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Relationship between stability and dimerization ability of silylenes

Julianna Oláh, Tamás Veszprémi *

Department of Inorganic Chemistry, Budapest University of Technology and Economics, Gellért tér 4, H-1521 Budapest, Hungary

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Abstract

Isodesmic reaction energies and dimerization energies were calculated for several silylenes using B3LYP/6-31G(D) and MP2/6-311+G(2D) quantum chemical methods. Two different dimerization routes, the disilene formation and the four-membered bridge structure, were considered. The dimerization energy for disilene formation correlates excellently with the stabilization energy and the singlet–triplet energy separation of the silylenes. No correlation, however, has been found between the dimerization energy of the bridged dimer formation and the isodesmic reaction energy or the singlet–triplet energy separation of silylenes.

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1. Introduction

Silylenes are frequent intermediates in thermal and photochemical reactions. Their existence was first proposed as transient molecules in organometallic chemistry and later they were observed in matrix at low temperature and still later in the 1990s as stable species. The first “bottleable” silylene **1a** (Scheme 1) was synthesized in 1994 by Denk et al. [1]. Subsequently **2a**, the saturated form of **1a**, was also isolated [2]. The first stable alkyl-silylene **3a** was synthesized by Kira et al. [3] in 1999.

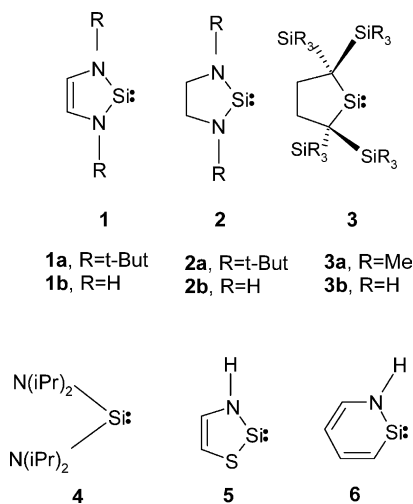
In 1990s, much effort was made to identify the main factors of the stabilization of divalent silicon species. The most important factor in the stabilization of singlet silylene is the π -electron donation from the substituent to the formally empty p-orbital of silicon [4]. This effect is the largest if the substituent is in α -position to the divalent center. On the other hand, triplet silylenes can be stabilized by electropositive substituents such as Li [4a] or Na [4b]. The stabilizing effect of alkyl groups is small, but it can be modified by other groups in β -position. The existence of **3a** is the clearest example for the stabilizing effect of β -silyl groups. The same effect

was found in the case of carbenes; Gordon's theoretical calculations indicate that β -silyl groups stabilize singlet carbenes to a large extent [5].

A second important factor of stability is the possible aromaticity. On the basis of electron density analysis, isodesmic reaction energies and bond lengths, Apeloig and coworkers [6] showed that aromaticity is important in the stabilization of molecules. The aromaticity of **1a** is about 60% of that of benzene. The analysis of NICS(2) indices of **1**, **2**, benzene and thiophene resulted in the same conclusion [7]. Electron density analysis of **1**, **2** and their benzo-condensed analogues revealed that though the overall electron density does not differ considerably in the saturated and unsaturated compounds, there is a large difference in the charge distribution of the σ - and π -system which can be interpreted by the +I and –M effects [8]. Boehme and Frenking [9] also confirmed these findings. According to them, the π -electron density in the p_{π} -orbital of the divalent Si is 0.54 in the unsaturated **1**, while in the saturated **2** it is only 0.33. Aromaticity is an important factor in the stabilization of silylenes, but it is not essential, as it is proved by the existence of **2a** and **3a**. The same fact was concluded from the isodesmic reaction energies of silaimidazol-2-ylidene and its isomeric silene and silane forms. The isodesmic reaction energies clearly indicated that silenes are the most aromatic compounds while silylenes are only moderately aromatic [10]. In the case of cyclic

* Corresponding author. Tel.: +36-1-463-1793; fax: +36-1-463-3642.

E-mail address: Tveszpremi@mail.bme.hu (T. Veszprémi).



Scheme 1.

compounds, ring stress is an important destabilizing factor. Systematic analysis of the ring stress led to the design of **6** [11] which was predicted to be as stable as **1**. Although in this molecule there is only one nitrogen atom next to the silyl center, the 6π -electrons allow cyclic delocalization and thanks to the six-membered ring the ring stress is minimized. Further kinetic stabilization can be expected using bulky groups which prevent the divalent species from dimerization, e.g. as it is in bis(diisopropyl-amino)silylene (**4**) [12].

The knowledge of the main factors of stability gives some opportunity for a systematic design and finally it may give hints for the synthesis of hitherto unknown divalent species.

Such process has been proposed in our previous work for carbenes [13]. Our results clearly indicate that in case of (sterically not hindered) carbenes there is an excellent linear correlation between the electronic effects stabilizing the carbenes and the dimerization energies. As a consequence, with the computation of a simple isodesmic reaction, one can predict the stability of an unknown carbene.

This motivated us to investigate the same relationship for silylenes. However, we shall prepare for some complications. While the dimerization product of carbenes is always a stable olefin, silylene dimers are usually as unstable as the monomer is. Furthermore, Trinquier [14] and Apeloig et al. [15] have suggested that for silylenes at least two different dimerization routes exist. In Fig. 1, Path 1 shows the “classical” way: the lone pair of the first molecule overlaps with the empty p-orbital of the other molecule forming a disilene. The product has a *trans*-bent geometry if the sum of the singlet–triplet separation of the parent silylene is larger than half of the total bond energy of the Si=Si double bond [16].

In Path 2, the lone pair orbital of the substituent of a silylene interacts with an empty Si(3p) orbital of the

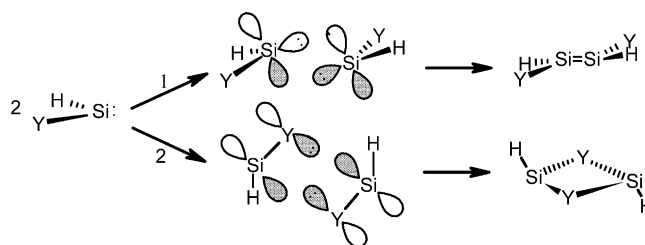


Fig. 1. Dimerization routes of silylenes.

other silylene forming a bridged structure. The bridged species are best described as donor–acceptor complexes [15a]. Since the dimerization process in both ways is barrierless and exothermic, the same correlation is expected as was found in case of carbenes. Obviously, some other complications are also possible, e.g. the two dimerization channels can compete with each other. This was experimentally observed by Takahashi et al. [17] who have pointed out that the dimerization process of silylenes might strongly depend on the temperature. At lower temperature, **4** dimerizes to disilene while at room temperature the bridged dimer is formed. New dimerization routes can also exist, e.g. in case of **2a**, where both paths are blocked [18]. Due to the large size of the *t*-butyl groups on **2a**, the molecules cannot approach to the appropriate Si–N distance and orientation without encountering severe steric repulsion. Therefore, the bridged isomer cannot be formed. Thus, first an insertion of the first silylene into the Si–N bond of the second molecule takes place leading to a new silylene. This new silylene is already able to dimerize to form a Si=Si double bond.

2. Calculations

Quantum chemical calculations were performed with the Gaussian 98 program package [19] at the B3LYP and MP2 levels of theory using the 6-31G(D) and 6-311+G(2D) basis sets. The nature of the stationary points were further checked with second derivative calculations to prove that the optimized geometries were real minima on the potential energy surface. Gibbs free energies were calculated using the ideal gas, rigid rotor and harmonic oscillator approximation. UHF and UMP2 methods were used for studying the triplet states. The spin contamination was carefully checked and it was found that the S^2 value was always around 2. As a consequence, contamination of higher spin states is negligible for these states.

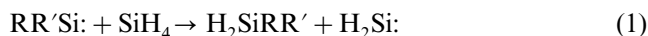
3. Results and discussion

The stabilization energy of silylenes has been calculated using the following isodesmic reaction:

Table 1

Isodesmic reaction energies (ΔE_i), dimerization energies (ΔE_{dim}), Gibbs free energies and singlet–triplet energy differences (ΔE_{s-t})^a

	ΔE_i	ΔE_{s-t}	ΔE_{dim} disilene	ΔG_{dim} disilene	ΔE_{dim} bridged
HSiH	0.0 (0.0)	20.1 (14.3)	−61.2 (−64.8)	−47.7	^b
HSiLi	−16.9 (−15.2)	−23.8 (−28.5)	−115.0 (−122.0)	−103.8	^b
HSiBeH	−1.1 (−0.4)	−0.003 (−4.5)	−83.1 (−88.9)	−68.8	^b
HSiCH ₃	0.9 (0.2)	22.3 (17.5)	−57.5 (−62.8)	−42.5	^b
HsiNH ₂	23.1 (20.9)	41.0 (37.3)	−20.3 (−23.0)	−8.9	−29.8 (−32.9)
HsiOH ^c	15.8 (14.2)	39.9 (35.0)	−28.6 (−30.2)	−16.5	−24.7 (−24.6)
HSiF	9.6 (8.6)	39.1 (33.0)	−36.4 (−35.1)	−22.6	−21.2 (−14.9)
HSiNa	2.6 (1.6)	−3.8 (−11.6)	−85.3 (−101.3)	−71.1	^b
HSiMgH	0.8 (0.8)	−0.7 (−6.7)	−81.8 (−91.4)	−68.1	^b
HSiAlH ₂	3.7 (3.3)	3.9 (−1.2)	−75.5 (−84.5)	−60.7	^b
HSiSiH ₃	1.6 (1.1)	13.5 (8.1)	−66.4 (−74.7)	−51.0	^b
HSiPH ₂	10.7 (9.1)	22.4 (18.4)	−44.1 (−52.6)	−31.2	−41.4 (−50.9)
HSiSH ^c	20.2 (19.0)	35.6 (32.0)	−24.0 (−29.0)	−12.5	−15.4 (−25.2)
HSiCl	12.0 (10.5)	33.7 (29.2)	−35.4 (−39.6)	−22.0	−12.6 (−18.8)
Si(NH ₂) ₂	31.0 (28.9)	55.6 (54.1)	^d	^d	−13.7 (−16.6)
Si(OH) ₂ ^c	29.5 (28.6)	65.5 (62.6)	^d	^d	−12.8 (−11.0)
Si(SH) ₂ ^c	29.7 (28.8)	43.1 (42.4)	−6.5 (−13.4)	2.0	−1.4 (−11.1)
SiF ₂	24.7 (23.5)	75.6 (67.9)	−6.56 (−1.6)	5.0	−11.1 (−2.8)
SiCl ₂	25.5 (23.1)	53.0 (49.7)	−10.3 (−14.2)	1.4	−1.1 (−7.6)
H ₂ NSiOH ^c	29.5 (28.7)	60.1 (58.3)	−0.6 (1.5)	8.8	−19.4 (−21.6)
H ₂ NSiSH ^c	31.5 (29.9)	50.1 (48.9)	−2.5 (−5.7)	7.8	−20.6 (−25.5)
HOSiSH ^c	27.3 (25.8)	51.3 (49.1)	−7.2 (−9.9)	3.8	−13.9 (−14.8)
1b	51.47	59.3 (67.0)	^d	^d	^d
2b	38.86	75.5 (71.1)	−1.8	8.9	−14.3
3b	13.31	32.4	−29.9	−8.3 ^e	^b
5	46.36	56.5 (64.5)	^d	^d	12.2
6	35.84	60.3 (61.4)	−3.9	6.8	22.2

^a At the B3LYP/6-31G(D) and MP2/6-311+G(2D) (in parentheses) level of theory. Data in kcal mol^{−1}.^b Bridged dimer was not considered.^c Data for the lowest energy conformer—HSiOH, HSiSH, H₂NSiOH, H₂NSiSH: *trans*-isomer; Si(OH)₂: *cis*–*trans*-isomer; Si(SH)₂: *trans*–*trans*-isomer; HOSiSH: the OH group in *cis*- and the SH group is in *trans*-position.^d No dimer was found.^e At the B3LYP/3-21G(D) level.

The calculated B3LYP/6-31G(D) results are summarized in Table 1. The table also contains the MP2/6-311+G(2D) results in parentheses. As expected, among the monosubstituted derivatives the largest stabilization is found by the R = NH₂ and SH groups. Disubstitution increases the stabilization. The effect of the second substituent is larger for OH, F and Cl and smaller for NH₂ and SH than that of the first one. The results suggest that the main stabilization effect is the saturation of the empty p-orbital of silicon which may reach a maximum value. Similar trend was observed for carbenes [13].

Compounds **1**–**3** which proved experimentally to be stable have much larger stabilization energy than all the other compounds. The only exception is **3b**, which may indicate that SiMe₃ groups stabilize silylene much more effectively than silyl groups and this stabilization is not only due to the large steric requirements of the SiMe₃ groups.

The saturation effect is not observed in the singlet–triplet energy differences (ΔE_{s-t}). This quantity, how-

ever, strongly depends on the calculational method. As it was stated earlier, precise, highly sophisticated MRCI calculations with large basis sets and relativistic corrections are necessary to correctly predict the experimental ΔE_{s-t} [20]. Therefore, the absolute values of our calculated ΔE_{s-t} are probably not precise but as the main sources of the error do not change significantly with the substitution [21], we can assume that the trends of our results are correct. From the data it is obvious that the isodesmic reaction energies and ΔE_{s-t} values are interrelated. It is interesting that **1b** which is more stable thanks to its aromaticity than **2b** has a smaller ΔE_{s-t} than **2b** at both levels of theory.

In Fig. 2, the energy of the isodesmic reaction (1) is plotted against the silylene dimerization energy and dimerization Gibbs free energy (Path 1). The two curves run parallel. Due to the entropy factor the Gibbs free energies are larger than the dimerization energies. The correlation is somewhat worse than in the case of carbenes [13].

Three different regions can be separated in the plot. The first region consists of silylenes with triplet ground

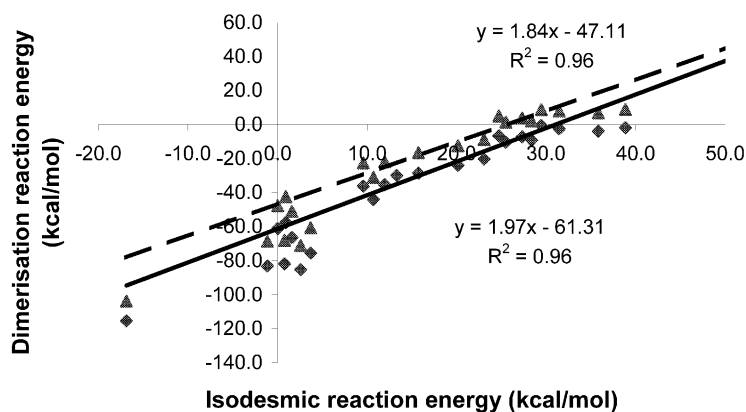


Fig. 2. Isodesmic reaction energy vs. the dimerization energy (◆) and Gibbs free energy (▲, dashed line) at the B3LYP/6-31G(D) level (Path 1).

state ($\Delta E_i < 4 \text{ kcal mol}^{-1}$). These compounds have an isodesmic energy close to zero (except for Li, where $\Delta E_i = -16.9 \text{ kcal mol}^{-1}$). In the following region between $\Delta E_i = 4$ and 35 kcal mol^{-1} , the dimerization energy (and the dimerization Gibbs free energy) changes linearly with the isodesmic reaction energy. The correlation coefficient calculated for this region is $R^2 = 0.97$ for both the dimerization energy and the dimerization Gibbs free energy (MP2: $R^2 = 0.91$). The third region of the diagram above $\Delta E_i = 35 \text{ kcal mol}^{-1}$ consists of the highly stable silylenes. In this part, the curve is getting flat; the dimerization energy is close to zero while the dimerization Gibbs free energy is positive, i.e. the dimerization process is thermodynamically not allowed. We could not find doubly bonded isomers in case of **1b** and **5**.

The singlet–triplet energy separation correlates well with the dimerization energy (see Fig. 3). The correlation is somewhat better for the MP2 results ($R^2 = 0.99$) than for the B3LYP data ($R^2 = 0.98$), and better than that found between the isodesmic reaction energy and the dimerization energy. Also, in this case the highly stable silylenes make the curve flat (we omitted these points from the correlation). Silylenes with triplet

ground state lie, however, on the line as this correlation takes the ground state of the molecules into consideration. Similar observation was reported by Karni and Apeloig [22].

As it was mentioned, Apeloig suggested that bridged dimers could be formed in the case of substituents having lone pairs. (Note that several bridged structures can be found on the potential surfaces of H- [23], Li-, Na-, MgH- and AlH₂-substituted dimers, but we excluded them from the recent discussion, since they are highly unstable and their electronic structure is essentially different from that of the investigated potentially stable molecules.) In this work, we considered bridged dimers of NH₂, OH, F, PH₂, SH and Cl mono- and disubstituted silylenes. Besides the homodisubstituted silylenes, we examined some heterodisubstituted species: RR'Si where R, R' = NH₂, OH, SH. From these several dimers can be formed which are all real minima on PES (see Table 2). As expected, the ($\mu\text{-NH}_2$)₂-bridged dimers are the lowest in energy and the ($\mu\text{-SH}$)₂-bridged are the highest. The stability of bridged dimers strongly depends on the bridging substituent and on its ability of donating a lone pair to the silicon. This explains why the dimerization energy of the monosubstituted silylenes

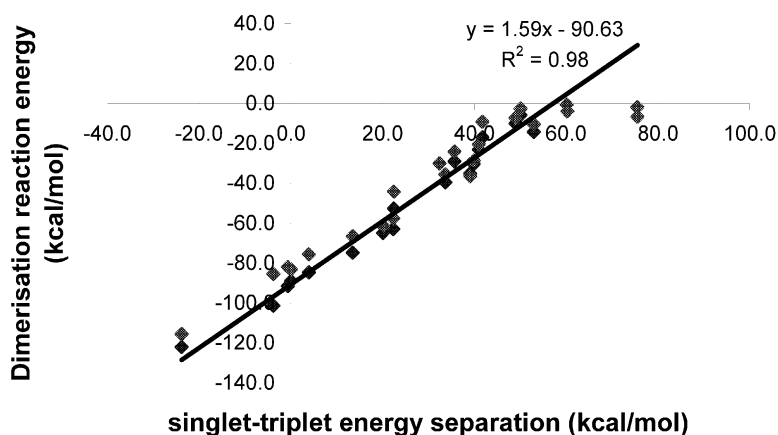


Fig. 3. Singlet–triplet energy separation vs. the dimerization energy at the B3LYP/6-31G(D) level (Path 1).

Table 2
Dimerization energies of heterodisubstituted silylenes (kcal mol⁻¹)

Silylene/bridging groups	ΔE_{dim} bridged
H ₂ NsiOH	
(μ -OH)(μ -NH ₂)	-13.1 (-13.6)
(μ -OH) ₂	-8.2 (-6.8)
H ₂ NsiSH	
(μ -SH)(μ -NH ₂)	-7.1 (-13.8)
(μ -SH) ₂ ^a	- (-1.5)
HOSiSH	
(μ -OH)(μ -SH)	-8.7 (-13.6)
(μ -SH) ₂	-1.6 (-9.0)

^a No bridged species was found at the B3LYP/6-31G(D) level.

increases in the F < Cl < OH < SH < NH₂ order (see the dotted line in Fig. 4). The PH₂ groups behave somewhat differently. The large dimerization energy and the relatively low stabilization energy are due to the fact that in HSiPH₂ the phosphorus is almost planar due to the interactions between the PH₂ lone pair and the SiH empty orbital. As a consequence, some energy must be surmounted to reach this conformation.

For the disubstituted silylenes the trend between stability and the dimerization energy changes in a similar fashion: with the increasing stability of silylene the stability of disilene decreases. However, there is no linear relationship between the two values. Although for R = NH₂, OH and R' = H Apeloig and Müller [15a] suggested that the reaction is barrierless and concerted, our results indicate that the mechanism of the bridged dimer formation may not be a simple one-step reaction for all the cases. Also, in the case of bulky substituents a barrier might exist along the reaction path, which may change the linear correlation between the stability of silylene and its dimer. The same is true for the singlet–triplet energy separation and the dimerization energy of bridged dimers (Fig. 5). Although we can observe a

tendency of the smaller dimerization energies with increasing ΔE_{s-t} , the correlation is far from linear.

4. Conclusion

The relationship between stability and resistance against the dimerization reaction of silylenes was studied with theoretical methods. It was found using B3LYP and MP2 quantum chemical calculations that for silylenes with singlet ground state a linear correlation exists between the isodesmic reaction energies and dimerization energies in the 4 < ΔE_i < 35 kcal mol⁻¹ region. The slightly worse correlation between the two values compared to the respective carbenes is due to the reduced stability of the Si=Si dimers. On both ends of the linearity region some deviation from linearity has been found. The singlet–triplet energy differences also correlate well with the dimerization energies, but in the case of the highly stable silylenes ($\Delta E_{s-t} > 60$ kcal mol⁻¹) the curves become flat. The results suggest that both the isodesmic reaction energy and the singlet–triplet energy separation can be used to predict the chemical stability of silylenes. No correlation, however, has been found between the dimerization energy of the bridged dimer formation and the isodesmic reaction energy or the singlet–triplet energy separation of silylenes.

Acknowledgements

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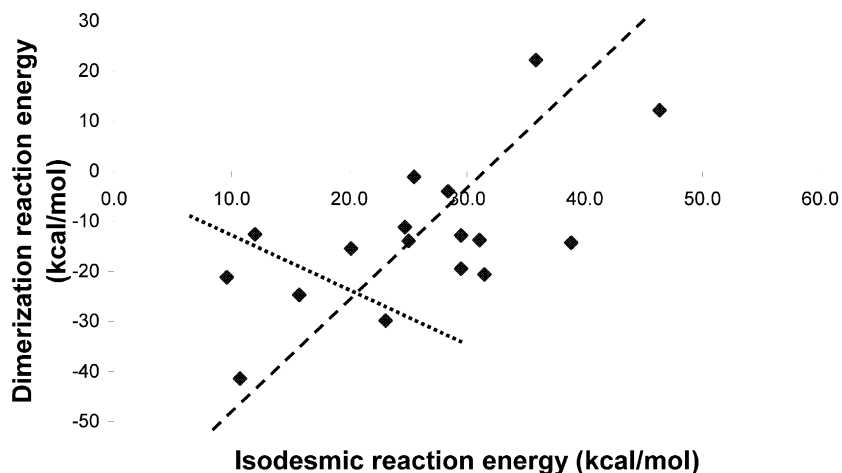


Fig. 4. Relationship between the isodesmic reaction (1) and the dimerization energy at the B3LYP/6-31G(D) level (Path 2).

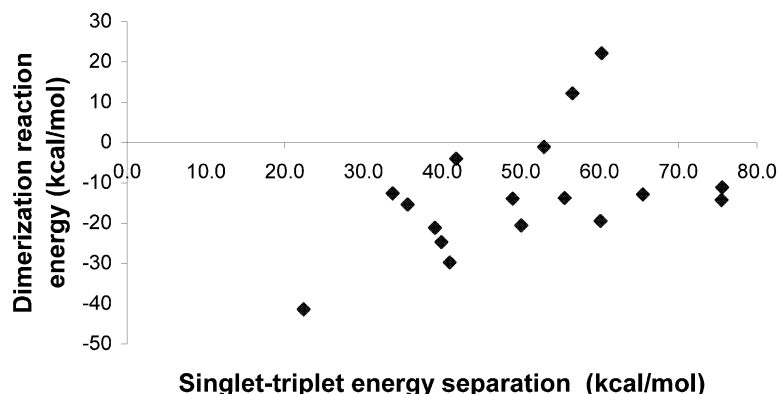


Fig. 5. Singlet–triplet energy separation vs. the dimerization energy at the B3LYP/6-31G(D) level (Path 2).

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