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Addition Reactions of Silylenoids H_2SiLiX (X = F, Cl) to Acetylene

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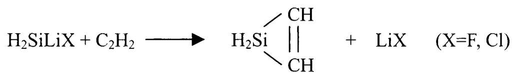
The addition reactions of silylenoids H_2SiLiX (X = F, Cl) to acetylene were studied by ab initio molecular orbital theory. The reaction mechanisms were revealed for the first time. The structures of reactants, transition states, and products were located and fully optimized at the G2(MP2) level. Based on the MP2(full)/6-31G(d) optimized geometries, harmonic vibrational frequencies of various molecules were obtained. The reaction paths were investigated and confirmed by intrinsic reaction coordinate (IRC) calculations. The barriers for the addition reactions were computed to be 77.3 (X = F) and 11.4kJ/mol (X = Cl) at the G2(MP2) level, respectively. Changes (ΔS, ΔH, and ΔG) in thermodynamic functions, equilibrium constant $K(T)$, and preexponential factor $B(T)$ and second-order reaction rate constant $k(T)$ in Eyring transition state theory were calculated over a temperature range of 100−1000 K, and then thermodynamic and kinetic properties of the reactions were analyzed.

1. Introduction

Silylene chemistry has long been of great interest.[1−4] The reactions of silylenes, for example, insertion, addition, and polymerization, are recognized as important and effective methods for the preparation of new silicon-bonded and heterocyclic silicon compounds. The formation of highly strained small ring molecules using π-type additions of silylenes to multiple bonds has also been an important topic of theoretical and experimental studies.[5−17] The studies have shown that the addition reactions of silylenes R_2Si (R = H, CH_3, t-Bu) proceed with no barriers, and the theoretical results are well consistent with the experiments. According to the theoretical calculations,[15−17] the additions of silylenes SiX_2 (X = F, Cl) to ethylene or acetylene, however, have nonzero barriers, and the barrier for SiF_2 addition is much larger than that for $SiCl_2$, indicating that the electronegativity of the substituted atoms in silylenes is more important than steric effects in determining barrier heights for the additions of silylenes.

Similar to silylene chemistry, carbene chemistry has also attracted people's considerable attention both theoretically and experimentally.[18] However, investigation shows that real intermediates of many organic reactions, which were originally recognized to be carbenes, are practically carbenoids. The active carbon intermediates caused by the exchanging reactions of chlorohydrocarbons and alkyllithium or similar compounds take part in reactions in the forms of chlorolithium carbenoids.[19−21] Over the past few decades, a considerable number of studies have been made on carbenoids.[22]

Silylenoids, silicon analogues to carbenoids, have been confirmed to be existent and predicted to be active intermediates in some organosilicon reactions.[23,24] When silylene coexists with alkali halide, they are impossibly separated from each other and will exist in the form of silylenoids. Most recently, the first experimental aspects of silylenoid chemistry in (alkoxysilyl)lithium compounds were reported by Tamao et al.[25] They found that [(*tert*-butoxy)diphenylsilyl]lithium not only behaves as a silylenoid but also has ambiphilic reactivity, which appears to be in concert with theoretical results. Then, further experimental studies on silylenoids have been carried out.[26] Recent theoretical calculations indicate that reactions of silylenoids H_2SiLiX (X = F, Cl) with H_2 resemble the insertion of H_2Si into H_2 except with high barriers,[27,28] preliminarily revealing the applicability of silylenoids. In the present work, the addition reactions of silylenoids H_2SiLiX (X = F, Cl) to acetylene to form silirene are investigated using ab initio calculations. We first calculated geometric parameters, vibrational frequencies, and energies of the reactants, transition states, and products for the addition reactions and confirmed the reaction paths by the intrinsic reaction coordinate (IRC) theory. Then, we carried out the thermodynamic and kinetic calculations using statistical mechanical methods and Eyring transition state theory, respectively. The reaction mechanisms were revealed for the first time.



2. Theoretical Methods

Optimized geometries and energies for the stationary points were obtained using G2(MP2) theory.[29] The corresponding harmonic vibrational frequency calculations at the MP2(full)/6-31G(d) level were carried out in order to verify whether the stationary points are local minima or saddle points. The reaction paths were examined by intrinsic reaction coordinate (IRC) calculations at the MP2(full)/6-31G(d) level. The Gaussian 98 series of programs were employed in all calculations.[30] The changes of thermodynamic functions, entropy (ΔS), entropy ($\Delta S^{\ddagger}$) for transition state, enthalpy (ΔH) and free energy (ΔG), and equilibrium constant ($K(T)$) were calculated by using the MP2(full)/6-31G(d) optimized geometries and harmonic vibrational frequencies of reactants and products with statistical

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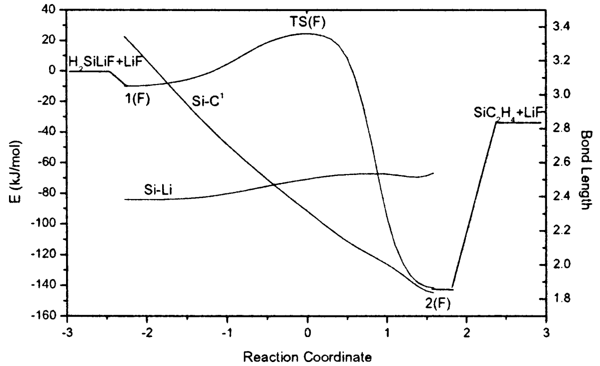


Figure 1. Relative energy (*E*) and bond length vs reaction coordinate in reaction path for the addition of H_2SiLiF to C_2H_2 (MP2(full)/6-31G(d)).

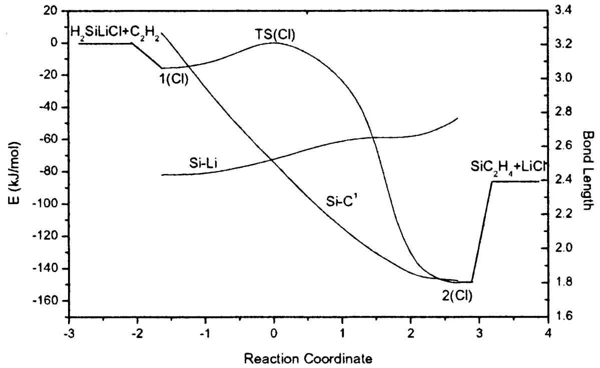


Figure 2. Relative energy (*E*) and bond length vs reaction coordinate in reaction path for the addition of $H_2SiLiCl$ to C_2H_2 (MP2(full)/6-31G(d)).

mechanical methods.[31] Using Eyring transition state theory, the preexponential factor $B(T)$ and second-order rate constant ($k(T)$) of the reactions were obtained.

3. Results and Discussion

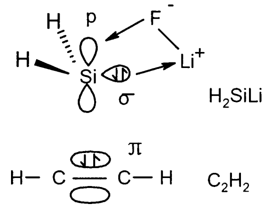
The calculations have shown that the three-membered ring structures of silylenoids H_2SiLiX ($X = F$, Cl) are experimentally detectable ones among all isomers in which H_2SiLiX takes part in chemical reactions.[23,24] So their three-membered ring structures are adopted in the present study. When H_2SiLiX and C_2H_2 approach to each other, complexes **1**(X) first form. As the reactions proceed, additions of H_2SiLiX to acetylene occur via the transition states TS, forming the complexes **2**(X). With LiX being dissociated apart from the Si atom, the complexes **2**(X) decompose, and the product silirene can be obtained

$$\underset{}{H_2SiLiX} + C_2H_2 \rightarrow \underset{\mathbf{1}(X)}{H_2SiLiX\cdot C_2H_2} \rightarrow \underset{TS}{[H_2SiLiX\text{-}C_2H_2]} \rightarrow$$

$$\underset{\mathbf{2}(X)}{SiC_2H_4\cdot LiX} \rightarrow \underset{\text{silirene}}{SiC_2H_4} + LiX$$

The reaction paths were confirmed by the IRC calculations, as shown in Figures 1 and 2. The apparent features for the reactions are that Si−Li bond distance gradually lengthens and Si−C distances gradually shorten as the reactions proceed. Sketch maps and atomic numbering of the stationary points are given in Figure 3. Their MP2(full)/6-31G(d) geometric parameters and energies are listed in Tables 1 and 2, respectively. All species have C_s symmetries except that silirene has C_{2v} symmetry and C_2H_2 and LiX have $C_{\infty v}$ symmetries.

3.1. Addition of H_2SiLiF to C_2H_2. Silylenoid H_2SiLiF is a complex of silylene H_2Si with a LiF molecule, where the positive Li end and the negative F end of the LiF molecule act on the σ orbital and the unoccupied 3p orbital of the singlet silylene H_2Si:, respectively. The Si 3p orbital is a main part of LUMO of H_2SiLiF. When the π orbital (HOMO) of C_2H_2 as a nucleophile attacks the Si 3p orbital from the back of the F atom, not along the direction of the Si 3p orbital, the orbital symmetry is allowed, and complex **1**(F) forms with no barrier. In complex **1**(F), the $Si-C^1$ distance is 3.381 Å, H_2SiLiF and C_2H_2 depart far from each other and there exists only a weak interaction between H_2SiLiF and C_2H_2. There is little variation in the structural parameters of H_2SiLiF and C_2H_2 moieties, relative to two separated entities. However, it can be found from the atomic charges in Table 3 that the donation of π electrons of C_2H_2 into the Si 3p orbital does occur. Compared with those of H_2SiLiF and C_2H_2, the negative charge of the C^1 atom decreases slightly, whereas the positive charge of the Si atom decreases by 0.019. The G2(MP2) energy of complex **1**(F) is 9.1kJ/mol lower than the two separated entities.



As the C_2H_2 molecule further approaches the Si 3p orbital, the C^2 atom moves toward the σ orbital on the Si atom so that the σ electrons are partially donated into the antibonding π^* orbital of C_2H_2 to reach the transition state TS(F), whose only one imaginary frequency is 275i cm^{-1}. Compared with those of H_2SiLiF and C_2H_2, the positive charge of Si atom and negative charge of C^2 atom in TS(F) increase by 0.17 and 0.223, respectively, whereas the negative charge of the C^1 atom increases only by 0.046. The C^1-C^2 bond lengthens to 1.258 Å and is gradually changing from triple to double bonds. The Si−F and Si−Li bonds increase by 0.148 and 0.115 Å, respectively. The Li and F atom approach to each other and the LiF moiety is departing away from Si atom. The forming $Si-C^1$ bond in the TS(F) shortens by 1.066 Å, relative to complex **1**(F). The predicted barrier height for the addition is 77.3kJ/mol at the G2(MP2) level.

After getting over the TS(F), complex **2**(F) forms with further departing of the LiF moiety from the Si atom and approaching of the C_2H_2 moiety toward the Si atom. Most of the σ lone pair electrons on the Si atom are transferred to C atoms, causing the Si atom have 1.498 positive charges. The calculations indicate that the G2(MP2) energy of complex **2**(F) is 137.0 kJ/mol lower than the sum of energies of the reactants, so the reaction is highly exothermic. The Si−C and C−C bonds in complex **2**(F) are almost equal to those in silirene, respectively. Si−Li and Si−F distances are 0.155 and 0.049 Å longer than those in H_2SiLiF, respectively. In fact, **2**(F) is a complex of silirene with LiF. When LiF separates away completely from Si atom, silirene can be obtained. However, the complex **2**(F), whose G2(MP2) energy is 91.7 kJ/mol lower than the sum of energies of silirene and LiF, is rather stable, which allows us to assume that, when silirene and LiF coexist, they will exist in complex **2**(F) unless some strong external factors occur.

3.2. Addition of $H_2SiLiCl$ to C_2H_2. Similar to the addition of H_2SiLiF to C_2H_2, complex **1**(Cl) forms when the occupied π orbital (HOMO) of C_2H_2 approaches the Si 3p orbital (LUMO) in $H_2SiLiCl$ from the back of Cl atom. In the **1**(Cl), there is also only a weak interaction between the HOMO and

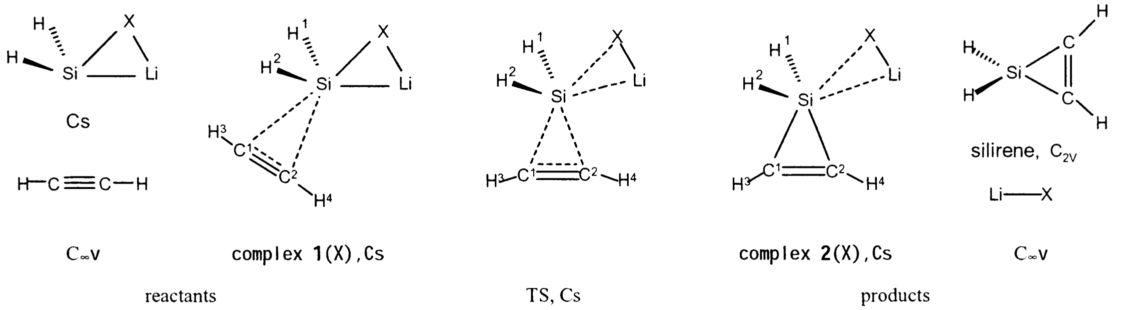


Figure 3. Sketch maps and atomic numbering of reactants, TS, and products (X = F, Cl).

TABLE 1: MP2(full)/6-31G(d) Optimized Geometries[a]

molecule	Si−H	Si−Li	Si-X	Li-X	Si−C^1	C−C	C^1-H	C^2-H	HSiH	YSiLi	XLiSi	YSiC^1	CCSi	HC^{1}Si	HC^{2}C^1
							X = F								
reactants															
C_2H_2						1.216	1.066								
H_2SiLiF	1.504	2.388	1.807	1.747					99.6	152.0	48.9				
1(F)	1.502	2.384	1.820	1.738	3.381	1.218	1.066	1.066	100.3	150.6	49.4	57.6	76.4	102.3	178.8
TS(F)	1.483	2.503	1.955	1.672	2.315	1.258	1.070	1.077	113.3	134.7	51.2	79.1	61.7	130.1	146.7
products															
2(F)	1.487	2.543	1.856	1.700	1.835	1.358	1.078	1.103	114.4	132.9	46.8	130.0	72.4	158.5	125.8
SiC_2H_4	1.482				1.817	1.343	1.085		111.2			158.3	68.3	155.7	135.1
LiF				1.566											
							X = Cl								
reactants															
$H_2SiLiCl$	1.500	2.433	2.297	2.249					100.6	159.9	58.6				
1(Cl)	1.498	2.433	2.336	2.229	3.332	1.218	1.067	1.066	101.2	157.2	60.0	59.3	77.6	101.2	178.1
TS(Cl)	1.492	2.525	2.805	2.130	2.508	1.234	1.069	1.069	103.7	138.1	73.6	73.7	65.1	110.9	159.0
products															
2(Cl)	1.472	2.767	3.401	2.083	1.813	1.346	1.084	1.095	115.0	106.4	87.9	157.3	70.4	156.1	129.6
LiCl				2.064											

[a] Bond lengths are in angstroms; bond angles are in degree. Y, imaginary atom; SiY, bisector of angle HSiH.

TABLE 2: Total Energies (a.u.) and Relative Energies (kJ/mol; in Parentheses) of Reactants, Transition States, and Products for Reactions of H_2SiLiX with C_2H_2

molecule	MP2(full)/6−31(d)	G2(MP2)
	X = F	
$H_2SiLiF+C_2H_2$	−474.36257 (0.0)	−474.69216 (0.0)
1(F)	−474.36636 (−9.9)	−474.69562 (−9.1)
TS(F)	−474.35325 (24.5)	−474.66271 (77.3)
2(F)	−474.41653 (−141.7)	−474.74433 (−137.0)
SiC_2H_4 + LiF	−474.37463 (−31.7)	−474.70942 (−45.3)
	X = Cl	
$H_2SiLiCl+C_2H_2$	−834.36768 (0.0)	−834.67774 (0.0)
1(Cl)	−834.37192 (−11.1)	−834.68136 (−9.5)
TS(Cl)	−834.36588 (4.7)	−834.67339 (11.4)
2(Cl)	−834.42262 (−144.2)	−834.72446 (−122.7)
SiC_2H_4 + LiCl	−834.40203 (−90.2)	−834.70690 (−75.6)

LUMO, as is clear from the long Si−C bond distance and little variation in structural parameters of $H_2SiLiCl$ and C_2H_2 moieties relative to the separated $H_2SiLiCl$ and C_2H_2 molecules, as shown in Table 1. From the lowering of energy relative to the reactants (see Table 2), it can be seen that complex **1**(Cl) has the same stability as complex **1**(F). This suggests that the stability for complexes formed from silylenoids H_2SiLiX and acetylene is not particularly dependent on the haloid atoms in H_2SiLiX.

TS(Cl) is the transition state for the addition of $H_2SiLiCl$ to C_2H_2, whose only imaginary frequency is 156i cm^{-1}. In TS(Cl), part of the σ lone pair electrons on Si atom is transferred to C^2 atom, just like the form of TS(F), making the Si atom more positive relative to the Si atom in $H_2SiLiCl$. The TS(Cl) is somewhat earlier than the TS(F), as is shown by the longer Si−C bond distance and the slightly shorter C−C bond relative to TS(F). The computed barrier height for the addition of $H_2SiLiCl$ to C_2H_2 is 11.4kJ/mol at the G2(MP2) level, 65.9kJ/mol lower than that for the addition of H_2SiLiF to C_2H_2, indicating that the former proceeds via an early transition state more easily than the latter. In addition, we can find that chlorine departs from the Si atom more easily than larger electronegative florine, as is clear from the 0.508 Å longer Si−Cl bond distance in TS(Cl) than in $H_2SiLiCl$. This is also in accordance with the low reaction barrier and early transition state for the addition of $H_2SiLiCl$ to C_2H_2. These suggest that halogen (X) in H_2SiLiX is the deciding factor in determining the barrier heights of these addition reactions.

The intermediate product for the addition of $H_2SiLiCl$ to C_2H_2 is the complex **2**(Cl), in which transferring of the σ lone pair electrons on the Si atom to C atoms causes the Si atom to have 1.273 positive charges. The exothermicity for the reaction is 122.7kJ/mol at the G2(MP2) level, 14.3kJ/mol lower than that for the addition of H_2SiLiF to C_2H_2, indicating that **2**(F) is more stable than **2**(Cl). In complex **2**(Cl), the Si−Cl and Si−Li distances are 1.104 and 0.334 Å longer than those in $H_2SiLiCl$, respectively; the Li−Cl bond distance is only 0.019 Å longer than that in the LiCl molecule; the $H_2SiC_2H_2$ moiety is very close to that of silirene. These suggest that **2**(Cl) is a complex of silirene with the LiCl molecule and there exists only a week interaction between $H_2SiC_2H_2$ and LiCl moieties. The G2(MP2) energy of complex **2**(Cl) is 47.1kJ/mol lower than the sum of energies of the separated $H_2SiLiCl$ and LiCl molecules. So we can come to the conclusion similar to **1**(F) that when silirene coexists with LiCl they will exist in complex **2**(Cl).

3.3. Vibrational Frequencies. The main vibrational frequencies of reactants, transition states, and products for the addition reactions are summarized in Table 4. Each frequency is attributed to one or two vibrations, and each molecule has its

TABLE 3: Atomic Natural Charges

molecule	Si	Li	X	H^1	C^1	C^2	H^3	H^4
				X = F				
reactants								
H_2SiLiF	0.444	0.871	−0.768	−0.274				
C_2H_2					−0.246		0.246	
1(F)	0.425	0.871	−0.773	−0.268	−0.240	−0.252	0.252	0.252
TS(F)	0.614	0.889	−0.805	−0.230	−0.292	−0.469	0.269	0.255
products								
2(F)	1.498	0.948	−0.786	−0.267	−0.609	−0.947	0.217	0.213
SiC_2H_4	1.219			−0.230	−0.616		0.236	
LiF		0.924	−0.924					
				X = Cl				
reactants								
$H_2SiLiCl$	0.217	0.883	−0.632	−0.234				
1(Cl)	0.210	0.886	−0.652	−0.232	−0.235	−0.254	0.256	0.253
TS(Cl)	0.297	0.889	−0.808	−0.221	−0.155	−0.357	0.286	0.290
products								
2(Cl)	1.273	0.908	−0.885	−0.197	−0.576	−0.806	0.246	0.234
LiCl		0.930	−0.930					

TABLE 4: Vibrational Frequencies (cm^{-1}; Relative Intensity in Parentheses) and Corresponding Vibrations

vibration	**1**(F)	**2**(F)	TS(F)	**1**(Cl)	**2**(Cl)	TS(Cl)	H_2SiLiF/C_2H_2	$H_2SiLiCl$	SiC_2H_4
C−H stretching	3569(0.4) 3481(32)	3207(10) 3025(28)	3472(25) 3343(34)	3567(0.7) 3479(44)	3284(0.8) 3134(16)	3529(29) 3454(71)	3570(0) 3482(96)		3276(2) 3253(2)
Si−H stretching	2214(100) 2207(98)	2290(100) 2279(66)	2314(100) 2291(39)	2241(100) 2230(85)	2394(100) 2369(58)	2278(100) 2258(53)	2200(100) 2204(99)	2231(100) 2222(90)	2231(100) 2323(57)
C−C stretching	1998(0.6)	1522(3)	1818(41)	1997(2)	1540(12)	1910(14)	2005(0)		1546(9)
SiH_2 scissor	1027(68)	1028(99) 917(34)	1008(19) 815(36)	1017(58)	1016(99)	991(52)	1036(68)	1024(59)	1040(61)
SiH_2 wagging	848(73)	644(48)	981(80)	775(64)	702(100) 723(68)	829(36) 822(27)	826(62)	749(49)	698(23) 717(78)
SiH_2 twisting	718(9)	914(0.8)	881(3)	665(3)	609(3)	720(1)	694(5)	639(2)	602(0)
C−H bending	750(25) 739(41) 388(0.4)	1260(5) 990(3) 500(75) 487(31) 388(19)	1008(19) 981(80) 694(37) 670(12) 430(21)	749(36) 744(68) 407(0.8)	1219(10) 973(20) 549(63)	762(51) 589(31) 580(1)	752(100)		1164(12) 963(0) 952(5) 594(9)
Si−C stretching		775(52)	500(2)		802(44) 661(73)				807(7) 726(23)
Si−Li stretching	374(9)	432(20)		361(36)		387(27)	359(13)	354(49)	
Si-X stretching	497(70)						517(51)	514(47)	
Li-X stretching	651(22)	689(26)	749(49)	520(48)	625(75)	561(49)	643(20)		

own characteristic vibrations, by which the structure of the molecule can be analyzed.

As can be seen in Table 4, each molecule has two C−H stretching vibrations, and the high frequency vibration is weaker. They will gradually shift to low frequencies as the addition reaction proceeds. The H_2Si moiety in the molecule can be confirmed by two strong characteristic Si−H stretching vibrations (symmetric and asymmetric Si−H stretching vibrations) at about 2200 cm^{-1} and H_2Si scissor vibrations at about 1000 cm^{-1}. Although the C−C stretching vibration in the C_2H_2 molecule cannot be observed at 2005 cm^{-1} because of the molecular symmetry, the C−C stretching vibrations of other molecules, despite being rather weak, can be seen because the C−C bonds here have not been the real triple bonds. The C−C vibrational frequency of **1**(F) or **1**(Cl) is close to that of C_2H_2, which correlates with the weak interaction between the LUMO of H_2SiLiX and the HOMO of C_2H_2 in **1**(F) or **1**(Cl). The C−C vibrational frequency of the transition state TS(F) (or TS(Cl)) is close to complex **1**(F) (or **1**(Cl)); that is, the C−C bond in TS(F) or TS(Cl) has partial triple bond character. This is in agreement with early transition states for the title reactions. However, the C−C vibration of **2**(F) or **2**(Cl) has become the typical double bond vibration, just like that of silirene. We can find from the data in Table 4 that the Si−C stretching vibrations can be observed only in **2**(F), **2**(Cl), TS(F), and silirene in the range from 500 to 807 cm^{-1}, which is in good agreement with their structures. It is interesting that IR intensity for SiH_2 twisting vibration in silirene is zero.

3.4. Thermodynamic and Kinetic Analyses for the Addition Reactions. Thermodynamic and kinetic analyses for the addition reactions can further illustrate their realizability and possibility. So we carried out the thermodynamic and kinetic calculations for these title reactions. The calculated thermodynamic functions, ΔS, $\Delta S^{\ddagger}$, ΔH, and ΔG, equilibrium constant $K(T)$, and second-order rate constant $k(T)$ for the reactions over a temperature range from 100 to 1000 K are listed in Table 5. All values are corrected by zero-point energies. It can be found from the data in Table 5 that ΔS and $\Delta S^{\ddagger}$ for the additions of H_2SiLiF and $H_2SiLiCl$ to C_2H_2 are negative values. This means that both of the additions are slightly entropy-decreased reactions. The calculated enthalpy changes (ΔH) for them are also all negative, indicating that the additions are exothermic. As the temperature rises, the exothermicity slowly decreases, and the ΔG values gradually increase and change from negative to positive values. For H_2SiLiF addition, ΔG values are negative at less than 600 K, and the reaction is spontaneous, whereas ΔG values are positive at more than 600 K, and the reaction is nonspontaneous. For $H_2SiLiCl$ addition, ΔG values are negative

TABLE 5: Thermodynamic and Kinetic Analyses

reaction	T K	$\Delta S^‡$ J/(mol K)	$k(T)$ cm^3/(mol s)	ΔH kJ/mol	ΔG kJ/mol	ΔS J/(mol K)	$K(T)$
$H_2SiLiF+C_2H_4$	100	−133.3	1.3×10^{-7}				
	200	−130.0	7.6×10				
	300	−142.4	8.8×10^4	−104.4	−57.01	−157.8	
	400	−143.4	3.6×10^6	−102.4	−38.15	−160.6	9.60×10^4
	500	−143.8	3.8×10^7	−99.9	−19.12	−161.6	9.94×10
	600	−143.8	2.0×10^8	−97.0	−0.042	−161.6	1.01
	700	−143.6	7.2×10^8	−93.8	19.01	−161.2	3.81×10^{-2}
	800	−143.4	1.9×10^9	−90.4	38.00	−160.4	3.30×10^{-3}
	900	−143.1	4.4×10^9	−86.7	56.91	−159.6	5.00×10^{-4}
	1000	−142.9	8.6×10^9	−82.9	75.74	−158.7	1.10×10^{-4}
$H_2SiLiCl+C_2H_2$	100	−124.1	7.8×10^4				
	200	−127.1	1.6×10^8				
	300	−128.6	2.7×10^9	−107.7	−67.07	−135.5	
	400	−129.1	1.3×10^{10}	−105.6	−50.48	−137.7	3.90×10^6
	500	−129.2	4.1×10^{10}	−103.0	−33.75	−138.4	3.36×10^3
	600	−128.9	9.3×10^{10}	−99.9	−17.00	−138.2	3.02×10
	700	−128.6	1.8×10^{11}	−96.6	−0.298	−137.6	1.05
	800	−128.3	3.1×10^{11}	−93.1	16.34	−136.8	8.58×10^{-2}
	900	−128.0	4.9×10^{11}	−89.5	32.89	−136.0	1.23×10^{-2}
	1000	−127.6	7.3×10^{11}	−85.7	49.35	−135.0	2.64×10^{-3}

at less than 700 K and the reaction is spontaneous, whereas ΔG values are positive at more than 700 K and the reaction is nonspontaneous. With the rising of temperature, addition rates increase obviously while $K(T)$ values decrease, in other words, addition yields decrease. So a suitable reaction temperature, for example, 500 K for H_2SiLiF addition and 600 K for $H_2SiLiCl$ addition, should be chosen for both reaction rates and yields.

In addition, $K(T)$ and $k(T)$ values for the addition of $H_2SiLiCl$ to C_2H_2 are larger than those for the addition of H_2SiLiF to C_2H_2 at the same temperature, respectively. This suggests that the addition of $H_2SiLiCl$ to C_2H_2 proceeds more easily and is more sensive to temperature. This is in accordance with the above analysis.

Figure 4 shows the factor $B(T)$ against temperature (T) for the title reactions over a temperature range from 100 to 1000 K. The relationship between the factor $B(T)$ and temperature T exactly conforms to the following equations in units of cm^3 mol^{-1} s^{-1}:

$$B(T) = 4.738 \times 10^{10}\ e^{0.00234T} \quad \text{(for the addition of } H_2SiLiF \text{ to } C_2H_2\text{)}$$

$$B(T) = 2.978 \times 10^{11}\ e^{0.00235T} \quad \text{(for the addition of } H_2SiLiCl \text{ to } C_2H_2\text{)}$$

So the rate constants for the title reactions over a temperature range from 100 to 1000 K can be given in units of cm^3 mol^{-1} s^{-1} as follows:

$$k(T) = 4.738 \times 10^{10}\ e^{(0.00234T-3921/T)} \quad \text{(for the addition of } H_2SiLiF \text{ to } C_2H_2\text{)}$$

$$k(T) = 2.978 \times 10^{11}\ e^{(0.00235T-1319/T)} \quad \text{(for the addition of } H_2SiLiCl \text{ to } C_2H_2\text{)}$$

4. Conclusions

The π-type addition reactions of silylenoids H_2SiLiX to acetylene for X = F and Cl have been investigated with ab initio calculations. The results show that the additions are very similar to the addition of silylene H_2Si to acetylene and can give the same final products but proceed with barriers. When H_2SiLiX and acetylene approaches each other, HOMO of acetylene interacts with LUMO (the Si 3p orbital) of H_2SiLiX, forming a complex. As the σ lone pair electrons on Si atom transfer to the antibonding π^* orbital (LUMO) of acetylene and the LiX moiety gradually separates from the Si atom, transition states are reached. The G2(MP2) barriers for H_2SiLiF and $H_2SiLiCl$ additions are computed to be 77.3 and 11.4 kJ/mol, respectively. It is suggested that halogen (X) in silylenoids H_2SiLiX is the deciding factor in determining the barrier heights of the additions. Surmounting transition states, complexes of silirene with LiX molecules will form, which are more stable than separated silirene and LiX molecules. When silirene coexists with LiX, they will exist in the complexes. The additions are exothermic. With the rising of reaction temperature, the additions accelerate but their yields decrease. A suitable reaction temperature, for example, 500 K for H_2SiLiF addition and 600 K for $H_2SiLiCl$ addition, should be chosen for both reaction rates and yields. The $H_2SiLiCl$ addition is more sensitive to temperature than the H_2SiLiF addition.

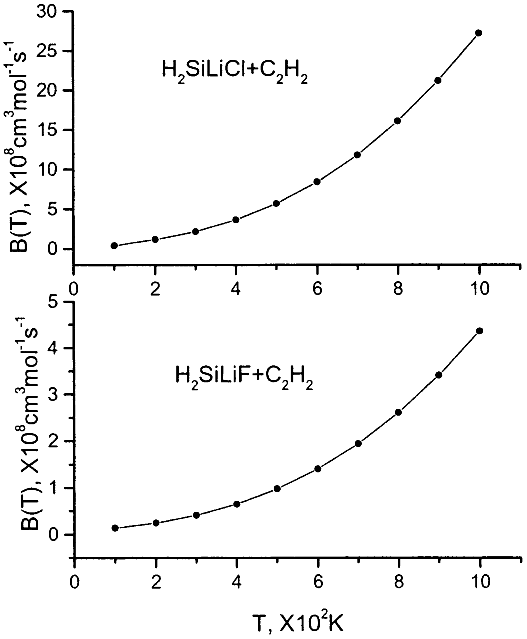


Figure 4. Factor $B(T)$ against temperature (T) for the additions of H_2SiLiX to C_2H_2(X = F, Cl).

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