

## Nucleophilic Substitutions on *o*-Nitrobenzeneselenenyl Halogenides (Cl and Br). A Kinetic Study

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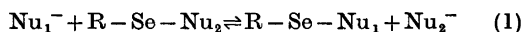
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The rate of reaction between *o*-nitrobenzeneselenenyl halogenides (Cl and Br) and 20 different nucleophiles has been measured in methanol using a stopped-flow spectrophotometer. For each of the nucleophiles examined, the kinetic plots showed the reaction to be of second order, first order in each of the reactants. A linear relationship between  $\log k_2$  and  $E^\circ$  (oxidation potential) was established for anionic nucleophiles having the same nucleophilic atom. The proton basicity of the nucleophile was found to be negligible in determining the reactivity towards  $\text{Se}^{\text{II}}$ , and within the experimental errors the rate constants were found to be the same when changing the leaving group from bromide to chloride. The mechanism has been discussed in terms of previous studies concerning substitution reactions on *o*-nitrobenzenesulfenyl substrates.

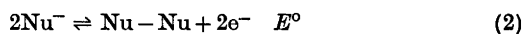
Nucleophilic substitution reactions on divalent selenium are generally believed to be much faster than the analogous reactions on divalent sulfur. Thus, kinetic studies involving nucleophilic substitutions on  $\text{Se}^{\text{II}}$  are far less numerous than those on divalent sulfur. Due to the large decrease in the rate of reaction between two negatively charged ions observed in a dipolar aprotic solvent as compared with a protic solvent,<sup>1</sup> kinetic experiments of the reaction between various polythionates containing divalent selenium atoms in the chain ( $^-\text{O}_3\text{S}-\text{Se}-\text{SO}_3^-$ ,  $^-\text{O}_3\text{S}-\text{Se}-\text{Se}-\text{SO}_3^-$ , and  $^-\text{O}_3\text{S}-\text{S}-\text{Se}-\text{S}-\text{SO}_3^-$ ) and ionic cyanide have successively been performed in acetonitrile.<sup>2,3</sup> Apart from these studies, no systematic kinetic work concerning nucleophilic attack on  $\text{Se}^{\text{II}}$  has been reported in the literature until now.

However, a number of nucleophilic displacement reactions on divalent selenium are known,

and a relative measure of the selenophilicity of various seleno bases has been obtained by studying systems of the type depicted by eqn. 1.<sup>4-6</sup>



With regard to nucleophilic attack on  $\text{S}^{\text{II}}$ , Foss<sup>7,8</sup> has pointed out that the reactivity of thio nucleophiles increases in the order of increasing oxidation potential of the systems:



that is, the nucleophilic reactivity increases with increasing ease of oxidation of the thio anion to the corresponding disulfide. Data from displacement reactions on  $\text{Se}^{\text{II}}$  appear to indicate a similar relationship.<sup>4-6,9</sup>

Sulfenyl sulfur has been characterised as a soft electrophilic centre, comparable to peroxide oxygen.<sup>10</sup> In nucleophilic substitution on the sulfenyl sulfur atom of the trithionate ion,  $^-\text{O}_3\text{S}-\text{S}-\text{SO}_3^-$ , in 50 wt % methanol-water, Ritter and Krueger<sup>11</sup> have pointed out that although polarizability of the nucleophile is the dominant factor, basicity is also important. According to the HSAB principle,<sup>12</sup> divalent selenium is believed to be an even softer electrophilic centre than divalent sulfur. Consequently, the hydrogen basicity of the nucleophile, as a factor determining the reactivity, is supposed to be less important for divalent selenium than for divalent sulfur.

Many equilibrium and kinetic studies concerning nucleophilic attack on  $\text{S}^{\text{II}}$  are available. It therefore appears reasonable to discuss kinetic data involving displacement on  $\text{Se}^{\text{II}}$  in relation to previous studies on  $\text{S}^{\text{II}}$ . The kinetic

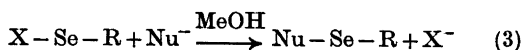
data so far<sup>2,3</sup> indicate that nucleophilic substitutions on Se<sup>II</sup> follow the same mechanism as proposed for nucleophilic attack on S<sup>II</sup>, which in most cases is believed to fit a synchronous bimolecular mechanism.<sup>13</sup> This is in agreement with the crystal structures of a number of selenium(II) complexes which have been determined.<sup>14-16</sup> The complexes may, according to Foss,<sup>17</sup> be regarded as reaction intermediates or models for the transition state in nucleophilic substitution on Se<sup>II</sup>.

In this paper we wish to report a kinetic study on the reaction between *o*-nitrobenzeneselenenyl halogenides (Br and Cl) and 20 different nucleophiles in methanol. The main purpose of the work is to obtain a quantitative measure for the nucleophilicity of the various seleno bases towards Se<sup>II</sup>, and to shed further light on the factors determining reactivity. Finally the reaction mechanism will be discussed.

## RESULTS

The substrate *o*-nitrobenzeneselenenyl halogenide was chosen because the products are

stable and many of them have been synthesised previously.<sup>18</sup> The products of the reaction between the various nucleophiles and the substrate, reaction (3), are listed in Table 1.



where R = *o*-nitrophenyl and X = Cl or Br

In all cases the reaction 3 showed excellent second order kinetics, first order in each of the reactants. The rate of reaction was followed at 430 nm applying a stopped-flow spectrophotometer. The experimental data on the reaction between *o*-nitrobenzeneselenenyl bromide and the various nucleophiles are tabulated in Table 2.

The nucleophilicity of the dithiocarbamates (Nos. 1 and 2) appears to be very much affected by the organic moiety linked to the nitrogen atom, and it seems to parallel the basicity of the corresponding secondary amines. The  $pK_a$  values of piperidine and dimethylamine are 11.12 and 10.73, respectively.

The di-*O*-ethylthiophosphate ion (No. 8) is more than twice as nucleophilic towards Se<sup>II</sup> as is the corresponding di-*O*-methyl anion (No.

Table 1. Products of the reaction between various nucleophiles and *o*-nitrobenzeneselenenyl bromide.

No.	Compound (R = <i>o</i> -nitrophenyl)	Ref.	M.p. °C <sup>b</sup>
1	R-Se-S-C(S)-(piperidyl)	<sup>a</sup>	148 (lit. 134) <sup>c</sup>
2	R-Se-S-C(S)-N(Me) <sub>2</sub>	<sup>a</sup>	189
3	R-Se-S-Ph	20	54-55
4	R-Se-CN	21	143
5	R-Se-S <sub>2</sub> O <sub>3</sub> K	18	ca. 190 dec.
6	R-Se-S-P(S)Me <sub>2</sub>	<sup>a</sup>	117
7	R-Se-S-P(S)(OMe) <sub>2</sub>	<sup>a</sup>	89
8	R-Se-S-SP(S)(OEt) <sub>2</sub>	<sup>a</sup>	62
9	R-Se-S-P(O)(OEt) <sub>2</sub>	18	Oil
10	R-Se-S-P(O)(O-iPr) <sub>2</sub>	<sup>a</sup>	Oil
11	R-Se-Se-P(O)(OMe) <sub>2</sub>	<sup>a</sup>	42
12	R-Se-Se-P(O)(OEt) <sub>2</sub>	<sup>a</sup>	Oil
13	R-Se-Se-P(O)(O-iPr) <sub>2</sub>	<sup>a</sup>	Oil
14	R-Se-S-SO <sub>2</sub> -Me	18	96
15	R-Se-S-SO <sub>2</sub> -Ph	18	147
16	R-Se-SCN	18	107
17	R-Se-SeCN	22	109-110
18	R-Se-S-C(NH <sub>2</sub> ) <sub>2</sub> Br	<sup>a</sup>	199
19	R-Se-Se-C(NH <sub>2</sub> ) <sub>2</sub> Br	<sup>a</sup>	216
20	R-Se-SO <sub>2</sub> -Ph	18	109

<sup>a</sup> This work. <sup>b</sup> The values of the melting points correspond with those given in the references quoted. <sup>c</sup> Ref. 19.

Table 2. Pseudo-first-order rate constant ( $k$ ) and second-order rate constant ( $k_2$ ) for the reaction between *o*-nitrobenzeneselenenyl bromide and different nucleophiles in methanol at 25 °C.

No.	Nucleophile	[Nu] × 10 <sup>3</sup> M	$k$ s <sup>-1</sup>	$k_2$ M <sup>-1</sup> s <sup>-1</sup>	$E^{\circ a}$ (V)																																																																																																																												
1	(piperidyl)-C(=S)-S <sup>-</sup>	0.50	22.4	4200	(+0.25)																																																																																																																												
		1.00	41.5			2	(Me) <sub>2</sub> N-C(=S)-S <sup>-</sup>	0.399	11.5	2667	(+0.21)	0.798	22.6	1.59	43.9	2.40	64.3	3	Ph-S <sup>-</sup>	0.585	40.1	7000	+0.3 <sup>b</sup>	1.17	76.5	2.33	170.2	4	CN <sup>-</sup>	0.50	3.58	994	+0.19 <sup>b</sup>	1.00	8.64	2.00	18.7	3.00	30.0	5	S <sub>2</sub> O <sub>3</sub> <sup>2-</sup>	0.30	0.376	125	-0.169 <sup>c</sup>	0.35	0.425	0.40	0.505	6	(Me) <sub>2</sub> P(=S)-S <sup>-</sup>	0.50	1.75	350	(-0.03)	1.00	3.66	2.00	7.08	3.00	10.43	7	(MeO) <sub>2</sub> P(=S)-S <sup>-</sup>	0.50	0.0854	14.5	(-0.37)	1.00	0.144	2.00	0.293	3.00	0.443	4.00	0.559	8	(EtO) <sub>2</sub> P(=S)-S <sup>-</sup>	0.50	0.150	35.3	(-0.28)	1.00	0.366	2.00	0.682	3.00	1.18	4.00	1.59	9	(EtO) <sub>2</sub> P(=O)-S <sup>-</sup>	1.00	0.0207	1.97	-0.53 <sup>d</sup>	2.00	0.0408	3.00	0.0573	10	(iPrO) <sub>2</sub> P(=O)-S <sup>-</sup>	0.50	0.0247	4.57	-0.50 <sup>d</sup>	1.00	0.0493	2.00	0.0939	3.00	0.136	11	(MeO) <sub>2</sub> P(=O)-Se <sup>-</sup>	0.50	0.439	120	-0.37 <sup>d</sup>	1.00	1.09	2.00	2.47	3.00	3.56	12	(EtO) <sub>2</sub> P(=O)-Se <sup>-</sup>	0.50	0.859	160	-0.34 <sup>d</sup>
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Table 2. Continued.

13	$\begin{array}{c} \text{O} \\    \\ (\text{iPrO})_2\text{P}-\text{Se}^- \end{array}$	0.50	1.21	222	-0.31 <sup>d</sup>
		1.00	2.21		
		2.00	4.48		
		3.00	6.67		
14	$\begin{array}{c} \text{O} \\    \\ \text{Me}-\text{S}-\text{S}^- \\    \\ \text{O} \end{array}$	1.00	0.0305	2.82	-0.54 <sup>e</sup>
		2.00	0.0566		
		3.00	0.0848		
		4.00	0.110		
15	$\begin{array}{c} \text{O} \\    \\ \text{Ph}-\text{S}-\text{S}^- \\    \\ \text{O} \end{array}$	0.50	0.0148	3.25	-0.49 <sup>e</sup>
		2.00	0.0683		
16	SCN <sup>-</sup>	1.00	0.00158	0.133	-0.77 <sup>f</sup>
		2.00	0.00519		
		4.00	0.00286		
17	SeCN <sup>-</sup>	0.50	0.00887	1.73	≈ -0.57 <sup>g</sup>
		1.00	0.0173		
18	(NH <sub>2</sub> ) <sub>2</sub> C=S	0.50	0.313	53.3	-0.42 <sup>h</sup>
		1.00	0.545		
		2.00	1.01		
		3.00	1.61		
19	(NH <sub>2</sub> ) <sub>2</sub> C=Se	0.50	11.9	2625	-0.24 <sup>i</sup>
		1.00	27.8		
		2.00	53.6		
20	$\begin{array}{c} \text{O} \\    \\ \text{Ph}-\text{S} \\    \\ \text{O} \end{array}$	0.25	0.00487	2.05	
		0.50	0.0108		
		1.00	0.0203		
		2.00	0.0407		

<sup>a</sup> The values in parentheses are estimated from  $k_2$  and Fig. 1. <sup>b</sup> Ref. 11. <sup>c</sup> Ref. 23, <sup>d</sup> Ref. 24, <sup>e</sup> Refs. 8 and 25, <sup>f</sup> Ref. 26, <sup>g</sup> Ref. 27, <sup>h</sup> Ref. 28, <sup>i</sup> Ref. 29.

7), which suggests that the nucleophilic nature

of the group  $\begin{array}{c} \text{S} \\ || \\ -\text{P}-\text{S}^- \end{array}$  is very sensitive to electronic effects. The high reactivity of the dimethyldithiophosphinate ion (No. 6) relatively to the above mentioned dithiophosphates, indicates that the inductive effect caused by the oxygen atoms in compounds Nos. 7 and 8 is superior to the mesomeric backbonding effect.

With regard to the reactivity of the di-*O*-alkylmonothiothiophosphates, Nos. 9 and 10, and the seleno analogues, Nos. 12 and 13, Table 2 shows that the nucleophilicities of these anions are also very sensitive to the organic moiety.

The seleno nucleophiles are more powerful nucleophilic agents towards Se<sup>II</sup> than are the corresponding thio nucleophiles, by a factor of nearly 100.

The difference in the nucleophilic nature of seleno and thio nucleophiles is, however, smaller in the case of the selenocyanate ion (No. 17) and the thiocyanate ion (No. 16). The former is about 13 times more reactive towards Se<sup>II</sup> than is the latter.

The small difference in the rate constants of the methanethiosulfonate ion (No. 14) and the benzenethiosulfonate ion (No. 15), shows that the electronic arrangement on the thiosulfonate group, -SO<sub>2</sub>-S<sup>-</sup>, is very little affected by the

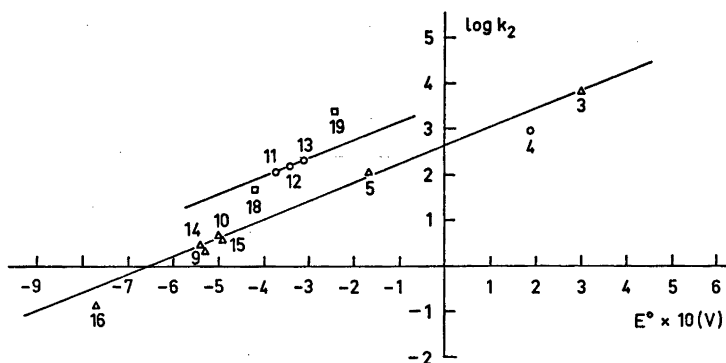
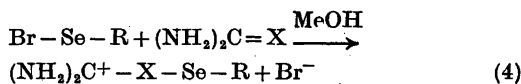


Fig. 1. Logarithm of the rate constants for the reaction of nucleophiles with *o*-nitrobenzeneselenyl bromide as a function of the oxidation potential of the nucleophile. The numbers correspond to those listed in Table 2.

organic group attached to the sulfonyl sulfur atom.

Table 2 further shows that the thiophenolate ion (No. 3) is the strongest nucleophile, and that the cyanide ion is nearly 10 times more nucleophilic than the thiosulfate ion. It is further seen that the rate constants of the benzenesulfinate ion (No. 20) and the selenocyanate ion (No. 17) are nearly identical in methanol.

In the case of the two neutral nucleophiles, *i.e.*, thiourea (No. 18) and selenourea (No. 19), the reaction product is a salt, eqn. 4.



where R = *o*-nitrophenyl and X = S or Se. According to Table 2, selenourea is about 50 times more reactive than thiourea.

The column to the right in Table 2 contains the oxidation potentials for the nucleophiles. The values which are placed in parentheses are estimated by means of the second order rate constants and Fig. 1. In all cases the oxidation potentials are based on the system represented by eqn. 2. In order to verify if there exists any relationship between  $k_2$  and  $E^\circ$ , a graphical representation of  $\log k_2$  versus  $E^\circ$  was made, Fig. 1.

The figure shows that the thio nucleophiles Ph-S<sup>-</sup>, S<sub>2</sub>O<sub>3</sub><sup>2-</sup>, (iPrO)<sub>2</sub>P(O)-S<sup>-</sup>, Me-SO<sub>2</sub>-S<sup>-</sup>, and (EtO)<sub>2</sub>P(O)-S<sup>-</sup> appear to conform to a linear relationship between  $\log k_2$  and  $E^\circ$ . With

regard to the di-*O*-alkylmonoselenophosphates, Fig. 1 clearly shows that these nucleophiles give a relationship different from that found for the thio nucleophiles. The values of the second order rate constants for the seleno nucleophiles are higher than predicted by the oxidation potentials relatively to the thio nucleophiles.

However, all the thio nucleophiles do not lie on the same line in the  $\log k_2 - E^\circ$  plot. Thiourea has a higher value of  $k_2$  than predicted by the oxidation potential, while  $k_2$  of the thiocyanate ion is lower than expected from the  $E^\circ$  value. The same trend is also found for the analogous seleno nucleophiles, *i.e.*, selenourea has a higher reactivity and selenocyanate a lower one than expected from their  $E^\circ$  values relatively to the di-*O*-alkylmonoselenophosphates.

The effect on the rate constants when changing the leaving group from bromide to chloride has been studied for some of the nucleophiles. The experimental data for the reaction between *o*-nitrobenzeneselenenyl chloride and five different nucleophiles are listed in Table 3. Table 4 clearly shows that when changing the leaving group from bromide to chloride, the effect on the second order rate constant is rather small. In all cases the ratio  $k_2(\text{Br})/k_2(\text{Cl})$  is close to 1.

Second order rate constants for 6 of the nucleophiles have also been determined at different temperatures, 15, 25, 30, and 35 °C, and activation parameters have been calculated, Tables 5 and 6. It is seen that both the enthalpy and entropy of activation change

Table 3. Pseudo-first-order rate constant ( $k'$ ) and second-order rate constant ( $k_2$ ) for the reaction between *o*-nitrobenzeneselenenyl chloride and different nucleophiles in methanol at 25 °C.

Nucleophile	Nu $\times 10^2$ M	$k'$ S <sup>-1</sup>	$k_2$ M <sup>-1</sup> s <sup>-1</sup>
S <sub>2</sub> O <sub>3</sub> <sup>2-</sup>	0.25	0.285	128
	0.50	0.643	
	1.00	1.213	
(MeO) <sub>2</sub> P(=O)-Se <sup>-</sup>	0.50	0.392	90.0
	1.00	0.892	
	2.00	0.208	
(iPrO) <sub>2</sub> P(=O)-S <sup>-</sup>	0.50	0.0332	5.0
	1.00	0.0522	
	2.00	0.0971	
(iPrO) <sub>2</sub> P(=O)-Se <sup>-</sup>	0.50	1.05	202
	1.00	2.02	
	2.00	4.16	
CN <sup>-</sup>	0.50	4.00	1066
	1.00	9.24	
	2.00	20.5	

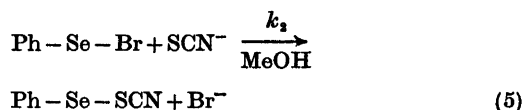
drastically when going from an ionic nucleophile to a neutral one.

Finally some attempts were made to study kinetically the reaction between benzeneselenenyl bromide and the above mentioned nucleophiles in methanol, but in all cases the rate was too high. Even when using the weakest nucleophilic agent of Table 2, SCN<sup>-</sup>, the reaction

Table 4. The effect of the leaving group in nucleophilic substitution on *o*-nitrobenzeneselenenyl bromide (chloride) in methanol at 25 °C.

Nucleophile	$k_2$ (Br) M <sup>-1</sup> s <sup>-1</sup>	$k_2$ (Cl) M <sup>-1</sup> s <sup>-1</sup>	$\frac{k_2(\text{Br})}{k_2(\text{Cl})}$
S <sub>2</sub> O <sub>3</sub> <sup>2-</sup>	125	128	0.97
(MeO) <sub>2</sub> P(=O)-Se <sup>-</sup>	120	90	1.33
(iPrO) <sub>2</sub> P(=O)-S <sup>-</sup>	4.57	5.0	0.91
(iPrO) <sub>2</sub> P(=O)-Se <sup>-</sup>	160	202	1.10
CN <sup>-</sup>	994	1066	0.93

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 reaction 5 is  $k_2 > 6 \times 10^4$  M<sup>-1</sup> s<sup>-1</sup>. Thus, upon changing the substrate from *o*-nitrobenzeneselenenyl bromide to benzeneselenenyl bromide, the second order rate constant of the thiocyanate ion increases at least by a factor of 10<sup>6</sup>.

## DISCUSSION

The data listed in Table 2 show that the relative order of reactivity of the anionic thio nucleophiles towards *o*-nitrobenzeneselenenyl halogenide is completely consistent with the nucleophilic sequence previously reported on the basis of exchange reactions on S<sup>II</sup>, Se<sup>II</sup> and Te<sup>II</sup> in protic solvents.<sup>4-8</sup> The nucleophilicity progressively increases in the order: SCN<sup>-</sup> < (EtO)<sub>2</sub>P(O)-S<sup>-</sup> < Me-SO<sub>2</sub>-S<sup>-</sup> < Ph-SO<sub>2</sub>-S<sup>-</sup> < (iPrO)<sub>2</sub>P(O)-S<sup>-</sup> < (MeO)<sub>2</sub>P(S)-S<sup>-</sup> <

Table 5. 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 <sup>2</sup> M	15 °C		25 °C		30 °C		35 °C	
		$k'$ s <sup>-1</sup>	$k_2$ M <sup>-1</sup> s <sup>-1</sup>	$k_2$ M <sup>-1</sup> s <sup>-1</sup>	$k'$ s <sup>-1</sup>	$k_2$ M <sup>-1</sup> s <sup>-1</sup>	$k'$ s <sup>-1</sup>	$k_2$ M <sup>-1</sup> s <sup>-1</sup>	
(NH <sub>2</sub> ) <sub>2</sub> C=S	0.5	0.252			0.333		0.363		
	1.0	0.521	48.9	53.3	0.609	60.5	0.672	66.9	
	2.0	0.912			1.14		1.27		
$\begin{array}{c} \text{O} \\ \parallel \\ (\text{iPrO})_2\text{P}-\text{S}^- \end{array}$	0.5	0.0151			0.0365		0.0432		
	1.0	0.0313	3.08	4.57	0.0627	6.10	0.0927	8.39	
	2.0	0.0608			0.118		0.152		
$\begin{array}{c} \text{O} \\ \parallel \\ (\text{iPrO})_2\text{P}-\text{Se}^- \end{array}$	0.5	0.648			1.26		1.49		
	1.0	1.33	133	222	2.52	250	3.00	305	
	2.0	2.67			4.85		6.11		
CN <sup>-</sup>	0.5	2.29			5.36		6.80		
	1.0	4.60	500	994	11.0	1110	14.6	1460	
	2.0	10.8			25.1		33.8		
(NH <sub>2</sub> ) <sub>2</sub> C=Se	0.5	9.24			13.7		15.20		
	1.0	19.8	1950	2625	29.7	2820	33.1	3225	
	2.0	38.8			55.6		61.5		

(EtO)<sub>2</sub>P(S)–S<sup>-</sup> < S<sub>2</sub>O<sub>3</sub><sup>2-</sup> < Me<sub>2</sub>P(S)–S<sup>-</sup> < Me<sub>2</sub>N–C(S)–S<sup>-</sup> < (piperidyl)–C(S)–S<sup>-</sup> < Ph–S<sup>-</sup>.

Among the thio nucleophiles whose oxidation potentials are known, there appears to be a linear correlation between log  $k_2$  and  $E^\circ$ , Fig. 1. On the basis that the proton basicity of these nucleophiles differs widely ( $pK_a \approx -6$  and  $pK_a = 7.5$  in the case of Me–SO<sub>2</sub>–S<sup>-</sup> and Ph–S<sup>-</sup>, respectively), this relationship suggests that the proton basicity of the nucleophiles does not play any role in substitution reactions on Se<sup>II</sup>.

One may notice that two of the thio nucleophiles, *i.e.*, the thiocyanate ion and especially

Table 6. Activation parameters for the reaction between *o*-nitrobenzeneselenenyl bromide and various nucleophiles in methanol at 25 °C.

Nucleophile	$\Delta H^*$ kcal/ mol	$\Delta S^*$ cal/ mol deg.	$\Delta F^*$ kcal/ mol
(NH <sub>2</sub> ) <sub>2</sub> C=S	3.3	-40	15.2
(NH <sub>2</sub> ) <sub>2</sub> C=Se	3.7	-30	12.8
(iPrO) <sub>2</sub> P(O)–S <sup>-</sup>	10.4	-21	16.7
(iPrO) <sub>2</sub> P(O)–Se <sup>-</sup>	6.8	-25	14.2
CN <sup>-</sup>	8.7	-16	13.4

thiourea do not appear to fit the log  $k_2$ – $E^\circ$  relationship represented by the other thio nucleophiles. Due to the instability of thiocyanogen, (SCN)<sub>2</sub>, in aqueous solution, the experimental  $E^\circ$ -value<sup>26</sup> of the thiocyanate ion may perhaps be too high, and this may explain the discrepancy. Thiourea, being an uncharged nucleophile, probably is far less solvated in methanol than the other anionic thio nucleophiles, and therefore, according to Parker,<sup>30</sup> it may be a relatively stronger nucleophilic reagent towards Se<sup>II</sup>. However, within these limitations the fit is very good.

The present results are in agreement with the findings of Foss<sup>7-8</sup> that in displacement reactions on divalent sulfur, thio anions of more positive  $E^\circ$  will displace thio anions of lower  $E^\circ$ .

Oxidation potentials of other thio anions may then be estimated by means of the second order rate constant and Fig. 1. The oxidation potentials of the nucleophiles (piperidyl)–C(S)–S<sup>-</sup>, Me<sub>2</sub>NC(S)–S<sup>-</sup>, Me<sub>2</sub>P(S)–S<sup>-</sup>, (MeO)<sub>2</sub>P(S)–S<sup>-</sup>, and (EtO)<sub>2</sub>P(S)–S<sup>-</sup> have been determined in this way, Table 2. The oxidation potential of the diethyldithiocarbamate ion has been measured as +0.33 V in 60 % ethanol by Gregg and Tyler.<sup>31</sup> The estimated  $E^\circ$  values of the dithiocarbamates in this work are somewhat lower.

The relationship between  $\log k_2$  and  $E^\circ$  is not a general one that applies for all type of nucleophiles. This is clearly demonstrated by the di-*O*-alkylmonoselenophosphates which appear to make their own correlation, Fig. 1. However, the slopes of the lines that correspond to the thio nucleophiles and the seleno nucleophiles are similar. On the basis that the hydrogen basicity of the nucleophile is negligible in determining the reactivity towards  $\text{Se}^{\text{II}}$ , it is not possible to explain why the thio and the seleno nucleophiles form different  $\log k_2 - E^\circ$  plots by discussing the data in terms of the Edwards<sup>22</sup> equation (6).

$$\log (k_{\text{Nu}}/k_{\text{H}_2\text{O}}) = \alpha E_n + \beta H \quad (6)$$

According to Edwards,<sup>22</sup>  $E_n$  and  $H$  are the nucleophilic and basic constants for the nucleophiles, and  $\alpha$  and  $\beta$  are the corresponding substrate constants. In the case of *o*-nitrobenzeneselenenyl bromide the present work gives  $\alpha$  and  $\beta$  values of  $\approx 3.9$  and  $\approx 0$ , respectively. The fact that the anionic thio nucleophiles and the seleno nucleophiles provide different  $\log k_2 - E^\circ$  plots, and the deviation of the points that correspond to thiourea and selenourea from these lines, suggests that a general representation of the nucleophilicity towards various substrates should contain at least two more parameters related to the nucleophiles. Concerning  $\text{Se}^{\text{II}}$  as the electrophilic centre, we may then conclude that the Edwards equation is unsuitable for determining the reactivity of the nucleophiles listed in Table 2.

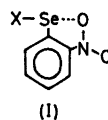
The rate at which a nucleophile attacks a carbon atom sometimes parallels the affinity of the nucleophile for protons. Especially in a series of anions whose reactivity atom is the same, the connection between rate constant and  $\text{p}K_a$  values of the nucleophiles is well established.<sup>23</sup> Concerning a softer electrophilic centre, *i.e.*,  $\text{Se}^{\text{II}}$ , the present data indicate that there exists an analogous relation between the rate constant and the oxidation potential that changes with the nature of the nucleophilic atom and with the charge on the nucleophile.

The nucleophilic reactivity of the cyanide ion towards  $\text{Se}^{\text{II}}$  in methanol, in terms of its oxidation potential, is more like the reactivity of thio nucleophiles than of the seleno nucleophiles, Fig. 1.

## Reaction mechanism

Both structural<sup>14-16</sup> and kinetic<sup>2,3</sup> data point to a nucleophilic attack on  $\text{Se}^{\text{II}}$  *trans* to the leaving group, followed by synchronous bond formation and breaking. Foss<sup>17</sup> has described the bonding in the transition state as a three-centre-four-electron bonding system.

*o*-Nitrobenzeneselenenyl compounds, like the analogous thio compounds, are usually found to be more stable than the unsubstituted compounds. This property of the *ortho*-substituted compounds is probably due to the formation of an intramolecular three-centre arrangement containing one of the oxygen atoms of the nitro group, the chalcogen atom, and the atom attached to the latter (I).<sup>24</sup>



Thus, in the present substrate the position *trans* to the leaving group is already occupied by an intramolecular interaction between Se and O. In order to attack *trans* to the leaving group, the intramolecular three-centre arrangement of the substrate has to break down in solution, or if the three-centre-system is still maintained in solution, the nucleophile has to push the nitro group aside. In the latter case there will be an additional energy term for the three-centre formation between the nucleophile, the selenium atom, and the leaving group. Thus, the free energy of activation in the case of the *ortho*-nitro substrate should be higher than in the case of the unsubstituted substrate. The present kinetic experiments on the reaction between unsubstituted benzeneselenenyl bromide and ionic thiocyanate, which is believed to follow a synchronous mechanism, are in line with these statements.

On the other hand, a mechanism involving a rate determining break-down of the  $\text{O} \cdots \text{Se} - \text{X}$  arrangement first-hand would predict the overall reaction to be of first order (independent of the nucleophile). However, such a mechanism is not in agreement with the kinetic data.

To gain further information about the reaction mechanism, the leaving group has been changed from bromide to chloride. The relative



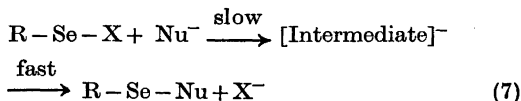
nucleophilicity of Cl<sup>-</sup> and Br<sup>-</sup> towards S<sup>II</sup> in protic medium has been found by Kice and co-workers<sup>36</sup> to have a factor of 35 in favour of Br<sup>-</sup>. Considering divalent tellurium as the central atom, a large increase in the *trans* bond-lengthening effect was observed when substituting iodide for bromide.<sup>36</sup> With regard to divalent selenium it is not unreasonable to assume a similar increase in the *trans* bond-lengthening effect when going from chlorine to bromine. Thus, a synchronous mechanism in the present reaction probably should give rise to a marked change in the rate constant upon changing the leaving group from bromide to chloride. However, Table 4 clearly shows that within the experimental errors the rate constants are nearly unaffected by changing the leaving group.

On the assumption that the free energy of activation,  $\Delta F^*$ , consists of an energy term associated to the break-down of the O...Se-X arrangement,  $\Delta F^*$  (O...Se-X), and a second energy term associated to the displacement of the leaving group,  $\Delta F^*$  (X), a synchronous bond formation and bond breaking can probably only take place on either of the following two conditions:

(1)  $\Delta F^*$  (O...Se-X) has to be much larger than  $\Delta F^*$  (X), and furthermore, the energy required to break up O...Se-Cl has to be nearly equal to the energy required to break up O...Se-Br. That is,  $\Delta F^*$  (O...Se-X)  $\gg$   $\Delta F^*$  (X) and  $\Delta F^*$  (O...Se-Cl)  $\approx$   $\Delta F^*$  (O...Se-Br). The high reactivity of benzeneselenenyl bromide relatively to the ortho-nitro substrate accords with the first statement.

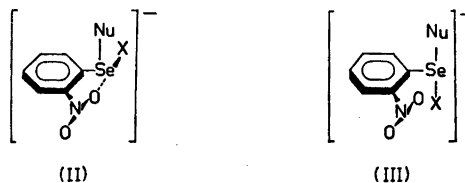
(2) The difference in the free energy of activation associated to the break-down of O...Se-Cl and O...Se-Br,  $\delta\Delta F^*$  (O...Se-X), must be nearly equal to the difference in the free energy of activation associated to the displacement of the two leaving groups Br and Cl,  $\delta\Delta F^*$  (X). That is,  $\delta\Delta F^*$  (O...Se-X)  $\approx$   $\delta\Delta F^*$  (X). In terms of the *trans* bond-lengthening effect of the ligands,<sup>36</sup> the break-down of O...Se-Cl should require a higher energy than is the case for the break-down of the O...Se-Br arrangement. Moreover, the energy required to displace a bromide ion from Se<sup>II</sup> is believed to be higher than the energy required to displace a chloride ion.

Alternatively, the present data can be explained by a two-step mechanism, eqn. 7.



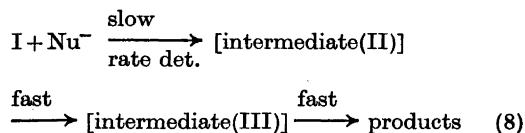
The first step, the intermediate formation, is thought to be the rate determining step, and the second step is a fast elimination of the leaving group. Such a two-step addition-elimination process has been labelled S<sub>A</sub>N by Kosower.<sup>37</sup> Bond formation thus precedes bond breaking.

X-Ray crystallographic studies on *o*-nitrobenzeneselenenyl compounds show that the Se-X bond lies in the plane of the nitro group and the benzene ring.<sup>34</sup> Two ways of approach to the Se atom may be considered, *i.e.*, (a) nucleophilic attack *trans* to the phenyl group which appears very unlikely due to the large *trans* bond-lengthening effect of this group commonly observed,<sup>17</sup> and (b) nucleophilic attack normal to the plane of the molecule. The intermediate in the latter case may be represented by the complex (II).



Concerning divalent selenium, such a configuration is, however, considered to be unlikely. Prior to the elimination of the leaving group, a fast rearrangement to the more energetic favourable form (III) may take place. The interaction between O and Se in (III) is probably smaller.

The overall mechanism may then be represented by eqn. 8.



A transition state similar to (III) has been suggested by Givens and Kwart<sup>38</sup> for the reaction between *o*-nitrobenzenesulfonyl chloride and the acetate ion.

Stable salts of phenyldiselenocyanatotellurate(II) and phenyldithiocyanatotellurate(II) have recently been prepared by Hauge and Vikane.<sup>39</sup> The structural geometry of these anions, which may be regarded as models for the transition state in nucleophilic substitution on divalent tellurium, have shown both of the anions to have a linear three-centre arrangement normal to the benzene ring in accordance with the intermediate (III).<sup>40</sup>

Likewise, Wynne and co-workers<sup>41,42</sup> have isolated a number of dihalo(aryl)selenate(II) and dihalo(aryl)tellurate(II) salts which probably have the same configuration around the chalcogen atom. The authors pointed out that 2,4-dinitrophenylselenenyl bromide was unreactive towards tetraorganylphosphonium halides, and the inability to isolate a dibromo(2,4-dinitrophenyl)selenate(II) is probably due to the presence of a coordinated *o*-nitro group and the instability of any higher coordinated species.<sup>43</sup>

No difference in the reaction mechanism has been suggested in the nucleophilic cleavage of unsubstituted and *o*-nitro substituted symmetrical disulfides by triphenylphosphine in aqueous dioxane.<sup>43</sup> The reactivity of these two disulfides towards Ph<sub>3</sub>P is reported to be nearly the same. Moreover, the poor correlation in the Hammett plot of the *o*-nitrobenzenesulfonyl substrates suggests that the electronic requirements for these reactions are almost unimportant, and this is in agreement with a synchronous displacement reaction on S<sup>II</sup>.<sup>38,44</sup>

The O...S—X arrangement of the *o*-nitrobenzenesulfonyl halide probably breaks down in solution, and a rotation about C—S takes place. The large difference in the rate constant between the unsubstituted benzeneselenenyl bromide and the *o*-nitro substituted substrate (a factor > 10<sup>6</sup>) may indicate that the O...Se—X arrangement is still maintained in solution. Thus, the difference in the electrophilic behaviour of *o*-nitrobenzenesulfonyl and the analogous selenenyl compounds may be interpreted on the basis of the relative ability of the chalcogens to form stable three-centre arrangements, which is believed to follow the order S ≪ Se < Te.<sup>17</sup>

Due to the difference in the solvation of the various nucleophiles in methanol, it is difficult to discuss the relative values of the activation parameters in Table 6. However, both  $\Delta H^*$  and

$\Delta S^*$  of the neutral nucleophiles (thiourea and selenourea) are smaller than for the anionic nucleophiles. The unfavourable entropy of activation of thiourea and selenourea may be explained by a strong solvation of the polar transition state relative to the initial state. It appears that the most strongly solvated nucleophile has the highest  $\Delta S^*$ , which appears reasonable. The low  $\Delta H^*$ -values of the neutral nucleophiles suggest that the transition states in these cases are relatively more stable than the transition states of the anionic nucleophiles. With regard to divalent tellurium as the central atom, Foss<sup>17</sup> has pointed out that neutral three-centre arrangements are usually more stable than anionic three-centre systems. Thus, the activation parameters may be related to a transition state of the three-centre type.

With regard to the reaction between *o*-nitrobenzeneselenenyl halogenide and the various nucleophiles, the present data cannot discriminate between the two possible mechanisms described above, *i.e.*, a synchronous bond formation and bond breaking and a two-step addition elimination process probably involving the selenium *d*-orbitals. However, in view of kinetic<sup>2,3</sup> and structural<sup>14–16</sup> data referred to earlier, the former mechanism appears to be the most reasonable one.

## EXPERIMENTAL

**Solvents.** Methanol "Merck" *p.a.* was used without further purification. Acetonitrile was purified as reported previously.<sup>1</sup>

**Substrates.** *o*-Nitrobenzeneselenenyl bromide was prepared from *o*-nitrophenyl selenocyanate and excess of bromine in dry chloroform.<sup>45</sup> The product was recrystallized three times from light petroleum (40–60°C). M.p. 65°C (lit.<sup>46</sup> 64–65°C).

*o*-Nitrobenzeneselenenyl chloride was kindly provided by Mr. R. Eriksen.<sup>46</sup>

Benzeneselenenyl bromide was synthesised from the diselenide and bromine in dry chloroform.<sup>47</sup> The compound was recrystallized three times from light petroleum (40–60°C). M.p. 60°C (lit.<sup>48</sup> 61–62°C).

**Nucleophiles.** The following sources of the nucleophiles were employed: (piperidyl)—CS<sub>2</sub>Na·2H<sub>2</sub>O,<sup>49</sup> Me<sub>2</sub>NCS<sub>2</sub>Na·2H<sub>2</sub>O,<sup>49</sup> Ph—SNa, Ph<sub>4</sub>AsCN,<sup>1</sup> (Ph<sub>4</sub>As)<sub>2</sub>S<sub>2</sub>O<sub>3</sub>, Me<sub>2</sub>PS<sub>2</sub>Na·2H<sub>2</sub>O,<sup>50</sup> (MeO)<sub>2</sub>PS<sub>2</sub>K,<sup>51</sup> (EtO)<sub>2</sub>PS<sub>2</sub>NH<sub>4</sub>,<sup>51</sup> (EtO)<sub>2</sub>P(O)—SNa,<sup>34</sup> (iPrO)<sub>2</sub>P(O)—SNa,<sup>34</sup> (MeO)<sub>2</sub>P(O)—SeNa,<sup>24</sup> (EtO)<sub>2</sub>P(O)—SeNa,<sup>24</sup> (iPrO)<sub>2</sub>P(O)—SeNa,<sup>24</sup> MeSO<sub>2</sub>SK,<sup>7</sup> PhSO<sub>2</sub>SPh<sub>4</sub>As,<sup>52</sup> Ph<sub>4</sub>AsSCN,<sup>53</sup> Ph<sub>4</sub>AsSeCN,<sup>53</sup> (NH<sub>2</sub>)<sub>2</sub>C=S ("Fluka", *puriss.*

*p.a.*), (NH<sub>2</sub>)<sub>2</sub>C=Se ("Fluka", *purum*, recrystallized from water), PhSO<sub>2</sub>Na·2H<sub>2</sub>O.<sup>7</sup>

Sodium thiophenolate was prepared *in situ* by dissolving equivalent amounts of thiophenol and sodium in methanol.

(Ph<sub>4</sub>As)<sub>2</sub>S<sub>2</sub>O<sub>3</sub> was precipitated from an aqueous solution of Ph<sub>4</sub>AsCl and a large excess of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>·5H<sub>2</sub>O. The dry compound was then dissolved in a small volume of absolute ethanol, and the insoluble sodium salts were filtered off. The solvent was removed in vacuum and the procedure was repeated twice. Iodometric analysis showed the compound to contain 97% (Ph<sub>4</sub>As)<sub>2</sub>S<sub>2</sub>O<sub>3</sub>. (Found: C 65.61; H 4.83; S 7.21. Calc. for C<sub>18</sub>H<sub>40</sub>O<sub>3</sub>S<sub>2</sub>As<sub>2</sub>: C 65.57; H 4.56; S 7.29).

**Products.** Most of the products of Table 1 were synthesised by the general procedure described by Foss.<sup>18</sup>

The dithiocarbamates, Nos. 1 and 2, Table 1, were recrystallized from benzene/light petroleum (40–60 °C) and pure benzene, respectively. The di-*O*-alkyldithiophosphates, Nos. 7 and 8, and the dimethyldithiophosphinate, No. 6, were recrystallized from benzene/light petroleum (40–60 °C).

The adducts of *o*-nitrobenzeneselenenyl bromide with thiourea and selenourea were isolated from acetonitrile. Equivalent amounts of the selenenyl bromide and the nucleophile were mixed, whereupon the product precipitated. The compounds were recrystallized from boiling acetonitrile. Both products, especially the adduct of selenourea, were slightly soluble in this solvent.

**Kinetics.** The rate of the reaction between the *o*-nitrobenzeneselenenyl substrates and the various nucleophiles was followed at 430 nm with a Durrum stopped-flow spectrophotometer. The kinetic runs were performed under pseudo-first order conditions applying a large excess of the nucleophile. The substrate concentration was about 1–3 × 10<sup>-4</sup> M. The second order rate constants were obtained by plotting the pseudo-first order constant against the concentration of the nucleophile. In all cases excellent second order kinetics were observed.

The reaction between benzeneselenenyl bromide and ionic thiocyanate was too fast to be followed at 460 nm by means of the stopped-flow technique. The second order rate constant of this reaction was calculated to be greater than 6 × 10<sup>4</sup> M<sup>-1</sup> s<sup>-1</sup>.

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