A Kinetic Study of the Reaction of Various *para*-Substituted *o*-Nitrobenzeneselenenyl Bromides with Thiourea and Benzenethiosulfonate as Nucleophiles

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The rate of reaction of various *para*-substituted *o*-nitrobenzeneselenenyl bromides with thiourea and benzenethiosulfonate as nucleophiles has been measured in methanol at 25 °C using the stopped-flow technique. In all cases the kinetic plots showed the reaction to be of second order, first order in each of the reactants. For both of the nucleophiles, the reaction is markedly accelerated by electron-releasing groups in the *para* position of the substrate. Substituents that are able to act through mesomeric effects showed a correlation between log k_2 and the Hammett σ values, while substituents that only act through σ-bonds, causing inductive effects, showed a relatively lower enhancement of reactivity. The slope in the Hammett plots for the former type of substituents was calculated to be $\varrho = -1.2$ and $\varrho = -0.34$ for thiourea and benzenethiosulfonate, respectively.

The electronic effects on the rate of reaction are discussed in terms of previous crystallographic studies of complexes of divalent selenium and tellurium, and previous kinetic studies on divalent sulfur. It is concluded that the present kinetic data are compatible with a transition state in which the bonding is of the three-center four-electron type.
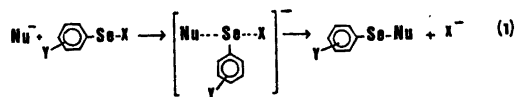
A large number of stable complexes with divalent selenium and tellurium as central atoms have been prepared, and the bonding in these complexes has been discussed by Foss and co-workers on the basis of X-ray crystallographic studies (for a review see Refs. 1 – 3). Furthermore, in 1962 Foss [4] pointed out that complexes of Te(II) may be regarded as model substances for the transition state in nucleophilic displacement at divalent chalcogen atoms. The crystallographic data clearly suggest that the transition state is linear with bonds probably of the

three-center four-electron type, *i.e.*, one occupied bonding orbital involving all three atoms, one occupied non-bonding orbital with all or most of the electron density on the entering atom and the leaving atom, and one empty anti-bonding orbital.[2]

According to Foss,[2] kinetic studies involving nucleophilic substitution on S(II), and structural evidence concerning the bonding in complexes of Se(II) and Te(II), are compatible in the description of the reaction mechanism for nucleophilic substitution on divalent chalcogen atoms.

In the later years we have undertaken a kinetic study concerning nucleophilic substitutions on Se(II) [5–9] and Te(II)[10]. The main purpose of this study is to find out if the kinetic data accord with the structural evidence in the description of the reaction mechanism. So far both structural and kinetic data point to the same reaction mechanism.

The present paper which may be regarded as part of this study, will deal with the timing of covalency changes in nucleophilic substitutions at divalent selenium and with the charge distribution around the selenium atom in the transition state relative to the ground state of the substrate. One way of studying this matter is through measurements of the effect of various substituents on the rate of a displacement reaction of the type:


$$\text{Nu}^- + \underset{Y}{\bigodot}\text{-Se-X} \longrightarrow \left[\underset{\underset{Y}{\bigodot}}{\text{Nu---Se---X}} \right]^- \longrightarrow \underset{Y}{\bigodot}\text{-Se-Nu} + \text{X}^- \quad (1)$$

The sign and the magnitude of the ϱ-value in the Hammett plot may tell something about the charge distribution around the selenium atom in the transition state.

A transition state that accords with the three-center four-electron bonding model, will probably give a ϱ-value that is near zero.

$$\left[\begin{array}{c} \overset{\textit{r-}}{Nu}\cdots \overset{}{Se}\cdots \overset{\textit{r-}}{X} \\ | \\ Ph \end{array} \right]$$

(I)
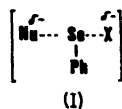
As indicated by (I), the non-bonding orbital of the three-center arrangement has most of its electron density on the outer atoms. Thus, the electron density around the selenium atom in the transition state is not very much different from the electron density around the selenium atom in the ground state.

Most of the existing kinetic work concerning nucleophilic displacement at divalent sulfur points to a synchronous displacement analogous to the S_N2 mechanism for sp^3 carbon. However, Ciuffarin et al.[11,12] have found that special sulfenyl chlorides probably undergo a two-step reaction when reacted with amines in benzene. They suggested that the intermediate may either be an ion pair or an addition complex formed through the use of the sulfur d orbitals.[11,12] If the displacement reaction is a two-step addition elimination process involving the selenium d orbitals, a negative charge on the selenium atom has to be stabilized. The Hammett plot should then give a large positive ϱ-value. Such a transition state is pictured by (II).

$$\left[\begin{array}{c} Nu - \overset{-}{Se} - X \\ | \\ Ph \end{array} \right]$$

(II)
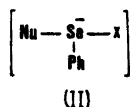
RESULTS AND DISCUSSION

In the present work we have studied the reaction between various para-substituted o-nitrobenzeneselenenyl bromides and thiourea and benzenethiosulfonate as nucleophiles, reaction (2).

$$Nu^- + p\text{-}X - R - Se - Br \xrightarrow[\quad 25\,°C \quad]{\text{MeOH}}$$

$$p\text{-}X - R - Se - Nu + Br^- \qquad (2)$$
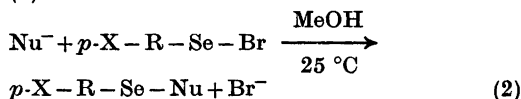
R = o-nitrophenyl
Nu = $(NH_2)_2C = S$ and $PhSO_2S^-$
X = CH_3O, CH_3, H, F, Cl, and NO_2.

Table 1 contains some data on the substrates. In the case of the neutral nucleophile, the product of reaction (2) is a salt. The rate measurements were performed in methanol at 25 °C applying a stopped-flow spectrophotometer.

Examination of the rate constants that are listed in Table 2 reveals that the rate for both of the nucleophiles obviously depends on the electron-withdrawing or electron-releasing character of the substituent attached to the aromatic ring. In both cases, electron-releasing substituents cause an increase in the rate. Furthermore, the effect of the substituents on the rate of reaction is somewhat stronger in the case of the neutral nucleophile.

The Hammett plot for the reaction between the various selenenyl bromides and thiourea is shown in Fig. 1. Hammett σ-values have been used.[25] The correlation of CH_3O, F, Cl, and NO_2, i.e., substituents that are able to act through mesomeric effects, is rather good. On the other hand, substituents that only cause inductive effects through σ-bonds, i.e., Me and H, deviate markedly from this correlation. This may suggest that σ^+ values rather then σ values should be used, but the $\log k_2 - \sigma^+$ plot did not show satisfactory results. A more reasonable explanation may be to suggest that the Hammett plot splits into two lines, an upper line that contains the points of the substituents that

Table 1. Some data on the substrates, $p\text{-}X - R - SeBr$, used in this work, (R = o-nitrophenyl). Recrystallized from diethyl ether, unless otherwise stated.

X	M.p./°C	$\lambda_{max}{}^a$/nm
CH_3O	114 (113.7 − 114.5)[b]	396
CH_3	90 (86.2)[c]	427
H	65[d] (64 − 65)[e]	417
F	68	427
Cl	102 (102.5 − 103.5)[c]	425
NO_2	118[f] (118)[g]	400[h]

[a] Measured in methanol. [b] Ref. 13. [c] Ref. 14. [d] Recryst. from light petroleum (40 − 60 °C). [e] Ref. 15. [f] Recryst. from diethyl ether/benzene. [g] Ref. 16. [h] The spectrum showed a shoulder at this wavelength.

Table 2. Pseudo-first-order rate constant, k', and second-order rate constant, k_2, for the reaction between various *para* substituted *o*-nitrobenzeneselenenyl bromides and the two nucleophiles thiourea and benzenethiosulfonate in methanol at 25 °C. (R = *o*-nitrophenyl).

X	[Nu]/ 10^{-2} M	$k'/$ s^{-1}	$k_2/$ M^{-1} s^{-1}
p-X – R – SeBr + (NH$_2$)$_2$C = S $\longrightarrow$			
p-X – R – Se – S – $\overset{+}{C}$(NH$_2$)$_2$ + Br$^-$			
CH$_3$O	0.675	2.57	
	1.17	4.08	342 ± 40
	2.11	6.28	
CH$_3$	0.675	0.842	
	1.17	1.32	116 ± 8
	2.11	2.32	
H[a]			53.3
F	0.675	1.38	
	1.17	2.24	185 ± 15
	2.11	3.50	
Cl	0.675	0.867	
	1.17	1.30	115 ± 15
	2.11	2.10	
NO$_2$	0.675	0.184	
	1.17	0.281	24 ± 3
	2.11	0.498	
p-X – R – SeBr + PhSO$_2$S$^-$ $\longrightarrow$			
p-X – R – Se – S – SO$_2$Ph + Br$^-$			
CH$_2$O	0.572	0.087	
	2.12	0.309	14.7 ± 0.5
	2.60	0.372	
CH$_3$	0.572	0.038	
	2.12	0.132	6.3 ± 0.3
	2.60	0.158	
H[a]			3.25
F	0.572	0.077	
	2.12	0.269	12.8 ± 0.6
	2.60	0.322	
Cl	0.572	0.0568	
	2.12	0.189	9.3 ± 0.6
	2.60	0.231	
NO$_2$	0.572	0.0369	
	2.12	0.125	6.3 ± 0.3
	2.60	0.168	

[a] Ref. 7.

operate through mesomeric effects, and a lower line that probably will contain points corresponding to substituents that cause only inductive effects on the aromatic ring. The sign and the magnitude of the slope of the line that fits the former substituents, $\varrho = -1.2$, indicate that the transition state is stabilized by electron-donating substituents. Furthermore, substit-
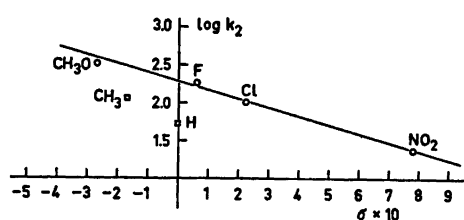
Fig. 1. Hammett plot for the reaction of various *para*-substituted *o*-nitrobenzeneselenenyl bromides and thiourea in methanol at 25 °C. σ-Values from Ref. 25.

uents that donate π-electrons to the electrophilic center appear to stabilize the transition state better than substituents that only donate electrons through σ-bonds.

Thiourea as nucleophile gives a neutral transition state complex. For the anionic nucleophile, benzenethiosulfonate, the transition state is a negatively charged complex. Even in this case the transition state is stabilized by electron-releasing groups in the *para* position, and the Hammett plot shows a similar trend as for thiourea, Fig. 2. The slope of the line through the points for the substituents that exert mesomeric effects, is, however, significantly less negative, $\varrho = -0.34$. Furthermore, all substituents of this type give a higher rate than do Me and H. Thus, relatively to the unsubstituted *o*-nitrobenzeneselenenyl bromide, substituents that act through electron-withdrawing mesomeric effects also accelerate the reaction. This points to some electron donation from the selenium atom to the aromatic π-
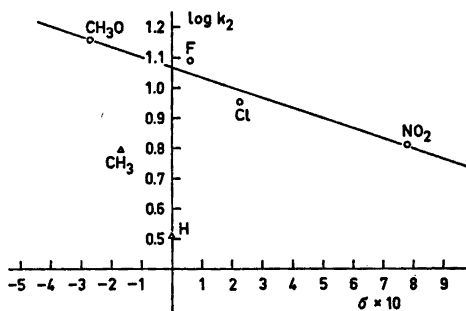

Fig. 2. Hammett plot for the reaction of various *para*-substituted *o*-nitrobenzeneselenenyl bromides and benzenethiosulfonate in methanol at 25 °C. σ-Values from Ref. 25.

orbitals in the transition state. However, the sign and the magnitude of the ϱ value strongly indicate that only a small part of the negative charge is located on the Se atom in the transition state complex.

With regard to nucleophilic substitutions on S(II), a lot of papers dealing with the electronic distribution around the sulfur atom in the transition state have been published. The electronic effects on the rate of reaction have in some cases been reported to be almost nil,[17] and in other cases a slightly positive ϱ value has been found.[18,19] Substitution reactions on S(II) in which both electron-releasing and electron-withdrawing groups in the *para* position accelerate the reaction have also been reported.[20,21] This type of behaviour has been interpreted as indicating different degrees of bond formation and fission in the transition state.

In the foregoing discussion the electronic effects of the nitro group in the *ortho* position of the selenenyl bromides have been ignored. We are aware of the fact, however, that the ground state of the substrates is stabilized by an intramolecular linear three-center arrangement involving one of the oxygen atoms of the nitro group, the selenium atom, and the bromine atom.[22] The electrophilic nature of these compounds has been discussed previously.[9] A nucleophilic attack *trans* or nearly *trans* to the leaving group is probably very hindered due to a strong solvation of the polar nitro group.[9] Thus, even though the nitro group is in the *meta* position relatively to the various substituents, electron donating groups probably make the nitro group more polar, and therefore more strongly solvated by methanol. This would lead to a slower reaction for substrates having electron-releasing groups in the *para* position. However, the opposite is really observed.

Electron donating groups in the *para* position may cause the selenium atom to be less electrophilic, and an equilibrium between intramolecularly bonded substrates and substrates which may undergo a rotation about the C — Se bond may be set up. The latter type of substrates are found to be much more reactive than the intramolecularly bonded substrates,[8] and an equilibrium as above should lead to a much faster reaction. As shown by Table 2, there is a rather small difference between the rate con-

stants of the various substrates. A drastic change in the initial state of the substrates would probably lead to a much greater difference in the rate constants.

In summary then, we find that the electronic requirements of the present reactions are best discussed on the basis of factors that stabilize the transition state and not the initial state of the substrates. In this way, the data are in complete consistency with the three-center four-electron bonding model as suggested by Foss on the basis of crystallographic studies.

EXPERIMENTAL

Solvent. Methanol Merck *p.a.* was used without further purification.

Substrates. The *para*-substituted *o*-nitrobenzeneselenenyl bromides were prepared from the corresponding selenocyanates and excess of bromine in dry chloroform.[15]

The aromatic selenocyanates, except for 2,4-dinitrophenyl selenocyanate, were prepared from diazotized anilines and potassium selenocyanate.[23] 2,4-Dinitrophenyl selenocyanate was synthesized by reacting 1-chloro-2,4-dinitrobenzene with potassium selenocyanate in warm ethanol as decribed by Fromm and Martin.[24]

Nucleophiles. Thiourea, $(NH_2)_2CS$, (Fluka, *puriss. p.a.*) and tetramethylammonium benzenethiosulfonate, $Me_4N^+PhSO_2S^-$,[9] were employed.

Kinetics. The rate of the reaction between the nucleophiles and the various aromatic selenenyl bromides was followed by measuring the decrease in the absorption near the λ_{max} of the substrates, Table 1, with a Durrum stopped-flow spectrophotometer. The kinetic runs were performed under pseudo-first order conditions, with excess of nucleophile, and the substrate concentrations were about $(2-4) \times 10^{-5}$ M. The second order rate constants appeared to increase slightly as the concentration of the nucleophile decreased. The k_2 values given in Table 2 are the average values of the three individual k_2 values, $k'/[Nu]$.

In the case of the anionic nucleophile, $PhSO_2S^-$, the final optical density of the solution was not stable. An increase in the optical density was observed for the two most concentrated solutions, which points to a consecutive reaction between the product and the nucleophile. However, this reaction is much slower than the original displacement reaction, and it has no influence in the calculation of the rate constant of the first step. This second reaction was not studied any further.

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