11	$\text{R-S-S-C}(\text{NH}_2)_2\text{Cl}$	178	methanol	23.9	24.1
12	R-S-SCN	95 ^b	carbon tetrachloride	—	—

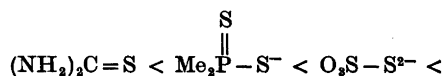
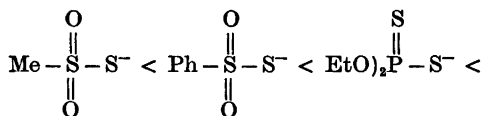
^a NC₅H₁₀ = piperidinyl. ^b Lit.²⁸ 93–94 °C.

Table 2. Pseudo-first-order rate constant (k') and second-order rate constant k_2 [S(II)] for the reaction between *o*-nitrobenzenesulfonyl chloride and different nucleophiles in methanol at 25 °C. The column to the right gives the second-order rate constants, k_2 [Se(II)] toward *o*-nitrobenzeneselenenyl bromide.

No.	Nucleophile	[Nu]/10 ⁻² M	k'/s^{-1}	k_2 [S(II)]/M ⁻¹ s ⁻¹	k_2 [Se(II)]/M ⁻¹ s ^{-1a}
1	C ₅ H ₁₀ N-C(=S)-S ^{-b}	0.50	4.17 × 10 ⁻³	0.889	4 200
		1.00	9.20 × 10 ⁻³		
		2.00	17.7 × 10 ⁻³		
2	Me ₂ N-C(=S)-S ⁻	0.401	1.29 × 10 ⁻³	0.444	2 667
		0.785	3.30 × 10 ⁻³		
		1.57	8.12 × 10 ⁻³		
3	Me ₂ P(=S)-S ⁻	1.00	2.17 × 10 ⁻⁴	2.13 × 10 ⁻³	350
		2.00	4.18 × 10 ⁻⁴		
4	(MeO) ₂ P(=S)-S ⁻	2.00	4.06 × 10 ⁻⁵	2.02 × 10 ⁻³	35.3
		3.00	6.20 × 10 ⁻⁵		
		4.00	8.03 × 10 ⁻⁵		
5	(EtO) ₂ P(=S)-S ⁻	2.00	4.06 × 10 ⁻⁵	2.02 × 10 ⁻³	35.3
		3.00	6.20 × 10 ⁻⁵		
		4.00	8.03 × 10 ⁻⁵		
6	Ph-S ⁻	0.555	0.116	22.8	7 000
		1.114	0.258		
		2.78	0.712		
7	S ₂ O ₃ ²⁻	0.50	0.841 × 10 ⁻³	0.164	125
		0.78	1.30 × 10 ⁻³		
		1.00	1.60 × 10 ⁻³		
8	Ph-SO ₂ -S ⁻	2.60	1.42 × 10 ⁻⁵	5.58 × 10 ⁻⁴	3.25
		4.00	2.30 × 10 ⁻⁵		
		6.07	3.36 × 10 ⁻⁵		
9	CH ₃ -SO ₂ -S ⁻	4.33	2.26 × 10 ⁻⁵	5.38 × 10 ⁻⁴	2.82
		6.07	3.36 × 10 ⁻⁵		
10	(EtO) ₂ P(=O)-S ⁻				1.97
11	(iPrO) ₂ P(=O)-S ⁻				4.57
12	(NH ₂) ₂ C=S	3.485	6.60 × 10 ⁻⁴	1.85 × 10 ⁻²	53.3
		4.45	7.99 × 10 ⁻⁴		
		7.25	13.3 × 10 ⁻⁴		
13	(MeO) ₂ P(=O)-Se ⁻	2.00	9.55 × 10 ⁻⁵	4.67 × 10 ⁻³	120
		3.00	13.73 × 10 ⁻⁵		
14	(EtO) ₂ P(=O)-Se ⁻	2.00	9.55 × 10 ⁻⁵	4.67 × 10 ⁻³	160
		3.00	13.73 × 10 ⁻⁵		
15	(iPrO) ₂ P(=O)-Se ⁻	2.00	9.55 × 10 ⁻⁵	4.67 × 10 ⁻³	222
		3.00	13.73 × 10 ⁻⁵		
16	CN ⁻	0.50	2.60 × 10 ⁻²	6.75	994
		1.00	7.06 × 10 ⁻²		
		1.41	9.40 × 10 ⁻²		

^a Ref. 7. ^b C₅H₁₀N=piperidinyl.

410 nm applying stopped-flow or conventional spectrophotometry. The rate constants of the reaction between the various nucleophiles and *o*-NO₂PhSCl are tabulated in Table 2. It is seen that the nucleophilicity of the thio nucleophiles progressively increases in the order:



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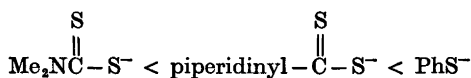


Table 2 further shows that the cyanide ion, No. 16, is a stronger nucleophile than the dithiocarbamates toward S(II), but is less nucleophilic than the thiophenolate ion.

Di-*O*-ethylmonoselenophosphate, No. 14, is more reactive than di-*O*-ethylthiophosphate, No. 5, but less reactive than dimethyldithiophosphate, No. 3, toward S(II).

The rate constants for three different types of nucleophiles, *i.e.*, (NH₂)₂C=S, Me₂NCS₂⁻, and CN⁻, have also been determined at different

Table 3. Pseudo-first-order rate constant (k') and second-order rate constant (k_2) for the reaction between *o*-nitrobenzenesulfonyl chloride and various nucleophiles in methanol at different temperatures.

Nucleophile	[Nu]/10 ⁻³ M	20 °C		25 °C		30 °C		35 °C		
		k'/s^{-1}	$k_2/M^{-1}s^{-1}$	$k_2/M^{-1}s^{-1}$	k'/s^{-1}	$k_2/M^{-1}s^{-1}$	k'/s^{-1}	$k_2/M^{-1}s^{-1}$	k'/s^{-1}	$k_2/M^{-1}s^{-1}$
(NH ₂) ₂ C=S	3.485	5.22 × 10 ⁻⁴	1.45 × 10 ⁻²	1.85 × 10 ⁻²	8.1 × 10 ⁻⁴	2.25 × 10 ⁻²	9.45 × 10 ⁻⁴	2.61 × 10 ⁻²		
	4.45	6.10 × 10 ⁻⁴			10.2 × 10 ⁻⁴		11.8 × 10 ⁻⁴			
	7.25	10.55 × 10 ⁻⁴			15.9 × 10 ⁻⁴		17.27 × 10 ⁻⁴			
S Me ₂ N-C-S ⁻	0.411	1.46 × 10 ⁻³	3.75 × 10 ⁻¹	4.44 × 10 ⁻¹	2.71 × 10 ⁻³	6.47 × 10 ⁻¹	2.89 × 10 ⁻³	8.09 × 10 ⁻¹		
	0.917	3.36 × 10 ⁻³			5.92 × 10 ⁻³		7.25 × 10 ⁻³			
	1.71	6.66 × 10 ⁻³			11.09 × 10 ⁻³		14.20 × 10 ⁻³			
CN ⁻	0.50	2.07 × 10 ⁻³	4.82	6.75	3.84 × 10 ⁻³	8.70	5.33 × 10 ⁻³	11.2		
	1.00	4.88 × 10 ⁻³			8.525 × 10 ⁻³		11.17 × 10 ⁻³			
	1.41	6.796 × 10 ⁻³			12.73 × 10 ⁻³		17.3 × 10 ⁻³			

temperatures, 20, 25, 30, and 35 °C, and the activation parameters have been calculated, Tables 3 and 4. Concerning these nucleophilic substitutions on *o*-NO₂PhSeCl, it is seen that the enthalpy of activation is rather similar while the entropy of activation is drastically increased when going from (NH₂)₂C=S to CN⁻.

Kinetic studies on Se(II). Kinetic studies have also been performed between the above-mentioned three nucleophiles and *o*-NO₂PhSeCl. The kinetic data and activation parameters are collected in the Tables 5 and 4, respectively.

The rate constants and the activation parameters for the reaction between *o*-NO₂PhSeBr and the same three nucleophiles are presented in Tables 6 and 4.

When the leaving group is changed from chloride to bromide, Tables 5 and 6 clearly show that the effect on the second order rate constant is rather small. At 30 °C the $k_2(\text{Cl})/k_2(\text{Br})$ ratios were found to be 1.20, 1.10, and 0.80 for (NH₂)₂C=S, Me₂NCS₂⁻, and CN⁻, respectively. Table 4 further shows that the activation parameters for the two thio nucleophiles are nearly unaffected by the change of the leaving group. The log $k_2 - 1/T$ correlation for the *o*-NO₂PhSeCl - CN⁻ reaction showed a curved plot, and activation parameters for this reaction have not been calculated.

The products of the reactions involving *o*-NO₂PhSeX as substrates have been described in the foregoing paper.⁷

log k₂[S(II)] - E° and log k₂[Se(II)] - log k₂[S(II)] relationships. With regard to nucleophilic substitution on *o*-NO₂PhSeCl, the anionic nucleophiles whose oxidation potentials, E° , are known, appear to conform to a rough linear relationship between log $k_2[\text{S(II)}]$ and E° , Fig. 1. However, one may notice that the point of the neutral thio nucleophile, (NH₂)₂C=S, appears to deviate markedly from this line.

Rate constants from the foregoing work⁷ for the reaction between the nucleophiles and *o*-NO₂PhSeBr are also listed in Table 2. In order to compare the electrophilic nature of S(II) and Se(II), the logarithm of the rate constants have been plotted against each other, Fig. 2. The figure shows that the log $k_2[\text{Se(II)}] - \log k_2[\text{S(II)}]$ plot of the thio nucleophiles splits up into two approximately parallel lines. The points for the monodentate nucleophiles lie on the lower line, while the points for

Table 4. Activation parameters for the reaction between *o*-nitrobenzenesulfonyl chloride, *o*-nitrobenzeneselenenyl chloride, and *o*-nitrobenzeneselenenyl bromide and various nucleophiles in methanol at 25 °C (R = *o*-nitrophenyl). 1 kcal = 4.184 kJ.

Nucleophile	ΔH^\ddagger kcal/mol	ΔS^\ddagger , cal/mol deg	ΔF^\ddagger kcal/mol
R-S-Cl + Nu ⁻ → RS-Nu + Cl ⁻			
(NH ₂) ₂ C=S	6.5	-45	19.9
Me ₂ N-C(=S)-S ⁻	8.8	-30	17.7
CN ⁻	8.3	-27	16.4
R-Se-Cl + Nu ⁻ → R-Se-Nu + Cl ⁻			
(NH ₂) ₂ C=S	3.5	-38	14.8
Me ₂ N-C(=S)-S ⁻	5.6	-24	12.7
R-Se-Br + Nu ⁻ → R-Se-Nu + Br ⁻			
(NH ₂) ₂ C=S ^a	3.3	-40	15.2
Me ₂ N-C(=S)-S ⁻	5.9	-23	12.8
CN ^{-a}	8.7	-16	13.4

^a Ref. 7.

Table 5. Pseudo-first-order rate constant (*k'*) and second-order rate constant (*k₂*) for the reaction between *o*-nitrobenzeneselenenyl chloride and various nucleophiles in methanol at different temperatures.

Nucleophile	[Nu]/ 10 ⁻² M	20 °C		25 °C		30 °C		35 °C	
		<i>k'</i> /s ⁻¹	<i>k₂</i> / M ⁻¹ s ⁻¹	<i>k'</i> /s ⁻¹	<i>k₂</i> / M ⁻¹ s ⁻¹	<i>k'</i> /s ⁻¹	<i>k₂</i> / M ⁻¹ s ⁻¹	<i>k'</i> /s ⁻¹	<i>k₂</i> / M ⁻¹ s ⁻¹
(NH ₂) ₂ C=S	1.00	0.696		0.80		1.04		1.19	
	2.10	1.284	61	1.41	66	1.708 ^a	73	2.03 ^a	87
	3.485	2.16		2.19		2.42		2.96	
$\begin{array}{c} \text{S} \\ \\ \text{Me}_2\text{N}-\text{C}-\text{S}^- \end{array}$	0.361			10.9		12.5		14.8	
	0.791			22.9	2 850	26.0	3 330	32.2	4 000
	1.264			35.5		40.9		48.3	
CN ⁻	0.50	3.08		3.50		3.93		6.03	
	1.00	6.73	672	7.48	750	8.93	888	12.1	1 200
	1.56	10.7		11.7		14.7		19.1	

^a [Nu] = 2.207 × 10⁻² M.

the bidentate nucleophiles lie on the upper line corresponding to about 10 times higher reactivity toward Se(II) at constant reactivity toward S(II). Fig. 2 further shows that di-*O*-ethylmonoselenophosphate, No. 14, behaves more like the bidentate dithio nucleophiles, and the reactivity of the cyanide ion appears to resemble the monodentate thio nucleophiles.

Solvent effect. Finally, some attempts were made to study the solvent effect on the reactions described above. The dipolar aprotic solvent acetonitrile was chosen because it has nearly the same dielectric constant as methanol, 36 and 33, respectively. The thiocyanate ion was applied as the nucleophile. For all the substrates studied, *i.e.*, *o*-NO₂PhSeX (X = Cl and Br) and

Table 6. Pseudo-first-order rate constant (k') and second-order rate constant (k_2) for the reaction between *o*-nitrobenzeneselenenyl bromide and various nucleophiles in methanol at different temperatures.

Nucleophile	[Nu]/ 10 ⁻³ M	20 °C		25 °C		30 °C		35 °C	
		k'/s^{-1}	$k_2/M^{-1}s^{-1}$	k'/s^{-1}	$k_2/M^{-1}s^{-1}$	k'/s^{-1}	$k_2/M^{-1}s^{-1}$	k'/s^{-1}	$k_2/M^{-1}s^{-1}$
(NH ₂) ₂ C=S ^a			48.9 ^b		53.3		60.5		66.9
$\begin{array}{c} \text{S} \\ \\ \text{Me}_2\text{N}-\text{C}-\text{S}^- \end{array}$	0.361	7.10		9.33		10.84		13.17	
	0.791	17.46	2 060	19.72	2 520	23.97	3 010	28.76	3 570
	1.264	25.3		31.68		37.36		44.38	
CN ^{-a}			500 ^b		994		1 110		1 460

^a Ref. 7. ^b Temp. 15 °C.

o-NO₂PhSCl, the reaction was too fast to be followed by means of the stopped-flow technique. Experimentally, we may then conclude that the second order rate constant of the reaction between the thiocyanate ion and the various substrates in acetonitrile is greater than $2 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$.

DISCUSSION

With regard to the thio nucleophiles, Table 2 shows that the relative order of reactivity toward S(II) and Se(II) is not quite the same. Fig. 2 further shows that the main reason for this disparity in reactivity toward S(II) and Se(II) is due to a higher nucleophilicity of the

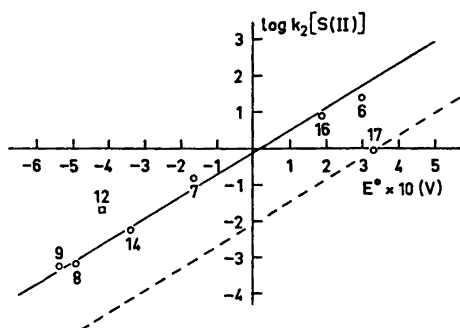


Fig. 1. Logarithm of the rate constants for the reaction of nucleophiles with *o*-nitrobenzenesulfonyl chloride as a function of the oxidation potential of the nucleophile. The numbers give the compounds as listed in Tables 2 and 7, and the E° -values correspond to those applied in Ref. 7.

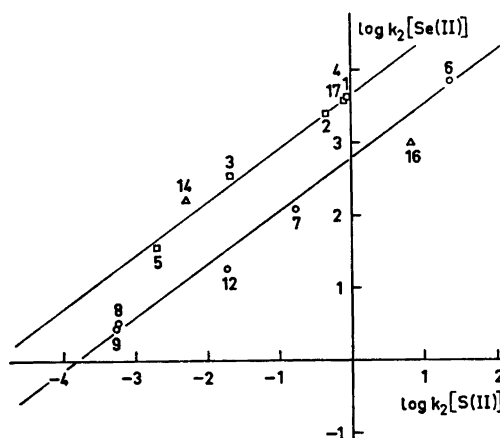
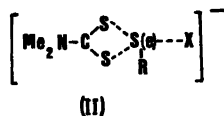


Fig. 2. Logarithm of the rate constants for the reaction of nucleophiles with *o*-nitrobenzeneselenenyl bromide as a function of the logarithm of the rate constants for the reaction of the same nucleophiles with *o*-nitrobenzenesulfonyl chloride. The numbers give the compounds as listed in Tables 2 and 7.

bidentate nucleophiles toward Se(II) at constant reactivity toward S(II).

The fact that the $\log k_2[\text{Se(II)}] - \log k_2[\text{S(II)}]$ correlation splits up into two lines may indicate that the mechanism, or the transition state, is not quite the same for the monodentate and the bidentate nucleophiles in their reactions with substrates of divalent sulfur and selenium. In the case of the monodentate nucleophiles, a transition state of the type (I), which is in agreement with previous studies, probably

occurs with both types of substrate. The bidentate dithio nucleophiles studied in this work have two equivalent donor sulfur atoms. Thus, we may for these suggest a transition state in which both of the donor atoms participate. If we consider the nucleophile, $\text{Me}_2\text{NCS}_2^-$, such a transition state may be represented by (II).



Generally, as central atom, the heaviest atom is the best complex former, and consequently a transition state of this type should be more favourable for Se(II) than for S(II). Thus, the enhancement in the reactivity of the bidentate nucleophiles toward Se(II) relative to S(II), considered in relation to the reactivity of the monodentate thio nucleophiles toward the same substrates, can be explained on the basis of a transition state of the type (II) in the case of Se(II) and a transition state of the type (I), eqn. (1), in the case of S(II).

The above explanation gains support from the crystallographic works by Husebye *et al.*¹²⁻¹⁴

Foss⁵ has suggested to describe the bonding in the transition state in nucleophilic substitution on S(II), Se(II), and Te(II) as a three-center four-electron bonding system. The parallellicity of the lines of the monodentate and the bidentate nucleophiles in Fig. 2 is an indication that the bonding in the transition states (I) and (II) is of the same type, *i.e.*, a three-center four-electron bonding system. The selenium *p*-orbital in the transition state for the reaction between the bidentate dithio nucleophile and selenenyl halides is assumed to overlap with orbitals of both of the donor atoms of the nucleophile. In the product, however, only one of the sulfur atoms may be bonded to the Se atom.

If the difference in the standard free energy changes for the reactions between *o*-NO₂PhSX and two of the nucleophiles is nearly equal to the difference in the standard free energy changes for the reactions between *o*-NO₂PhSeX and the same two nucleophiles, nucleophilic substitution reactions on Se(II) should be less selective than those on S(II) due to the higher rates of the former.¹⁶ This agrees with the

magnitude of the slope of the lines in Fig. 2, slope ≈ 0.72 , which is a value less than 1.

Furthermore, the slope of the lines in Fig. 2 can be related to the ability of the electrophilic centers to form a bonding system of the three-center four-electron type, which is believed to be $\text{S} < \text{Se} < \text{Te}$.⁸

The anionic nucleophiles appear to conform to a rough linearity in the $\log k_2[\text{S(II)}] - E^\circ$ plot, Fig. 1. Since the proton basicities of these differ widely, ($\text{p}K_a \approx -6$ and $\text{p}K_a = 7.5$ in the case of ¹⁷MeSO₂-S⁻ and ¹⁸Ph-S⁻, respectively), the relationship suggests that the proton basicity of the nucleophiles contributes very little in determining the reactivity toward S(II). Consequently, divalent sulfur should be characterized as a soft electrophilic center, in terms of the HSAB language.¹⁹ These findings accord with the conclusion of Kice and Large²⁰ that sulfenyl sulfur is a soft electrophilic center, comparable to peroxide oxygen. Ritter and Krueger¹⁸ have pointed out that although polarizability of the nucleophile is the dominant factor, basicity is also important in nucleophilic substitutions on the trithionate ion.

The present kinetic data also agree with the results of previous exchange reactions of Foss.^{21,22}

$$\log (k_{\text{Nu}}/k_{\text{H}_2\text{O}}) = \alpha E_n + \beta \text{H} \quad (4)$$

In the Edwards¹⁷ equation (4), the kinetic data for nucleophilic substitution on S(II) by anionic nucleophiles, Fig. 1, give $\alpha[\text{S(II)}]$ and $\beta[\text{S(II)}]$ values of ≈ 5.7 and ≈ 0 , respectively. The α and β values for Se(II) have previously been found to be ≈ 3.9 and ≈ 0.7 . Thus, the β values for S(II) and Se(II) are both

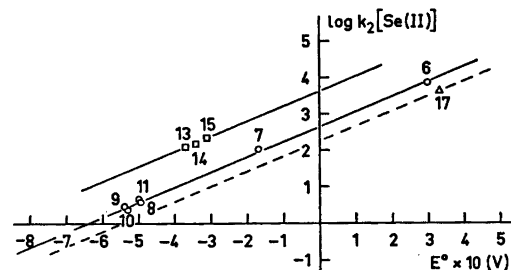


Fig. 3. Logarithm of the rate constants for the reaction of nucleophiles with *o*-nitrobenzeneselenenyl bromide as a function of the oxidation potential of the nucleophile. The numbers give the compounds as listed in Tables 2 and 7.

Table 7. Pseudo-first-order constant, k' , and second-order rate constant, k_2 , for the reaction between $\text{Et}_2\text{NCS}_2^-$ and $o\text{-NO}_2\text{PhSCl}$ and $o\text{-NO}_2\text{PhSeBr}$ in methanol at 25 °C. (R = *o*-nitrophenyl).

No.	Nucleophile	$[\text{Nu}]/10^{-3} \text{ M}$	$k'/10^{-3} \text{ s}^{-1}$	$k_2/\text{M}^{-1} \text{ s}^{-1}$
$\text{R}-\text{S}-\text{Cl} + \text{Nu}^- \rightarrow \text{R}-\text{S}-\text{Nu} + \text{Cl}^-$				
17	$\text{Et}_2\text{NCS}_2^-$	2.13	1.68	0.818
		2.76	2.26	
		4.55	3.74	
$\text{R}-\text{Se}-\text{Br} + \text{Nu}^- \rightarrow \text{R}-\text{Se}-\text{Nu} + \text{Br}^-$				
17	$\text{Et}_2\text{NCS}_2^-$	2.13	8.56	4 050
		2.76	11.1	
		4.55	18.3	

nearly zero, while the α value for S(II) is significantly higher than that for Se(II).

In order to verify if the bidentate dithio nucleophiles fit the $\log k_2 - E^\circ$ correlations of the other thio nucleophiles, Figs. 1 and 3, the rate constants for the reactions between $\text{Et}_2\text{NCS}_2^-$ and the substrates $o\text{-NO}_2\text{PhSCl}$ and $o\text{-NO}_2\text{PhSeBr}$ were determined, Table 7. The oxidation potential of $\text{Et}_2\text{NCS}_2^-$ has been determined by Gregg and Tyler;²³ the value found was +0.33 V. As is seen from Figs. 1 and 3, the point of $\text{Et}_2\text{NCS}_2^-$, No. 17, deviates markedly from the lines of the other anionic thio nucleophiles. Especially in the case of S(II) as electrophilic center, $\text{Et}_2\text{NCS}_2^-$ has a much lower rate constant than predicted from

Table 8. Oxidation potentials, $E^\circ[\text{S(II)}]$ and $E^\circ[\text{Se(II)}]$, for various bidentate dithio nucleophiles estimated on the basis of their rate constants towards $o\text{-NO}_2\text{PhSCl}$ and $o\text{-NO}_2\text{PhSeBr}$ and the dashed lines of Figs. 1 and 3, respectively.

Nucleophile	$E^\circ[\text{S(II)}]/\text{V}$	$E^\circ[\text{Se(II)}]/\text{V}$
$\text{C}_5\text{H}_{10}\text{N}-\text{C}(=\text{S})-\text{S}^-^a$	+0.34	+0.33
$\text{Me}_2\text{N}-\text{C}(=\text{S})-\text{S}^-$	+0.29	+0.28
$\text{Me}_2\text{P}(=\text{S})-\text{S}^-$	+0.065	+0.060
$(\text{EtO})_2\text{P}(=\text{S})-\text{S}^-$	-0.11	-0.19

^a $\text{C}_5\text{H}_{10}\text{N}$ = piperidinyl.

the E° value relative to the other thio nucleophiles. On the assumption that the slope of the line in the $\log k_2[\text{S(II)}] - E^\circ$ plot and in the $\log k_2[\text{Se(II)}] - E^\circ$ plot only depends on the electrophilic center, the oxidation potentials of the other dithio nucleophiles, except for $(\text{EtO})_2\text{PS}_2^-$, correspond very well with each other, Table 8.

Davis²⁴ has presented a theoretical and general justification of the Edwards equation, and he renamed this four-parameter equation the "Oxibase Scale". Davis suggested that this scale could be used in discussing kinetic data concerning nucleophilic substitutions on S(II). However, the experimental data from this work are not in line with this equation. Firstly, the proton basicity of the nucleophile appears to be of negligible effect in determining the reactivity towards S(II) and secondly, there appears to be a correlation between the rate constant and the oxidation potential that changes with the nature of the nucleophile. Thus, concerning S(II) and Se(II) as electrophilic centers, we may then conclude that a simple four-parameter equation analogous to the Edwards equation, is unsuitable in determining the reactivity of the nucleophiles listed in Table 2. Other parameters have to be included.

On the basis of the foregoing discussion, and together with previously published data for nucleophilic substitution on Se(II),⁷ the following conclusions may be drawn.

S(II) as electrophilic center. All types of nucleophiles discussed in this paper, *i.e.*, monodentate and bidentate nucleophiles, probably form a transition state of the type (I). The logarithms of the rate constants of the anionic monodentate nucleophiles, when plotted against their oxidation potentials, conform to a rough linearity. The bidentate dithio nucleophiles probably give a $\log k_2[\text{S(II)}] - E^\circ$ relationship different from that found for other anionic nucleophiles. Neutral nucleophiles, probably due to solvation effects, seem to deviate from these correlations.

Se(II) as electrophilic center. A transition state as pictured by (II) is suggested for the bidentate dithio nucleophiles, while a "normal" transition state of the type (I), appears to occur for the other nucleophiles of Table 2. The bonding in the two transition states (I) and (II) is probably basically of the same type,

i.e., based on a single *p*-orbital of the electrophilic center. Anionic seleno nucleophiles, *i.e.*, di-*O*-alkylmonoselenophosphates, monodentate thio nucleophiles, and bidentate dithio nucleophiles, form different parallel lines in the log $k_2[\text{Se(II)}] - E^\circ$ plot. Neutral nucleophiles, probably due to solvation effects, seem to deviate from these correlations.

Activation parameters. The data in Table 4 show that for the two thio nucleophiles there is a decrease in ΔH^\ddagger and an increase in ΔS^\ddagger as the substrate changes from *o*-NO₂PhSCl to *o*-NO₂PhSeCl. Thus, both ΔH^\ddagger and ΔS^\ddagger are more favourable in the case of the Se(II)-substrate. The decrease in ΔH^\ddagger is the largest factor in causing a higher reactivity of *o*-NO₂PhSeCl.

The decrease in ΔH^\ddagger for the thio nucleophiles, when going from *o*-NO₂PhSCl to *o*-NO₂PhSeCl, points to a more stabilized transition state in the latter case, and furthermore, the increase in ΔS^\ddagger can be related to a more tight transition state in substitution reaction on S(II), relatively to Se(II).

When the leaving group was changed from chloride to bromide, only very small effects on the rate constants in substitution reactions on Se(II) were observed. Table 4 shows that the activation parameters of (NH₂)₂C=S and Me₂NCS₂⁻ are nearly unchanged when chloride is replaced with bromide.

Reaction mechanism. The rate constant of the SCN⁻-*o*-NO₂PhSeBr reaction in methanol at 25°C was observed to be 0.133 M⁻¹ s⁻¹.⁷ By means of Fig. 2 the rate constant of the SCN⁻-*o*-NO₂PhSCl reaction at the same condition can be estimated to $\approx 10^{-5}$ M⁻¹ s⁻¹. This means that when changing the solvent from MeOH to MeCN, the solvent effects on the rate constants can be given by the ratios

$$\frac{k_2[\text{Se(II)}]_{\text{MeCN}}}{k_2[\text{Se(II)}]_{\text{MeOH}}} > 1.5 \times 10^6$$

and

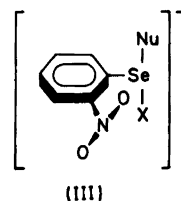
$$\frac{k_2[\text{S(II)}]_{\text{MeCN}}}{k_2[\text{S(II)}]_{\text{MeOH}}} > 2 \times 10^{10}$$

respectively. These tremendous increases in the rate constants observed in MeCN relatively to MeOH, cannot be attributed only to a different solvation of the thiocyanate ion in these solvents, because the thiocyanate ion is only

36 times more reactive toward methyl iodide in MeCN than in MeOH.²⁵ Some other factors associated with the substrates are probably involved.

The intramolecular three-center system, X-S(e)-O, of the present substrates is probably maintained in solution, otherwise a higher reactivity of these substrates would be observed.⁷ Due to a strong solvation of the polar NO₂-group in a protic solvent, such as MeOH, a nucleophilic attack *trans* to the leaving group is probably very hindered. In acetonitrile the NO₂-group is not H-bonded to the solvent, and the nucleophile has only to push the oxygen atom of the nitro group slightly aside in order to get in contact with the chalcogen atom. Thus, supposing a nucleophilic attack *trans* to the leaving group, a large solvent effect is to be expected. A mechanism involving an attack at the chalcogen atom normal to the plane of the molecule would probably not lead to such a large solvent effect on the rate of reaction.

Thus, the present results together with previously published and discussed data,⁷ suggest the mechanism of the reaction between *o*-nitrobenzenesulfonyl and *o*-nitrobenzeneselenenyl halides and nucleophilic reagents to involve a nucleophilic attack *trans* or nearly *trans* to the leaving group, accompanied by a synchronous rotation about the chalcogen-carbon bond. The transition state may be represented by (III).



The above view concerning the solvation of *o*-NO₂PhS(e)X in protic solvents may also explain the unusual stability of these compounds in protic solvents, relatively to the unsubstituted analogous.²⁶

o-Nitrobenzenesulfonyl (-selenenyl) substrates that have leaving groups with larger *trans* bonding-lengthening effects than Cl and Br, are expected to form a less stable intramolecular three-center system, X-S(e)-O.⁸ The chalcogen-oxygen bond is then weakened, and in

solution a rotation about the chalcogen-carbon bond may occur, causing a higher reactivity of these types of substrates. This will be discussed in a later paper.²⁷

EXPERIMENTAL

Solvents. Methanol "Merck" *p.a.* was used without further purification. Acetonitrile was purified as reported by Coetzee.²⁹

Substrates. *o*-Nitrobenzenesulfonyl chloride "Fluka" *puriss.* was recrystallized from light petroleum (40–60°C). *o*-Nitrobenzeneselenenyl chloride was kindly provided by Mr. R. Eriksen.³⁰ *o*-Nitrobenzeneselenenyl bromide was synthesized from *o*-nitrophenyl selenocyanate and excess of bromine in dry chloroform.³¹ The product was recrystallized three times from light petroleum (40–60°C).

Nucleophiles. The following nucleophiles were employed: (Piperidyl) $\text{CS}_2\text{Na}_2 \cdot 2\text{H}_2\text{O}$,³² $\text{Me}_2\text{NCS}_2\text{Na} \cdot 3\text{H}_2\text{O}$,³² $\text{Et}_2\text{NCS}_2\text{Na} \cdot 3\text{H}_2\text{O}$,³² $\text{Me}_2\text{PS}_2\text{Na} \cdot 2\text{H}_2\text{O}$,³³ $(\text{EtO})_2\text{PS}_2\text{NH}_4$,³⁴ PhSNa , $(\text{PhAs})_2\text{S}_2\text{O}_3$,⁷ $\text{Me}_4\text{NPhSO}_3\text{S}$, $\text{Me}_4\text{NMeSO}_3\text{S}$, $(\text{EtO})_2\text{P}(\text{O})\text{SeNa}$,³⁵ Ph_4AsCN ,³⁶ and $(\text{NH}_4)_2\text{C}=\text{S}$ ("Fluka" *puriss. p.a.*) Sodium thiophenolate was prepared *in situ* by dissolving equivalent amounts of thiophenol and sodium in methanol. $\text{Me}_4\text{N PhSO}_3\text{S}$ and $\text{Me}_4\text{N MeSO}_3\text{S}$ were prepared from the respective potassium salts and dry Me_4NCl in methanol. KCl separated and was filtered off. The solvent was removed in vacuum. $\text{Me}_4\text{NPhSO}_3\text{S}$ was recrystallized from methanol. M.p. 182°C. (Found: S 25.83. Calc. for $\text{C}_{16}\text{H}_{17}\text{NO}_3\text{S}_2$: S 25.88). $\text{Me}_4\text{NMeSO}_3\text{S}$ was recrystallized from acetonitrile. M.p. 275°C. (Found: S 34.75. Calc. for $\text{C}_6\text{H}_5\text{NO}_3\text{S}_2$: S 35.55).

Products. The compounds Nos. 1, 2, 3, and 4 of Table 1 were synthesized by the general procedure described by Foss³⁷ for preparing *o*-nitrobenzeneselenenyl sulfur compounds.

The compounds Nos. 7, 8, and 9 were prepared in a similar way, as above, using ethyl acetate and methanol, but in these cases the compounds did not crystallize spontaneously. Potassium or sodium salts of the nucleophiles and *o*-nitrobenzenesulfonyl chloride were used. The reaction mixtures were evaporated to dryness in vacuum, and the salts were separated from the products by means of chloroform in the case of Nos. 7 and 8 and ether in the case of No. 9.

The unsymmetrical disulfide, compound No. 5, was prepared by using acetic acid as solvent as proposed by Happer, Mitchell and Wright.³⁸ 2.20 g of thiophenol was dissolved in 8 ml of glacial acetic acid, and 3.77 g of *o*-nitrobenzenesulfonyl chloride was dissolved in 50 ml of glacial acetic acid. The thiol solution was added to the sulfonyl chloride solution, and the reaction mixture was stirred for 15 min at room temperature. The solvent was removed in vacuum, and the compound appeared as an

oily substance. On dissolving in diethyl ether and cooling in a dry-ice acetone bath, pure crystalline material was obtained, yield 4.07 g or 78%, based on the amount of sulfonyl chloride.

Compounds Nos. 10 and 12, Table 1, were prepared as reported previously.^{39,28} Compound No. 11 was synthesized in the same way as described for the analogous selenium compound.⁷

The tetraphenylarsonium salt of the *o*-nitrobenzenesulfonyl thiosulfate ion, compound No. 6, was prepared from *o*-nitrobenzenesulfonyl thiocyanate, sodium thiosulfate, and tetraphenylarsonium chloride according to the following procedure. 1.06 g of sulfonyl thiocyanate (5×10^{-3} mol) was dissolved in a mixture of 8 ml of ethyl acetate and 4 ml of methanol. 1.36 g of $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ (5.5×10^{-3} mol) and 2.40 g $\text{Ph}_4\text{AsCl} \cdot \text{H}_2\text{O}$ (5.5×10^{-3} mol) were dissolved in about 25 ml of water. The sulfonyl thiocyanate solution was added to the aqueous salt solution under vigorous stirring for 5 min, during which the Ph_4As -salt of the *o*-nitrobenzenesulfonyl thiosulfate ion precipitated as a yellowish-green substance, which was filtered off, washed carefully with water, and drained. The compound was recrystallized from acetonitrile by the addition of some ether. Yield, 2.58 g, or 80% based on the amount of *o*-nitrobenzenesulfonyl thiocyanate.

The products of the reactions using *o*-nitrobenzeneselenenyl halides as substrates have been synthesized previously.⁷

Kinetics. The reaction between *o*-nitrobenzenesulfonyl chloride and the various nucleophiles was in most cases followed by measuring the decrease in the absorption at 410 nm with a Beckman spectrophotometer, using 1 cm thermostated cells. In the case of the two strongest nucleophiles, *i.e.*, Ph-S^- and CN^- , the rate was determined with a Durrum stopped-flow spectrophotometer. The kinetic runs were performed under pseudo-first order conditions, with excess of nucleophile. The substrate concentration was about $(2-4) \times 10^{-5}$ M. The plots of $\log(D_\infty - D_t)$ against time gave in all cases straight lines, and the pseudo-first order rate constants k' , were determined from these diagrams. The second-order rate constants, k_2 , were calculated from the slope of the best straight line through the origin in the $k' - [\text{Nu}]$ plots.

The rate of the reaction between *o*-nitrobenzeneselenenyl halides and the various nucleophiles was followed at $\lambda = 430$ nm applying the stopped-flow technique. The kinetic runs were performed under the same conditions as described earlier.⁷

The activation parameters were determined from the best straight line plots of $\log k_2$ against $1/T$.

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