Physical Chemistry

Quantum-chemical calculations of the mechanism of some reactions of the insertion of silylenes and dichlorosilylenes into a single bond

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Carbenes and silylenes can participate in some insertion reactions both in singlet and in triplet electronic states. The reactivity of silylenes depends on the nature of their substituents. AM1 and PM3 semiempirical calculations were performed for the reactions of silylene and dichlorosilylene insertion into the H—Cl bond of the hydrogen chloride molecule and the C—O bond of the furane molecule. The data obtained was used to propose probable mechanisms of these reactions.

Key words: mechanism of silylene and carbene insertion; AM1 and PM3 calculations.

As has been repeatedly pointed out in the literature on organosilicon compounds, the processes of their synthesis are usually high-temperature gas-phase reactions, in which silylenes are reactive particles.[1—7] Silylenes participate both in the principal reaction and in side reactions. Techniques have been developed for generating these highly reactive intermediates in the gas phase, and acceptors have been found that are systems able to trap silylenes to form thermally stable compounds. Since silylenes are highly unstable, experimental studies of the reaction mechanisms involving these compounds present difficulties. Therefore, quantum-chemical calculations can be helpful in studying the structure and reactivity of silylenes.

One of the most important reactions for practical purposes is the insertion of silylene or dichlorosilylene into a single bond in the preparation of different organosilicon compounds, including heterocyclic compounds with functional groups at the silicon atom. Table 1 lists the calculated and experimental energy characteristics[8] of the insertion reactions of singlet methylene and silylene into H—C and H—Si bonds. It is seen that the weaker the bond into which the insertion occurs and the higher the reactivity of the attacking particle, the lower the activation barrier and the higher the thermal effect of the reaction. We note here only one conclusion of fundamental importance in the theory of silylene and carbene reactions, which implies that the *ab initio* self-consistent field (SCF) method is incapable of describing the energy barriers of these reactions. For this purpose, correlation corrections must be included using the Moller—Plessett perturbation theory, the configuration interaction method, or multiconfigurational SCF methods.

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Table 1. Energetics of the insertion reactions (experimental values are given in parentheses)[8]

Reaction	$E^{\neq}$/kJ mol^{-1}			$\Delta E[\Delta H]$/kJ mol^{-1}
	SCF 3-21G	SCF 6-31G*	MP3/6-31G*//3-21G	
SiH_2+H—CH_3	189.4	180.2	115.0 (71—79)	−204.8 [−208.6]
SiH_2+H—SiH_3	64.0	—	0 (0)	−227.8 [−188.9]
CH_2+H—CH_3	38.0	38.0	0(0)	−483.2 [−427.2]
CH_2+H—SiH_3	8.8	—	0(0)	−522.9 [−501.6]

Note. $E^{\neq}$ is the activation energy of the reaction, ΔH is the heat of formation.

When considering the reactivity of carbene-like particles, it is necessary to take into account that for the singlet states of carbenes and silylenes, the insertion reaction predominates, and for their triplet states, the competitive formation of radicals is also possible (see, for example, Ref. 1). The energetics of the detachment of a hydrogen atom from methane and silane by triplet methylene and silylene have been calculated previously.[9] The results of these calculations by the unrestricted Hartree—Fock method using the MP3/6-31G**//3-21G procedure are presented in Table 2.

Comparing the data in Tables 1 and 2, one can conclude that the detachment reactions are energetically less favorable than the competitive insertion processes. It should be taken into consideration that the silylene ground state is singlet, *i.e.*, ΔE_{ST} must be added to its activation energy $E^{\neq}$ for the detachment reaction. For silylene halides, the value of ΔE_{ST} is even larger, and their participation in the detachment reactions is even less probable. The account of the latter is important only in the analysis of the reactivity of hypothetical metallosilylenes, the simplest of which, *viz.*, dilithiumsilylene, must have the triplet ground state.

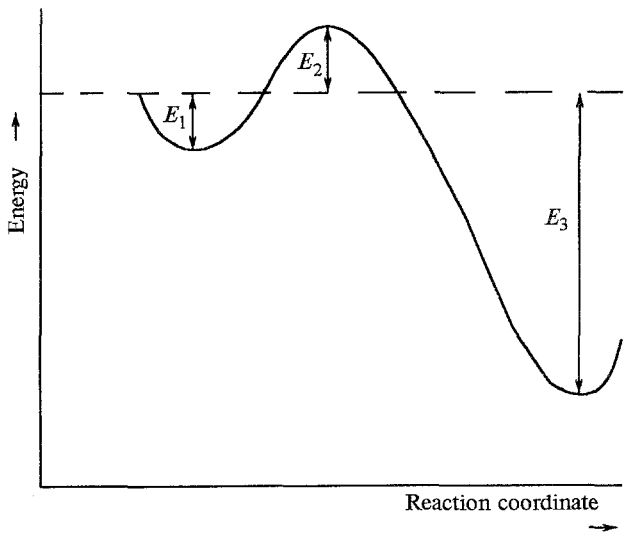


Fig. 1. The section of the potential energy surface for the reaction of the insertion of silylene into the H—X bond obtained by *ab initio* methods.[11]

Table 2. Energetics of the reactions of the detachment of H atoms by carbene and silylene[9]

Reaction	$E^{\neq}$/kJ mol^{-1}	ΔH/kJ mol^{-1}
$CH_2+CH_4 \rightarrow CH_3+CH_3$	74.8	−8.4
$SiH_2+CH_4 \rightarrow CH_3+SiH_3$	136.3	88.6
$CH_2+SiH_4 \rightarrow CH_3+SiH_3$	38.0	−88.2
$SiH_2+SiH_4 \rightarrow SiH_3+SiH_3$	66.5	11.7

Table 3. Energetics of the reactions of the insertion of singlet carbenes and silylenes into the H—H bond of the hydrogen molecule[10]

Reaction	$E^{\neq}$ /kJ mol^{-1}	ΔH /kJ mol^{-1}	ΔH_{exp} /kJ mol^{-1}
CH_2+H_2	8	−497	−496
$CHF+H_2$	64	−358	−351
CF_2+H_2	197	−226	−259
SiH_2+H_2	51	−214	−204
$SiHF+H_2$	130	−174	−199
SiF_2+H_2	274	−113	−195

We now turn to considering the effect of substituents on silylene reactivity. Table 3 gives the energy characteristics of the insertion reactions of singlet methylene, silylene, fluorocarbenes, and fluorosilylenes into the H—H bond of the hydrogen molecule,[10] which are the results of correlated *ab initio* calculations by the MP4/6-31G*//3-21G procedure with the subsequent inclusion of zero-point corrections. It can be seen that the activation energy of the reaction increases significantly with a systematic increase in the number of electronegative substituents.

The mechanism of the insertion of silylene into H—X bonds, where X is an atom more electronegative than Si is more complex.[11] The energy profile of this process is shown schematically in Fig. 1, and the corresponding energies are listed in Table 4 (the calculations were performed using the MP4/6-31G* procedure). At

Table 4. Energy characteristics of the reactions of the insertion of silylene into X—H bonds (see Ref. 11)

Molecule	Bond	E/kJ mol^{-1}		
		E_1	E_2	E_3
NH_3	N—H	−104	54	−251
H_2O	O—H	−54	38	−293
HF	F—H	−29	12	−351
PH_3	P—H	−75	8	−222
H_2S	S—H	−38	21	−251
HCl	Cl—H	−8	25	−288

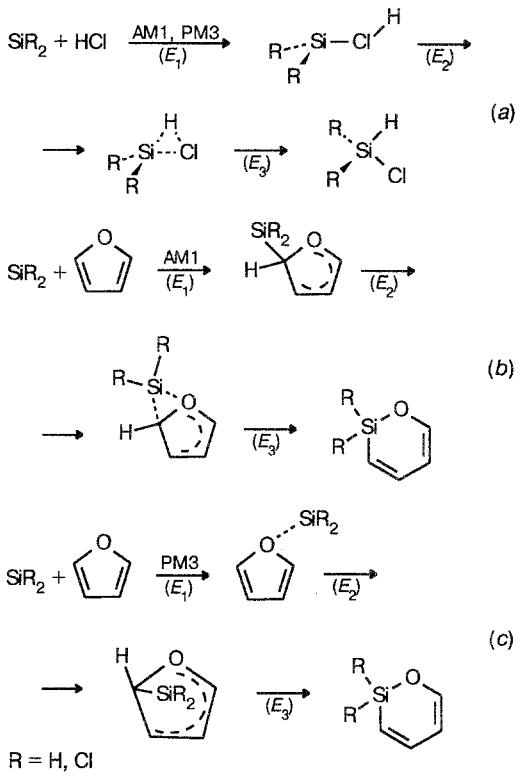
the first stage of the reaction, the metastable ilide-like structure (energy E_1) is formed, which, through a cyclic transition state (formation energy E_2), rearranges to the final products. As the polarity of the H—X bond, where X is a second-row atom, increases, the stability of the metastable intermediate decreases, as well as the activation barrier (E_3) to its rearrangement. When X is a third-row atom, this feature is less pronounced.

It should be noted that all of the calculations mentioned above were performed by *ab initio* SCF MO LCAO methods including correlation effects in extended basis sets. Such calculations of the most practically interesting processes, *e.g.*, the insertion of chlorosilylene into the C—Cl bond of chlorobenzene and the C—O bond of furane (especially in its fused derivatives) are not really possible technically at present. Hence, only semiempirical quantum-chemical methods can be used, the most appropriate of which are the modifications of the MNDO method: AM1[12] and PM3.[13] Although these modifications are far from perfect, their use for qualitative calculations is quite reasonable (*cf.* Ref. 14).

Using semiempirical AM1[12] and PM3[13] methods, we calculated the parameters of the reaction of the insertion of singlet silylene and dichlorosilylene into the H—Cl bond of hydrogen chloride (Scheme 1, reaction *a*) and into the C—O bond of furane (reactions *b* and *c*); the tentative mechanisms of the reactions were discussed. The geometries of the reactants and transition states were optimized by minimizing the total energies and the magnitude of the energy gradient, respectively, in internal coordinates. The criterion for the transition states was the matrix of second derivatives of the energy with respect to all internal coordinates (one negative eigenvalue).

The calculations indicated that the insertion of silylene and dichlorosilylene into HCl proceeds in two stages (see Scheme 1, *a*), with an $R_2Si...ClH$ intermediate formed in the first stage that involves a gain in energy. Then this compound rearranges to chlorosilane through a cyclic three-membered transition state. The activation barrier to this rearrangement is rather low. Table 5 gives the calculated formation energies of all of the mentioned compounds (see Scheme 1).

Scheme 1



It is interesting to note that somewhat different mechanisms of the insertion of SiH_2 and $SiCl_2$ into the furane molecule were obtained depending on the method of calculation. According to the AM1 calculations, in the first stage of the reaction, a σ-complex type intermediate arises with a four-coordinate C(α) atom and the functional groups of this atom perpendicular to the furane plane. Next, this intermediate rearranges into the

Table 5. Energy characteristics of the reactions of the insertion of silylene and dichlorosilylene into the H—Cl bond of HCl and the C—O bond of furane (Fu) calculated by semiempirical methods AM1 and PM3

Reaction	Bond	E/ kJ mol^{-1}		
		E_1	E_2	E_3
			AM1 method	
SiH_2+HCl	H—Cl	−78	−54	−338
$SiCl_2$+HCl	H—Cl	−58	5	−225
SiH_2+Fu	C—O	−88	−44	−445
$SiCl_2$+Fu	C—O	−25	0	−338
			PM3 method	
SiH_2+Fu	C—O	−57	−56	−442
$SiCl_2$+Fu	C—O	−61	−47	−313

transition state, in which the angle between the planes of the furane ring and CSiO is in the range 55—70°. Then the final product, 1-sila-2-oxa-3,5-cyclohexadiene, is formed. The energy difference between the intermediate and the transition state is 44 kJ mol^{-1} for SiH_2 and 25 kJ mol^{-1} for $SiCl_2$.

The PM3 calculations predict a somewhat different mechanism of $SiCl_2$ insertion into furane (see Scheme 1, *c*). In particular, the geometry of the intermediate is characterized by $SiCl_2$ attacking the O atom with an angle between the Si—O bond and the furane plane of ~170°. The transition state of this reaction is closer in structure to a σ-complex with the C(α) atom of the furane ring, but the projection of the Si—C bond to the furane plane lies inside the ring. In this case, the energy difference between the intermediate and the transition state is also rather small ($\Delta E_{PM3}(SiH_2)$ = 1 kJ mol^{-1}, $\Delta E_{PM3}(SiCl_2)$ = 14 kJ mol^{-1}), which once again supports the unfeasibility of studying the mechanism of this reaction experimentally.

Comparison of the data in Tables 4 and 5 indicates that the AM1 calculations correctly reproduce the order of the variation of the activation energies, but they underestimate the energies of intermediates, transition states, and final products by 50—80 kJ · mol^{-1} compared to the *ab initio* calculations and the experiment. The energy profile of the reaction obtained by semiempirical calculations is similar to that presented in Fig. 1. This method is more precise in reproducing the energies of the initial reactants: $\Delta H_{calc}(SiCl_2+HCl)$ = −298 kJ mol^{-1}, $\Delta H_{exp}(SiCl_2+HCl)$ = −257 kJ mol^{-1}, $\Delta(\Delta H)$ = −41 kJ mol^{-1}; $\Delta H_{calc}(SiCl_2+Fu)$ = −183 kJ mol^{-1}, $\Delta H_{exp}(SiCl_2+Fu)$ = −156 kJ mol^{-1}, $\Delta(\Delta H)$ = −26 kJ mol^{-1}). This offers an explanation for the appearance of negative values of E_2 in Table 5.

The obtained results suggest that the considered reactions proceed either without any energy barrier at all, or with only small energy consumption, *i.e.*, silylenes and dichlorosilylenes insert readily into the H—Cl bond of hydrogen chloride and the C—O bond of furane.

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