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Quantum-chemical calculations of the electronic structure and reactivity of silylenes

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The origin of the different reactivities of carbenes and silylenes has been discussed. Molecular orbital calculations have been carried out in order to estimate the effects of substituents on the singlet-triplet splittings ΔE_{ST} in these molecules. The data of *ab initio* calculations have been used to establish the linear correlation between ΔE_{ST} values for carbenes and silylenes. Both qualitative and quantitative appraisals of the applicability of the semiempirical MNDO method to calculations of ΔE_{ST} values for carbenes and silylenes have been derived. ΔE_{ST} values for a large number of substituted carbenes and silylenes have been computed by the PM3 method, one of the latest versions of the MNDO approach (Ref. 14).

Key words: substituted carbenes and silylenes; electronic structure; molecular orbital calculations.

Theoretical investigations of organosilicon systems were initiated in the seventies.[1] Being devoted to the individual properties of organosilicon compounds, these early studies were mainly carried out within the common framework of investigations of the structure and reactivity of typical organic molecules. From the early eighties, increasing attention was given to the specific features of silicon compounds, accounting, in particular, for the fact that the majority of the synthetic processes of organosilicon compounds are high-temperature gas-phase reactions in which silylenes play the role of active particles.[2–6] According to the data presented in Table 1, this peculiarity arises from the fact that in the decomposition of paraffins the formation of radicals is energetically favorable, whereas for organosilicon molecules the "silylene pathway" is preferable.[7]

Silylenes are the closest analogs of carbenes. The results of experimental studies of the structure and reactivity of the latter have been reviewed and discussed in detail.[2–6] Possible electronic configurations of carbenes and silylenes are shown schematically in Fig. 1. The reactivity of these compounds depends primarily on

Table 1. Enthalpies (ΔH/ kJ mol^{-1}) of radical, carbene, and silylene decomposition pathways

Process	ΔH
$SiH_4 \longrightarrow SiH_3^{\cdot} + H^{\cdot}$	380
$SiH_4 \longrightarrow SiH_2\colon + H_2$	205
$CH_4 \longrightarrow CH_3^{\cdot} + H^{\cdot}$	439
$CH_4 \longrightarrow CH_2\colon + H_2$	493

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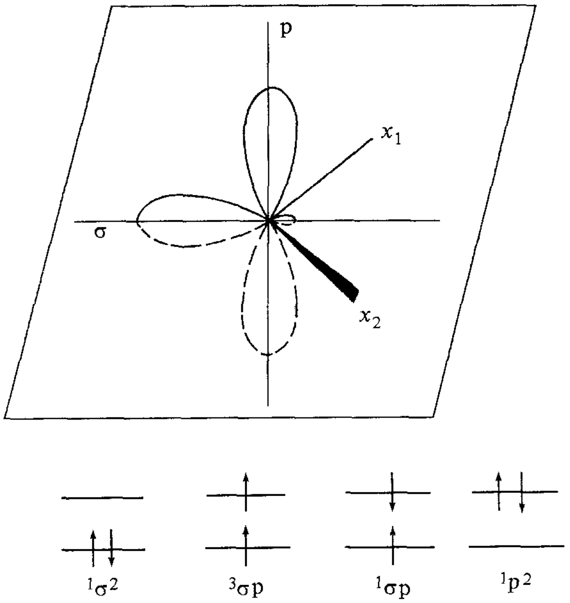

Fig. 1. Possible electronic configurations of carbene-like systems.[6]

the electronic configuration and spin multiplicity of their ground states, which, in turn, are determined by the difference in energies of the s and p orbitals of the silicon or carbon atom, the values of the one-center exchange integral, and the characteristics of the substituent at the carbene or silylene center that affect the delocalization of electron density in the system. As is evident from Fig. 1, the most important factor is the energy gap between the $^1\sigma^2$ and $^3\sigma p$ states, so the relative stability may be estimated by the singlet-triplet splitting ΔE_{ST}. For a large number of substituted carbenes a linear dependence between ΔE_{ST} and the resonant constants of substituent σ^0_R has been established.[8] These constants reflect the electronegativity of the substituents, so the stability of the singlet ground state and the absolute value of ΔE_{ST} increase with electronegativity in agreement with the results of previous theoretical studies.[9]

Less is known experimentally about silylenes, and the corresponding data are less accurate than those on carbenes. Hence, the application of quantum-chemical approaches for estimating ΔE_{ST} of silylenes is of special interest. The ΔE_{ST} values for several silylenes calculated by *ab initio* methods in extended basis sets with the inclusion of correlation effects[10,11] are listed in Table 2 together with the same data for analogous carbenes.[12]

Table 2. Singlet-triplet splittings (ΔE_{ST}/ kJ mol^{-1}) calculated *ab initio* for silylenes and carbenes[10—12]

Silylene	ΔE_{ST}	Carbene	ΔE_{ST}
SiH_2	−74.6	CH_2	53.5
SiHF	−140.0	CHF	−38.5
SiF_2	−309.3	CF_2	−186.0
SiHCl	(−122.9)*	CHCl	−6.7
$SiCl_2$	(−170.5)	CCl_2	−56.4
$SiLi_2$	43.1	CLi_2	(166.4)

* Estimated by relation (1).

The methylene (as well as, probably, other alkylcarbenes) and the hypothetical dilithium carbene have the triplet ground states (positive ΔE_{ST}), see Table 2. At the same time, almost all silylenes (except the hypothetical dilithiated species) have the singlet ground states since the electropositivity of the silicon atom is remarkably higher than that of the carbon atom. The data compiled in Table 2 make it possible to establish a linear correlation between the ΔE^{Si}_{ST} for silylenes and ΔE^{C}_{ST} of carbenes:

$$\Delta E^{Si}_{ST} = 4.0 \cdot \Delta E^{C}_{ST} - 116.5 \quad (r = 0.995). \tag{1}$$

The estimation of ΔE_{ST} by Eq.(1) given in Table 2 in parentheses coincides with the calculated and thermochemically measured values[11] within 4—6 kJ mol^{-1} accuracy, whereas the deviation in practical measurements of this quantity is much higher.

Ab initio calculations of sufficiently complex systems are time-consuming and, in some cases, even technically impossible. The only alternative is to resort to semiempirical quantum-chemical approaches. Table 3 contains ΔE_{ST} values for carbenes and silylenes computed by the MNDO method. Comparing the entries of Tables 2 and 3, one can easily see that although the MNDO approach correctly reproduces the trends in ΔE_{ST} variation along the rows of carbenes and silylenes,

Table 3. Singlet-triplet splittings (ΔE_{ST}/ kJ mol^{-1}) calculated by the MNDO method for silylenes and carbenes

Silylene	ΔE_{ST}	Carbene	ΔE_{ST}
SiH_2	−8.8	CH_2	139.5
SiHF	−85.4	CHF	41.5
SiF_2	−227.4	CF_2	−129.0
SiHCl	−62.3	CHCl	87.2
$SiCl_2$	−125.4	CCl_2	30.8
$SiLi_2$	104.6	CLi_2	79.0

Table 4. Heats formation of R^1—Si—R^2 silylenes calculated by the PM3 method (kJ mol^{-1})

R^1	R^2	Singlet			Triplet	
		RHF	CI(2×2)	CI(4×4)	RHF	UHF
H	H	213	148	135	127	114
H	Li	340	241	240	240	206
H	F	−362	−379	−405	−398	−408
F	F	−941	−955	−968	−923	−930
H	CH_3	49	−33	−35	−34	−51
H	SiH_3	177	68	55	66	38
H	NH_2	32	−47	−51	−53	−70
NH_2	NH_2	−160	−238	−237	−241	−257
CH_3	CH_3	−111	−195	−198	−193	−214
SiH_3	SiH_3	84	−12	−14	−13	−53

Table 5. Singlet-triplet splittings (ΔE_{ST}/ kJ mol^{-1}) of R^1—Si—R^2 silylenes calculated by the PM3 method (kJ mol^{-1}) and correlation coefficients *r* for the $y = ax + b$ dependence

R^1	R^2	RHF*	CI(2×2)*	CI(4×4)*	RHF**	CI(2×2)**	CI(4×4)**	ΔE_{ST}[15]
H	H	86	20	8	100	34	21	−69
H	Li	100	1	0	134	36	34	41
H	F	35	19	−7	46	29	3	−158
F	F	−18	−32	−44	−11	−25	−37	−309
H	CH_3	84	1	0	101	18	17	−83
H	SiH_3	112	3	−9	139	30	16	−43
H	NH_2	85	6	−2	102	23	19	−169
CH_3	CH_3	82	−2	−5	103	19	16	−92
SiH_3	SiH_3	97	1	−1	137	41	39	−24
NH_2	NH_2	81	3	4	97	19	20	—
a		2.222	3.431	5.295	1.893	4.438	4.188	
b		−264.6	−107.1	−65.4	−279.7	−201.8	−160.2	
r		0.8842	0.5089	0.7756	0.9120	0.8549	0.9059	

* Calculated by the RHF method. ** Calculated by the UHF method.

it overestimates the stability of triplet states by 50—80 kJ mol^{-1}.

For this reason we attempted to investigate some substituted silylenes using one of the most recent modifications of the MNDO scheme, namely, the PM3 version,[14] for calculations of their heats of formation and singlet-triplet splittings (see Table 4). The singlet states were calculated within the restricted Hartree-Fock method (RHF) with the limited 2×2 or 4×4 configuration interaction (CI), while the triplet states were studied within the "half-electron" approximation (a version of the RHF approach) and the unrestricted Hartree-Fock method (UHF). The ΔE_{ST} values (*x*) obtained using these methods were correlated with those determined *ab initio* for analogous systems[15] in order to find the correlation coefficients *r* for the $y = ax + b$ dependence, see Table 5. Obviously, the qualitatively best results were reached when ΔE_{ST} was evaluated as $E_S^{RHF} - E_T^{UHF}$ or $E_S^{CI(4\times4)} - E_T^{UHF}$ (Table 5, columns 4 and 6, respectively), although quantitatively these results are still not satisfactory. This is likely a consequence of deficiencies in the PM3 parameterization which prevent the optimization of geometric parameters with desirable accuracy (the optimization routine was terminated at relatively high gradient norms).

Furthermore, our data reveal that the use of the UHF scheme for the triplet states results in a noticeably better correlation between the nonempirical and empirical data, whereas the inclusion of the CI procedure for singlet states makes it even worse. The PM3 method markedly overestimates the ΔE_{ST} values with respect to *ab initio* approaches. This is primarily the consequence of the lowering of the triplet state energy pertinent to the semiempirical UHF schemes (see, for example, Ref. 16). At the same time, this method is likely to be acceptable for qualitative theoretical studies of the mechanisms of reactions between organic compounds and silylenes.

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