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A COMPARISON OF TRANSITION STATES IN NUCLEOPHILIC DISPLACEMENT BY ALKENES AT BIVALENT SULFUR AND SELENIUM[1]

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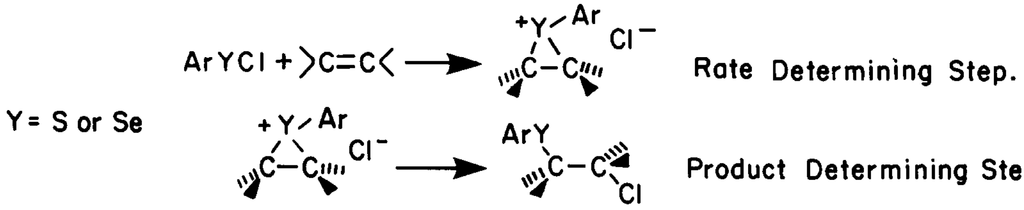
Abstract *Evidence is presented that S-Cl bond breaking and C-S bond making are about equal in the transition state of the addition of ArSCl to 1-(4-X-phenyl)propenes while SeCl bond breaking is more advanced than C-Se bond making in the analogous reaction of ArSeCl.*

The reaction of ArSCl and ArSeCl and alkenes are examples of electrophilic additions to carbon-carbon double bonds[2]. Viewed in this way, a simple two step mechanism has been proposed for these reactions[3]. The first step leading to formation of a thiiranium ion (for ArSCl) or a seleniranium ion (for ArSeCl) is rate-determining[4] and the second step is product determining.



These reactions can be viewed equally well as a nucleophilic displacement at bivalent S or Se by an alkene[5]. Such a view allows us to visualize a continuum of mechanisms as shown by the energy-reaction coordinate diagram in the Figure[6]. At corner A of the diagram are located the starting compounds. The intermediate seleniranium or thiiranium ion-chloride ion pair is found at corner D. Breaking the Y-Cl bond corresponds to movement along the edge AB to form the ion, ArY^+, chloride ion and alkene[7]. Approaching the alkene and ArYCl without breaking the Y-Cl bond corresponds to movement along the edge AE to form an episulfurane or episelenurane at corner E. Two such diagrams exist. One for Y=S and the other for Y=Se. For convenience, we have superimposed them. Three mechanisms that differ only in the relative amounts of Y-Cl bond breaking and C-Y bond making are contained on this Figure. An S_N1-like mechanism is presented by the path AB, BD, an S_N2-like mechanism is represented by

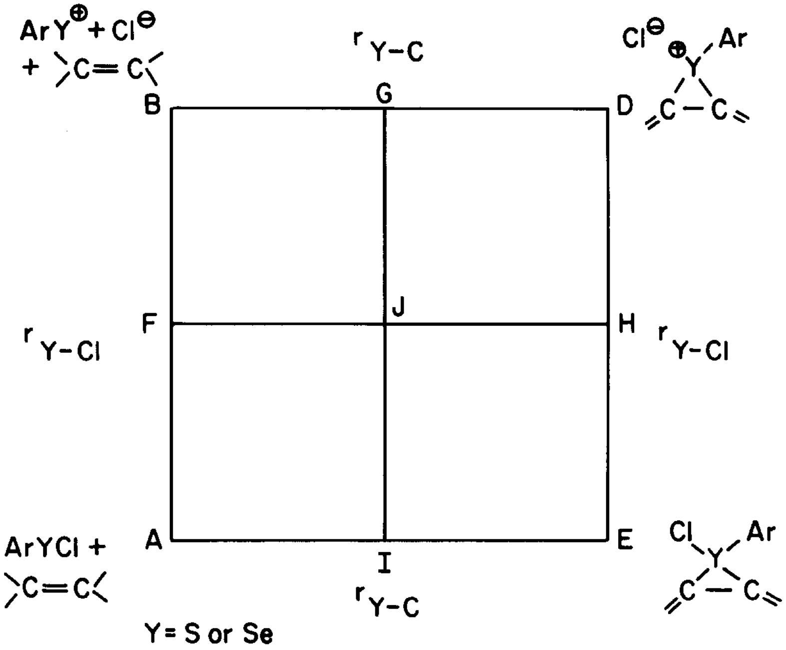


FIGURE *Energy Reaction Coordinate Diagram for Nucleophilic Displacement by Alkenes at Bivalent Sulfur or Selenium.*

the diagonal AJD, and path AE, ED represents an addition elimination mechanism. We can determine the relative locations of the rate determining transition states on such an energy reaction coordinate diagram for the reactions of ArSCl and ArSeCl with phenyl substituted styrenes by examining the effect of substituents in the phenyl ring of both the styrenes and ArSCl and ArSeCl.

The data for the addition of 4-substitutedbenzenesulfenyl chlorides to E- and Z-1-phenylpropene are given in the Table.

TABLE Second Order Rate Constants for the Addition of 4-Substitutedbenzenesulfenyl Chloride to E- and Z-1-Phenylpropene in CH_2Cl_2 at 25°C.

	1-Phenylpropene	
X	Z-isomer $k_2(M^{-1}\ s^{-1})$	E-isomer $k_2(M^{-1}\ s^{-1})$
CH_3O	8.75 + .09	27.6 + .3
CH_3	10.8 + .8	27.4 + .3
H	9.68 + .09	25.2 + .5
Cl	10.7 + .9	33.4 + .7
CF_3	11.2 + .8	26.1 + .4

Clearly substituents in the phenyl ring of ArSCl have little effect on the rate of reaction. Small values (either positive or netative) of ρ or no correlation are characteristic of many reactions of arenesulfenyl chlorides[8]. In contrast, the rate data for the reaction of 4-substitutedbenzeneselenenyl chlorides and Z- and E-1-phenylpropene in CH_2Cl_2 at 25°C correlate with σ^+ to give ρ^+ values of -1.53 (E) and -1.39 (Z)[9]. The values of ρ for the additions of C_6H_5SCl and C_6H_5SeCl to E- and Z-1-(4-X-phenyl)propene are very similar. For C_6H_5SeCl[9], ρ^+ is -1.51 (Z) and -1.91 (E) in CH_2Cl_2 at 25°C while for ClC_6H_4SCl[2], ρ^+ is -1.97 (Z) and -2.89 (E) in $C_2H_2Cl_4$ at 25°C. These data indicate that for the addition of ArSeCl, positive charge is developed at both the α-carbon of the styrene and Se in the transition state. In the transition state for the addition of ArSCl positive charge is developed at only the α-carbon. Little or no positive charge is developed at S.

The lack of a substituent effect in the reaction of ArSCl is an indication that C-S bond making and S-Cl bond breaking are about equal in the transition state. This corresponds to an S_N2-like mechanism whose reaction path is along or near the diagonal AJD. In order for the α-carbon of a substituted styrene to have positive charge, C-Y bond making must occur in the transition state. This corresponds to the rectangle GDEI for both S and Se. The negative value of ρ^+ for the reaction of ArSeCl indicates positive charge on the Se atom. For this to occur substantial Se-Cl bond breaking must occur in the transition state. The region in the diagram where this occurs is the rectangle BDHF. The transition state for the reaction of ArSeCl is located where these two regions overlap; the region in the rectangle GDHJ. Thus in this region any transition state structure in which Se-Cl bond breaking is more advanced than C-Se bond making is in accord with our data.

Other data allow us to restrict further the region in which the transition state for the ArSeCl reaction is located. Kinetically, Se^{II} is known to be more easily oxidized to Se^{IV} than S^{II} to S^{IV}[10]. Furthermore tetravalent Se Compounds are more stable than analogous S compounds[11]. As a result, changing Y from S to Se should move the position of transition state in the direction of corner E. Thus while the S transition state should be near the diagonal, the Se transition state should be in the region bounded by triangle JDH.

This analysis suggests that there is a continuum of mechanisms for the reactions of ArSCl and ArSeCl and alkenes (and other nucleophiles). In the reaction of ArSCl and 1-(4-X-phenyl)propenes, bond breaking and bond making to S are nearly equal. It should be noted that if bond making exceeds bond breaking, for substituents in ArSCl $\rho > o$ while the reverse leads to $\rho < o$. This behavior has been observed experimentally[12]. For the analogous addition of ArSeCl, C-Se bond making lags behind Se-Cl bond breaking in the transition state.

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