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play a major role in the energetics of both stages.

Note

Quantum-chemical study of organic reaction mechanisms. Part 2. Addition of selenium dichloride to acetylene



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ABSTRACT

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Introduction

In Part 1 of this series, we have studied theoretically the mechanism of the reaction between selenium dihalides with vinyl ethers being of keen interest from both theoretical and synthetic points of views [1]. Indeed, the addition reactions of selenium dihalides to unsaturated compounds attract steady research interest since they represent a straightforward route to new organo-selenium compounds [2-4]. It has been recently demonstrated that novel electrophilic selenium dichloride and dibromide, are selective and efficient reagents for the formation of the carbon–selenium bond [2-4]. Although selenium dihalides undergo disproportionation in solutions and cannot be isolated in pure form, freshly prepared selenium dichloride and dibromide can be used *in situ* for selective synthesis of organoselenium compounds including selenium-containing heterocycles [2-4].

The addition of selenium dihalides to acetylene [3] as well as substituted acetylenes [4] proceeds with high regio- and stereoselectivity. The reaction of selenium dichloride with acetylene was accomplished in carbon tetrachloride to furnish hitherto unknown

The mechanism of the addition of selenium dichloride to acetylene has been studied theoretically at the

DFT-B3LYP/6-311+G(d,p) level. The reaction proceeds as anti-anti-addition via the formation of the in-

termediate selenirenium compounds with the four-coordinated selenium atom. Both thermodynamically

and kinetically, a favorable E-2-chloroselenenyl chloride is formed on the first stage of the reaction. The

experimentally observed *E,E*-bis(2-chlorovinyl) selenide is kinetically more favorable as compared to *E,Z*-

isomer. Possible alternative reaction mechanisms require much higher energy barriers. Stereoselectivity of the process is achieved through the kinetic control of the reaction. In the reaction profile of a pref-

erable route leading to a kinetically favorable E,E-bis(2-chlorovinyl) selenide the entropy factor doesn't

selective *anti*-addition (Scheme 1). Acetylene represents a fundamental molecule and multipurpose chemical feedstock as well, and the reaction of selenium dichloride with acetylene is very important from both theoretical and prac-

E,E-bis(2-chlorovinyl)selenide (98% yield), a product of the stereo-

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with acetylene is very important from both theoretical and practical viewpoints. In continuation of our previous study [1], we report here the results of a theoretical study of the addition of selenium dichloride to acetylene performed at the DFT level. Noteworthy, there were no quantum chemical calculations of additions of selenium dihalides (or Se²⁺ electrophile) to the triple bond, and the present paper is a first quantum chemical consideration of the reactions of selenium dihalides with acetylenes.

It is well documented that the electrophilic addition of sulfenyl halides to the triple bond proceeds via the formation of thiirenuim cations [5,6]. Selenium analogs, selenirenium cations, have been also supposed as intermediates and even isolated in some cases [5,7]. However, there is a strong evidence that electrophilic addition of selenenyl halides to the triple bond may include the formation of

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$$2\text{HC} \equiv \text{CH} + \text{SeCl}_2 \xrightarrow{\text{CCl}_4} \xrightarrow{\text{Cl}_{\text{Se}}} \xrightarrow{\text{Cl}_{\text{Se}}}$$





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the three-membered intermediates with a four-coordinated selenium atom [5,8].

There are many similarities between the addition of areneselenenyl and arenesulfenyl chlorides to alkynes. According to the kinetics data, in both cases, the rate law is of a second order, and the polar effect of alkyl substituents predominates at the ratedetermining step [5,8]. However, the effect of alkyl substituents on the rate is more pronounced for the addition of arenesulfenvl chloride than for areneselenenyl chlorides. Besides, in contrast to addition of the sulfur electrophiles, the effect of substituting identical groups at the triple bonds on the rate of addition of benzeneselenenyl chloride is not cumulative [5,8]. The difference in the effect of alkyl substituents on the rate and product composition strongly suggests that the mechanism of electrophilic addition of selenium electrophiles involves at least two steps with one intermediate. Since the same step cannot be both rate- and productdetermining, it is suggested that the first step is a ratedetermining while the second one is a product-determining. Because the products are formed by stereospecific but nonregiospecific anti-addition, a selenirenium ion with a fourcoordinated selenium atom was postulated as the intermediate prior to the product-determining step [5,8]. It was thus a challenging task to verify this assumption at the high theoretical level which was a prime goal of the present study.

Results and discussion

The mechanism of the addition of selenium dichloride to acetylene: first stage

To elucidate the mechanism of the addition of selenium dichloride to acetylene which proceeds with high stereoselectivity in carbon tetrachloride, we undertook quantum chemical studies of the mechanism of this reaction within the DFT framework. The addition of selenium dichloride to acetylene was considered as a two-stage process involving the addition of SeCl₂ to one molecule of acetylene in the first stage followed by the addition of the mono-adduct to the second molecule of acetylene in the second stage.

Theoretically, the addition of selenium dichloride to acetylene can yield two stereoisomeric products, namely, $\mathbf{3}$ (Z) and $\mathbf{3}$ (E) (Scheme 2).

Quantum chemical calculations performed at the B3LYP/6-311+G(d,p) level taking into account solvent effect (CCl₄) within the polarizable continuum model (PCM) have shown that the reaction product **3** (*E*) is by 1.1 kcal/mol energetically more stable over product **3** (*Z*). Nevertheless, the difference in energy of the subject stereoisomers is almost negligible that does not allow one to speak about more stable formation of **3** (*E*) due to a thermodynamic control of this stage of the reaction. Moreover, there are no direct experimental data supporting the above assumption, since the addition reaction of selenium dichloride to acetylene proceeds before the formation of a bis-adduct, and the attempts to stop the reaction in the first stage met with no success [3a]. This is why we have studied in detail the energy profile of the first reaction stage using analysis of potential energy surface (PES), which is shown in Fig. 1.



Scanning of PES shows that the first stage of the interaction between acetylene **1** and selenium dichloride **2** can proceed via two different directions, and the choice of a route is defined by the type of the formed pre-reaction complex.

Indeed, we have managed to localize two different pre-reaction complexes, namely **4** and **5**, which differ in a spatial location of the reacting molecules with their relative energies being of -1.9and -1.1 kcal/mol, respectively. In the pre-reaction complex **4**, the linear acetylene molecule is located perpendicular to the SeCl₂ plane, and the selenium atom deviates symmetrically from carbon atoms of the multiple bond by 3.2 Å (Fig. 2). In addition, some minor changes of geometrical parameters of the interacting compounds are observed. On the other hand, in the pre-reaction complex **5**, the acetylene molecule is located in parallel with one of the Se–Cl bonds of selenium dichloride. Such an arrangement leads to the increase in distance between selenium atom and acetylene carbons by more than 0.3 Å. Further on, the pre-reaction complexes **4** and **5** are transformed in a way to follow two different reaction routes.

As is seen in Fig. 1, the pre-reaction complex **4** is transformed into the stable reaction intermediate **6** of selenirenium type via the transition state **TS1** with an activation barrier of 15.0 kcal/mol. It is noteworthy, that the generation of the activation complex **TS1** is accompanied by a considerable decrease of the interatomic Se–C distance (by 0.9 Å), whereas the Cl–Se–Cl bond angle increases by 26° making the acetylene molecule being oriented almost perpendicular to the reactant plane, to deviate significantly from a linear structure (Fig. 2).

It is noteworthy that in the intermediate compound **6**, the selenium atom exists in four-coordinated state forming two Se–C bonds. This conclusion is supported by the presence of bond and ring critical points on Bader diagrams calculated using the AIM method [9]. Indeed, two bond critical points (0.129 a.u.) and one ring critical point (0.123 a.u.) on the AIM graph of **6** shown in Fig. 3 strongly supports the formation of the selenirenium cycle.

Another support of the Se–C bonds formation in **6** follows from the NBO analysis performed at the B3LYP/6-311+G(d,p) level which gives 1.91951 e occupancy for both Se–C bonds.

It is important that halogen atoms in the selenirenium intermediate 6 are located practically along one line, while in a free selenium dichloride the bond angle Cl-Se-Cl totals to 101°. Similar effect was observed earlier in the seleniranium intermediate formed by the interaction of selenium dihalides with vinvl ethers [1]. It can be explained by the formation of the coordination bonds of selenium atom with carbon atoms of the alkene multiple bond which leads to the alteration of configuration at the selenium atom from the tetrahedral to the trigonalbipyramidal one. At the same time, halogen atoms are located in axial positions forming the Cl-Se-Cl bond angle of 171°. Formation of the Se-C bonds is also confirmed by noticeable lengthening of the multiple bond of the acetylene fragment (0.08 Å) and decrease of the C–C–H bond angle (30°) characterizing significant deviation of the acetylene molecule from a linear structure in the reaction intermediate 6.

Ring-opening of the intermediate **6** can lead to the formation of either *syn*-addition product **3** (*Z*) via the transition state **TS3** with high potential barrier of 25.8 kcal/mol or thermodynamically more favorable *anti*-addition product **3** (*E*) via the transition state **TS2** with considerably lower potential barrier of 19.2 kcal/mol.

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