



Note

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



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ABSTRACT

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 intermediate 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 preferable route leading to a kinetically favorable *E,E*-bis(2-chlorovinyl) selenide the entropy factor doesn't play a major role in the energetics of both stages.

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Introduction

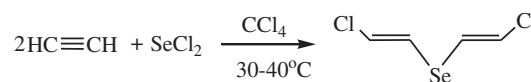
In Part 1 of this series, we have studied theoretically the mechanism of the reaction between selenium dihalides with vinyl ethers being of keen interest from both theoretical and synthetic points of views [1]. Indeed, the addition reactions of selenium dihalides to unsaturated compounds attract steady research interest since they represent a straightforward route to new organoselenium 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

E,E-bis(2-chlorovinyl)selenide (98% yield), a product of the stereoselective *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 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 Se^{2+} 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 sulfonyl halides to the triple bond proceeds via the formation of thiirenium 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



Scheme 1.

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