

Electrophilic Nature of *o*-Nitrobenzeneselenenyl Compounds.

A Kinetic Study

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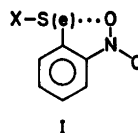
The rate of reaction between *o*-nitrobenzeneselenenyl bromide, $o\text{-NO}_2\text{PhSeBr}$, and various *para* substituted benzene sulfinates has been studied using stopped-flow and conventional spectrophotometry. The rate constants in methanol are related to σ substituent constants giving a Hammett plot with a slope of -1.0 . The rate constants are also related to the asymmetric S—O stretching frequencies in the sodium salts of the sulfinates. It is concluded that the transition state is stabilized by mesomeric electron donating substituents in the nucleophile.

The reaction between $o\text{-NO}_2\text{PhSeX}$, X = SCN, $p\text{MeOPhSO}_2$, PhSO_2S , and $(\text{NH}_2)_2\text{C}=\text{S}$, and dimethyldithiocarbamate, $\text{Me}_2\text{NCS}_2^-$, has also been studied kinetically in methanol. The leaving group effects on the rate constants have been discussed in terms of *trans* bond-lengthening effects of ligands bonded to divalent chalcogen atoms.

Upon changing the solvent from methanol to a dipolar aprotic medium, acetonitrile, an extremely large rate enhancing effect on the reaction between $o\text{-NO}_2\text{PhSeBr}$ and PhSO_2^- was observed. The low reactivity of $o\text{-NO}_2\text{PhSeBr}$ in the former medium relatively to the latter is explained by a strong solvation of the nitro group in the protic solvent, protecting the Se atom from an attack *trans* to the leaving group.

It is concluded that the intramolecular three-center arrangement of the substrate, $\text{X}-\text{Se}\cdots\text{O}$, is maintained in solution for X = Cl and Br, while it breaks down in solution for X = SCN, $p\text{MeOPhSO}_2$, PhSO_2S , and $(\text{NH}_2)_2\text{C}=\text{S}$.

The geometry of *o*-nitrobenzenesulfonyl¹ (selenenyl)² compounds in the crystalline state appears to show an intramolecular nearly linear three-center arrangement between one of the oxygen atoms of the nitro group, the chalcogen atom, and the atom of the group attached to the chalcogen atom, (I).



Kinetic studies concerning nucleophilic substitutions on $o\text{-NO}_2\text{PhSeCl}$ ³ and $o\text{-NO}_2\text{PhSeX}$,⁴ X = Cl and Br, reported previously, appeared to show that the intramolecular three-center arrangement is still maintained in solution. The influence on the rate constant when the leaving group is changed from Cl to Br, when the substrate is changed from $o\text{-NO}_2\text{PhSeBr}$ to PhSeBr , and when the solvent is changed from a protic to a dipolar aprotic solvent, conforms to an attack of the nucleophile *trans* to the leaving group in a synchronous bond formation and bond breaking process.^{3,4} The extraordinary high reactivity of $o\text{-NO}_2\text{PhSeCl}$ and $o\text{-NO}_2\text{PhSeBr}$ in acetonitrile relative to methanol, is suggested to be due to a strong solvation of the polar nitro group in the protic solvent. The free energy of activation in methanol is then mainly determined by the energy required to desolvate the nitro group.³ The unusual high stability of the *o*-nitrobenzenesulfonyl (selenenyl) halogenides relative to the unsubstituted substrates in protic solvent has been explained in this way.

In this paper we will report some further data concerning the electrophilic nature of *o*-nitrobenzeneselenenyl compounds. The donor property of the nucleophile is varied systematically by using different *para* substituted aromatic sulfinates. In this way we hope to get information concerning the electronic trans-

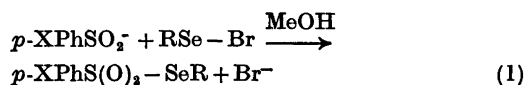
mission of substituent effects through the sulfinate group, and to shed further light on the polar effects in the transition state.

So far only halides, Cl and Br, have been used as leaving groups in kinetic studies of substitution reactions on *o*-nitrobenzeneselenenyl compounds. We will also in this paper report some interesting kinetic results obtained by use of other types of leaving groups.

Finally, some data concerning solvent effects on the reaction between benzenesulfinate and *o*-NO₂PhSeBr will be discussed.

RESULTS AND DISCUSSION

The o-NO₂PhSeBr-sulfinate reaction. Aromatic sulfinates react with *o*-nitrobenzeneselenenyl bromide, *o*-NO₂PhSeBr, in a bimolecular substitution reaction as described in eqn. (1).



X = MeO, Me, H, F, and Cl. R = *o*-nitrophenyl.

As indicated by the product the sulfur atom of the sulfinate group is believed to be the nucleophilic atom toward the divalent selenium

atom of the substrate. In all cases the products were stable, yellowish-green crystalline compounds, Table 1.

The rate data of reaction (1) at 25 °C in methanol are collected in Table 2. The reactions showed excellent second order kinetics, first order in each of the reactants. The rate of reaction was followed at 430 nm applying a spectrophotometer. Only *para*-substituted nucleophiles were used in order to avoid steric hindrance in the transition state.

The rate constants for the reaction of various aromatic sulfinates with *o*-NO₂PhSeBr show that electron-donating substituents in the

Table 1. Reaction products of the reaction between various substituted benzenesulfinates and *o*-nitrobenzeneselenenyl bromide.

Compound R = <i>o</i> -nitrophenyl	M.p./°C	Sulfur %	
		Calc.	Found
<i>p</i> -MeOPhSO ₂ SeR	ca. 115 dec.	8.60	8.73
<i>p</i> -MePhSO ₂ SeR	115 (lit. 118) ^a	—	—
PhSO ₂ SeR	106 (lit. 109) ^a	—	—
<i>p</i> -FPhSO ₂ SeR	88	8.88	9.02
<i>p</i> -ClPhSO ₂ SeR	ca. 120 dec.	8.50	8.69

^a Ref. 14.

Table 2. Pseudo first order rate constant, *k*', and second order rate constant, *k*₂, for the reaction between *o*-nitrobenzeneselenenyl bromide and different aromatic sulfinates in methanol at 25 °C.

No.	Nucleophile	[Nu]/10 ⁻³ M	<i>k</i> '/10 ⁻³ s ⁻¹	<i>k</i> ₂ /M ⁻¹ s ⁻¹
1	<i>p</i> -MeOPhSO ₂ ⁻	0.50	2.67	6.40
		1.00	6.74	
		2.00	12.9	
2	<i>p</i> -MePhSO ₂ ⁻	0.50	1.59	3.20
		1.00	3.20	
		2.00	6.40	
3	PhSO ₂ ⁻	0.25	0.487	2.05
		0.50	1.08	
		1.00	2.03	
		2.00	4.07	
4	<i>p</i> -FPhSO ₂ ⁻	0.25	0.386	1.71
		0.50	0.835	
		1.00	1.75	
5	<i>p</i> -ClPhSO ₂ ⁻	0.25	0.342	1.25
		0.50	0.623	
		1.00	1.23	

sulfinate increase the rate, while electron-attracting substituents decrease the rate. Thus, the rate depends on the electron density on the sulfur atom. The difference in the rate constant between the strongest and the weakest nucleophile is, however, rather small, *i.e.* $k_2(p\text{-MeO})/k_2(p\text{-Cl})=5.1$.

The rate data, except those for $p\text{-MeOPhSO}_2^-$ are correlated by the σ values⁵ giving a Hammett plot of slope -1.0 , Fig. 1. The obvious lack of correlation of $p\text{-MeOPSO}_2^-$ may suggest that σ^+ values rather than σ values should be used, but the $\log k_2 - \sigma^+$ plot showed a

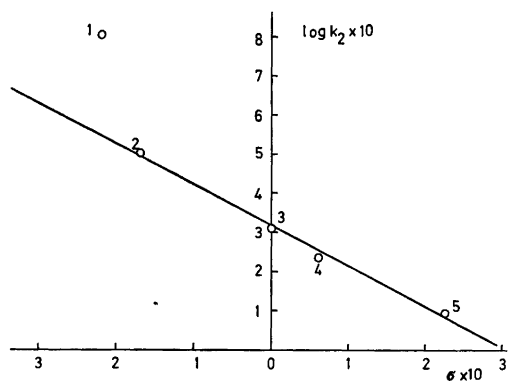


Fig. 1. Hammett plot for the reaction of *o*-nitrobenzeneselenenyl bromide and substituted benzenesulfonates in methanol at 25°C. σ values from Ref. 5. The numbers correspond to those listed in Table 2.

worse correlation. A combination of σ and σ^+ values, analogous to the Yukawa and Tsuno⁶ equation, would probably give the best correlation.

The sign and magnitude of the slope, $\rho = -1.0$, Fig. 1, indicate that the sulfur atom in the transition state is more positive charged relatively to the initial state. This is consistent with some degree of bond formation in the transition state.

The asymmetric S—O stretching frequencies of the sodium salts of the various substituted benzene sulfonates are listed in Table 3. It is seen that electron-donating substituents produce frequency shifts to higher wave numbers. Fig. 2 shows that, except for $p\text{-MeOPhSO}_2^-$, there appears to be a linear relationship between $\log k_2$ and $\nu_{as}(\text{S—O})$. The nucleophilic-

Table 3. Asymmetric S—O stretching frequencies, ν_{as} , in sodium salts of aromatic sulfonates, and pK_a values of the corresponding acids.

Compound	ν_{as}/cm^{-1} ^a	pK_a ^b
$p\text{-MeOPhSO}_2\text{Na}$	1150	2.72
$p\text{-MePhSO}_2\text{Na}$	1045	2.80
PhSO_2Na	1018	2.76
$p\text{FPhSO}_2\text{Na}$	1015	—
$p\text{ClPhSO}_2\text{Na}$	1000	2.76

^a The measurements were performed in nujol.

^b Ref. 7.

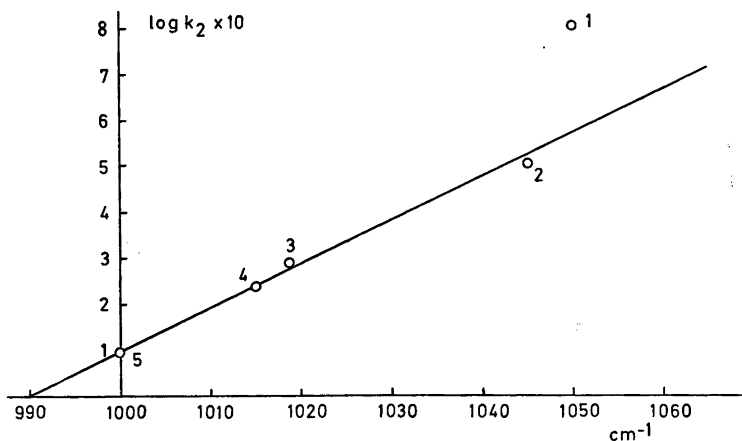


Fig. 2. Logarithm of the rate constants for the reaction of benzenesulfonates with *o*-nitrobenzeneselenenyl bromide as a function of the asymmetric S—O stretching frequencies of the sulfonates. The numbers correspond to those listed in Table 2.

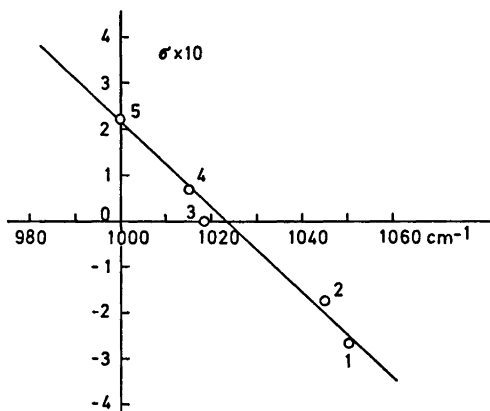


Fig. 3. The Hammett σ values as a function of the asymmetric S-O stretching frequencies of aromatic sulfonates. The numbers correspond to those listed in Table 2.

city of aromatic sulfonates toward Se(II) increases as the wave number of the S-O stretching frequencies increases.

As demonstrated in Fig. 3 the Hammett σ values conform to a linear relationship with $\nu_{as}(S-O)$.

It has been argued that due to the tetra-

hedral structure of the sulfonate group, $-\overset{\text{O}}{\underset{\text{O}}{\text{S}}}\text{:}^-$,

the "lone electron pair" of the sulfur atom is not available for a conjugation between π electrons of the benzene ring and those of the oxygen atoms.⁷ Fig. 3 does, however, show that some mesomeric effects do operate on the sulfonate group in the sodium salts. Furthermore, Figs. 1 and 2 suggest that mesomeric electron donation appears to be a more important factor in stabilizing the transition state relatively to inductive electron donation.

On the other hand, the deviation of the point that corresponds to $p\text{-MeOPhSO}_3^-$, may perhaps be explained by assuming a transition state analogous to that proposed for the $R_2\text{NCS}_2^- - o\text{-NO}_2\text{PhSeBr}$ reaction, (II).⁸

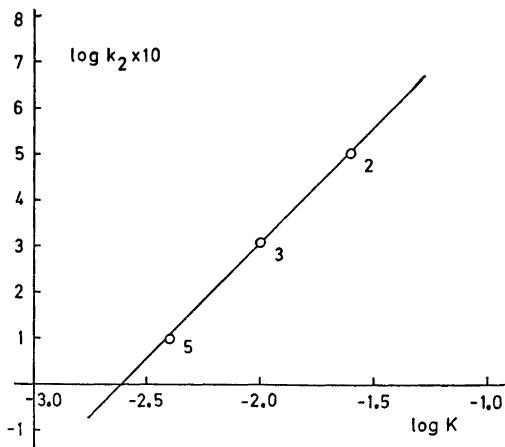
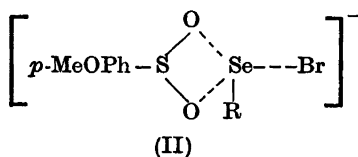
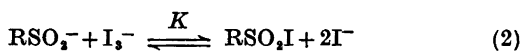


Fig. 4. Logarithm of the rate constants for the reaction between aromatic sulfonates and *o*-nitrobenzeneselenenyl bromide as a function of the logarithm of the equilibrium constant for the sulfonate-iodine reaction. The numbers correspond to those listed in Table 2.

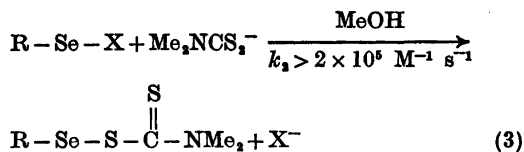
The sulfonate-iodine equilibria have been studied in aqueous solutions by Foss,⁶ eqn. (2)



Concerning aromatic sulfonates, there seems to be a linear connection between the free activation energy for substitution reactions on Se(II) and the free energy of the sulfonate-iodine reaction, Fig. 4.

The pK_a values of the corresponding acids of the nucleophiles are also listed in Table 3. By comparing the rate constants and pK_a values, no Brønsted correlation was found. On the basis of infrared and ultraviolet spectra, Detone and Hadze⁹ suggested that the proton is bonded to one of the oxygen atoms in the acid, *i.e.* $\text{R}-\overset{\text{O}}{\parallel}\text{S}-\text{OH}$. Consequently, the pK_a values in Table 3 do not represent the proton basicity of the nucleophilic sulfur atom of the sulfonate, and this may explain the lack of linearity in the $\log k_2 - pK_a$ plot.

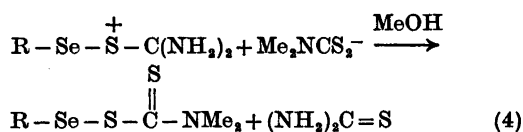
Leaving group effects. The reactions studied are shown by eqn. (3).



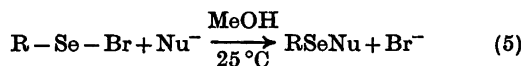
X = SCN, *p*-MeOPhSO₂, and PhSO₂S. R = *o*-nitrophenyl.

In all cases the reaction was too fast to be followed by means of a stopped-flow spectrophotometer. One may then conclude that the second order rate constant is greater than $2 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$.

Analogous results were also found for the reaction (4)



The leaving groups and the nucleophile of reactions (3) and (4) are also nucleophilic reagents toward *o*-NO₂PhSeBr, and the rate constants for these as nucleophiles at 25 °C in methanol are listed below.⁴



$$k_2(\text{SCN}^-) = 0.133 \text{ M}^{-1} \text{ s}^{-1}$$

$$k_2(p\text{-MeOPhSO}_2^-) = 6.40 \text{ M}^{-1} \text{ s}^{-1}$$

$$k_2(\text{PhSO}_2\text{S}^-) = 3.25 \text{ M}^{-1} \text{ s}^{-1}$$

$$k_2((\text{NH}_2)_2\text{C=S}) = 53.3 \text{ M}^{-1} \text{ s}^{-1}$$

$$k_2(\text{Me}_2\text{NCS}_2^-) = 2667 \text{ M}^{-1} \text{ s}^{-1}$$

Thus, concerning nucleophilic substitution reactions on *o*-nitrobenzeneselenenyl derivatives by Me₂NCS₂⁻, the rate constants of reactions (3), (4), and (5) clearly show that SCN, *p*-MeOPhSO₂, PhSO₂S, and (NH₂)₂C=S are better leaving groups than Br. Furthermore, Br⁻ does not react with the substrates of eqns. (3) and (4).

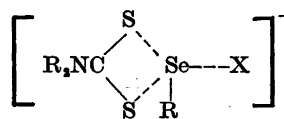
These results, at first sight, appear to contradict the general statement that exchange reactions on Se(II) are thermodynamically controlled. However, the kinetic data can be explained in terms of *trans* bond-lengthening effect of ligands participating in a three-center four electron bonding system around a divalent chalcogen atom (for a review see Refs. 10 and 11).

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As pointed out earlier, crystallographic data point to an intramolecular three-center arrangement around the selenium atom in the substrate, (I).⁵ The strength of the Se...O bond is, according to *trans* influence of ligands, affected by the group X. If X is more strongly bonded to Se, then the Se...O bond must be relatively weaker. In a thermodynamically controlled reaction, the strength of the X-Se bond in the transition state parallels the nucleophilicity of X toward Se(II). It is therefore reasonable to assume that the *trans* bond-lengthening effect increases in the order: Br < SCN < PhSO₂S < *p*-MeOPhSO₂ < (NH₂)₂C=S. Thus, the rate data can be explained by supposing the intramolecular X-Se...O arrangement to break down in solution for X = SCN, PhSO₂S, *p*-MeOPhSO₂, and (NH₂)₂C=S. The substrates then undergo a free rotation about the Se-C bond. The *trans* influence is smaller for X = Cl and Br, and the X-Se...O arrangement is for these substrates believed to be maintained in solution. Thus, a nucleophilic attack *trans* to the leaving group of *o*-NO₂PhSeBr involves an additional energy term in the free activation energy associated the strength of the Br-Se...O bonding system, while nucleophilic substitutions on the substrates in eqns. (3) and (4) do not involve such an additional energy term due to free rotation about the Se-C bond.

It is of interest to note that in the crystalline form the thiocyanate salt of [*o*-NO₂PhSe-S-C(NH₂)₂]⁺ forms a nearly linear S-Se...O arrangement,³ while the present data indicate that the cation undergoes a free rotation about the Se-C bond in methanol.

The transition state in substitution reactions on Se(II) with R₂NCS₂⁻ as nucleophiles is proposed to be of the type (III).³



(III)

Both of the donor atoms of the bidentate nucleophile are directed toward the Se atom. In the product, however, only one of the S atoms of the dithiocarbamate is believed to be bonded to the Se atom.

The present results, together with the data of the two previous papers in this series,^{3,4} clearly suggest that the nucleophile attacks *trans* to the leaving group, and that the X—Se···O arrangement in solution is strongly affected by the nature of X. Thus, so far both kinetic and structural data are compatible in the description of the mechanism for nucleophilic substitution on S(II), Se(II), and Te(II), as taking place through a linear three-center arrangement of nucleophile, electrophile, and leaving group, based on a single *p*-orbital of the electrophile. Concerning this picture Foss¹² once stated; "Nucleophilic reactivity may then relate to the ability of the reagent to engage the *p*-orbital in bonding, at the expense of the bond at 180°."

Solvent effects. Due to strong solvation of the polar nitro group in protic solvents, *o*-NO₂PhSeBr is expected to be less reactive in this type of medium relatively to dipolar aprotic solvents. An extremely large solvent effect is indeed reported for the *o*-NO₂PhSeBr—SCN⁻ reaction when going from MeOH to MeCN.³

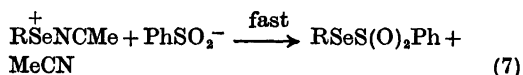
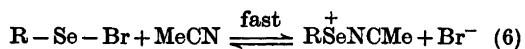
The *o*-NO₂PhSeBr—PhSO₂⁻ reaction has in the present work been studied kinetically at 25°C in the solvents; MeOH, MeCN, and MeNO₂. The dielectric constant of these solvents is nearly the same. The following second order rate constants were observed;

$$k_2(\text{MeOH}) = 2.05 \text{ M}^{-1}\text{s}^{-1}$$

$$k_2(\text{MeCN}) > 2 \times 10^5 \text{ M}^{-1}\text{s}^{-1}$$

$$k_2(\text{MeNO}_2) \approx 1.4 \times 10^5 \text{ M}^{-1}\text{s}^{-1}$$

Thus, the rate constant increases by a factor greater than 10⁵ when going from MeOH to MeCN. It is hard to believe that this large enhancement in the rate constant is only due to a different solvation of the nucleophile in MeOH and MeCN. Acetonitrile which, according to Gutmann,¹³ has donor property, DN_{SbCl₅} = 14.1, may be involved in the reaction process. A reaction mechanism passing through an equilibrium involving a selenium ion—acetonitrile adduct may be suggested, eqns. (6) and (7).



A mechanism of the type described by eqns. (6) and (7) may be favoured in solvents having large donor numbers. However, nitromethane, which has very poor donor properties, DN_{SbCl₅} = 2.7, also gives a large enhancement in the rate constant relatively to methanol (a factor of nearly 10⁵). It is therefore difficult to reconcile these results with a mechanism of the type described by eqns. (6) and (7). Thus, as suggested previously, the most reasonable explanation for the tremendous solvent effect on the electrophilicity of *o*-NO₂PhSeBr is to assume a strong solvation of the nitro group in MeOH, which hinders the nucleophile from attacking *trans* to the leaving group.

Conclusion. The electrophilic nature of *o*-nitrobenzeneselenenyl compounds may then be summarized as follows:

1. The intramolecular three-center arrangement, X—Se···O, is believed to be maintained in solution for X=Cl and Br.

2. The X—Se···O arrangement probably breaks down in solution for ligands more strongly bonded to the Se atom, *i.e.* SCN⁻, *p*-MeOPhSO₂⁻, PhSO₂⁻S, and (NH₂)₂C=S.

3. Nucleophilic attack appears to take place *trans* to the leaving group.

4. *o*-NO₂PhSeX, X=Cl and Br, is much more stable against nucleophilic attack in protic solvents than in dipolar aprotic solvents.

EXPERIMENTAL

Solvents. Methanol "Merck" *p.a.* was used without further purification. Acetonitrile was purified by distillation from P₂O₅ and CaH₂.¹⁵ Nitromethane "Fluka", (*puriss* ≥ 99.5 %), was used without further purification.

Substrates. *o*-NO₂PhSeBr was prepared and purified as reported previously.⁴

o-NO₂PhSeSCN and *o*-NO₂PhSeSS(O)₂Ph were synthesized by the method described by Foss.¹⁴

The adduct of *o*-NO₂PhSeBr with (NH₂)₂C=S, (NH₂)₂CSSePhNO₂-*o* Br, was isolated and purified as described previously.⁴

Nucleophiles. Sodium sulfates, which were recrystallized from methanol/ether, were employed. PhSO₂Na and *p*-MePhSO₂Na were commercial products obtained from "Fluka". The other aromatic sulfates, *i.e.* *p*-FPhSO₂Na, *p*-ClPhSO₂Na, and *p*-MeOPhSO₂Na, were prepared from the corresponding sulfonyl chlorides and aqueous sodium sulfite as reported by Smiles and Gibson.¹⁶

$\text{Ph}_4\text{AsPhSO}_2$ was prepared as described previously,¹⁷ and $\text{Me}_2\text{NCS}_2\cdot\text{Na}\cdot 2\text{H}_2\text{O}$ was a gift from Dr. O. Vikane of this Department.

Products. The products of the reactions between the sulfinates and *o*- NO_2PhSeBr were isolated according to the procedure of Foss.¹⁴ *p*- $\text{MeOPhSO}_2\text{SePhNO}_2$ was recrystallized from ethanol, and the other products in Table I were recrystallized from a benzene/methanol mixture.

The products of the reaction between $\text{Me}_2\text{NCS}_2^-$ and the various selenenyl substrates have been reported previously.⁴

Kinetics. The rate of the reaction between *o*- NO_2PhSeBr and the various aromatic sulfinates in MeOH was followed by measuring the decrease in the optical density, *D*, at the wavelength 430 nm using a Beckman DB-GT Grating Spectrophotometer. The kinetic runs were performed with matched 1 cm silica cells thermostated by circulating water from a thermostat controlled to $\pm 0.1^\circ\text{C}$.

The runs were performed under pseudo first order conditions applying large excess of the nucleophile. The substrate concentration was about $1-3 \times 10^{-4}$ M. Values of the first order rate constant, *k'*, were obtained from the slopes of the plots of $\log(D_\infty - D_t)$ against time. Plots of *k'* against [Nu] were linear and passed through the origin. The second order rate constants were calculated from the slope of these lines.

Attempts were made to follow the reaction between *o*- NO_2PhSeX , X = SCN, *p*- MeOPhSO_2 , PhSO_2S , and $(\text{NH}_2)_2\text{C}=\text{S}$, and $\text{Me}_2\text{NCS}_2^-$ in MeOH using a Durrum stopped-flow spectrophotometer, but the reactions were too fast. The measurements were performed at a fixed wavelength in the range 410–430 nm. The concentrations were 2.0×10^{-4} M of the substrate and 5.0×10^{-3} M of the nucleophile. The second order rate constants of these reactions could then be calculated to be greater than $2 \times 10^5 \text{ M}^{-1}\text{s}^{-1}$.

$\text{Ph}_4\text{AsPhSO}_2$ was used as the nucleophilic reagent in the kinetic studies of the *o*- $\text{NO}_2\text{PhSeBr} - \text{PhSO}_2^-$ reaction in MeCN and MeNO_2 . The measurements were performed at 430 nm. The reaction in MeCN was too fast to be followed by means of the stopped-flow technique, $k_2 > 2 \times 10^5 \text{ M}^{-1}\text{s}^{-1}$.

In MeNO_2 a logarithmic curve was observed, and the second order rate constant was estimated to be $\approx 1.4 \times 10^5 \text{ M}^{-1}\text{s}^{-1}$.

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