Substituent Effects on The Ring-Opening Mechanism of 1-Bromo-1-Lithiosilirane to Silaallenes: DFT Study

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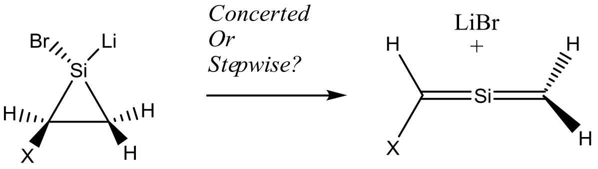
The chemistry of silaallenes has been attracting more interest in past few decades due to their unique structural properties compared to carbon analogs [1]. Recently, our group has proposed the concerted and stepwise mechanism about the ring-opening mechanism of lithium bromocyclopropylidenoids, 1-bromo-1lithiosilirane, and 2-bromo-2-lithiosilirane to allenes and silaallenes with the help of DFT calculations, respectively. The effects of substituents were reported for carbon analogs. Briefly, the stability of the reactive intermediate, i.e., the carbene, is dependent on the substituent. Cyclopropylidenes bearing an electron-donating group are extremely unstable and ring-open readily to the allene [2]. In addition to that, it is proposed in another study that the ring opening mechanism of 1-bromo-1-lithiosilirane to 2-silaallene can proceed in a stepwise fashion. On the contrary, the ring opening mechanism of 2-bromo-2-lithiosilirane to 1-silaallene can proceed in a stepwise fashion [3].



In this study, the ring-opening reactions of lithium bromosilaranes to silaallenes have been investigated computationally at B3LYP/6-31G(d) level of theory. Formally, two pathways can be considered: the reaction can be concerted or stepwise with intermediacy of a free carbene. In both case, loss of bromine ion determines the kinetic of the reaction. To analyze the possibility of the reactions, we worked on the potential energy surfaces for the elimination of LiBr from substituted 1-bromo-1-lithiosiliranes (X= -H, -Br, -SiH_3, -CH_3, -CF_3, -Cl, -F, -CN) at the B3LYP/6-31G(d) level of theory. With using DFT molecular orbital calculation, we estimate that the energy barrier for conversion from –CN substituted siliranes to TS1 has 18.1 kcal/mol which is the highest activation energy and –Br substitued siliranes has lowest energy barrier by 10.4 kcal/mol. The reaction of –SiH_3 and –CN substituted siliranes can be proceed concerted and stepwise fashion, whereas X= -H, -Br, -CH_3, -CF_3, -Cl, -F are only stepwise reaction type. Finally, we discussed required energies and reaction process from 1-Bromo-1-lithiosiliranes to silaallenes in accordance with Doering-Moore-Skattebol method.

[1] For reviews, see:
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