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The First Electrochemical Study of a Silene. An Unusually Low Oxidation Potential, Comparable to Those of Strong Organic π-Electron Donors

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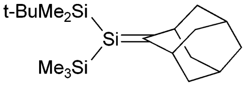
Summary: The first electrochemical study of a compound containing a Si═C double bond, i.e., (t-BuMe$_2$Si)(Me$_3$Si)Si═2-Ad, reveals an extremely low oxidation potential of 0.28 V (vs Ag/AgCl), which is comparable to those of of the best known organic electron donors.

Since the first report of firm evidence for the existence of compounds with a Si═C double bond (silenes) in 1967,[1] several physical properties of transient and stable silenes have been determined.[2−4] However, one of the most basic physical properties of silenes, their redox potentials, have not been studied yet. Here we report the first cyclic voltammetry (CV) measurements of a stable silene, (t-BuMe$_2$Si)(Me$_3$Si)Si═2-Ad (**1**),[5] which provide important insight into the electronic structure of silenes.



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CV measurements (Figure 1) of silene **1**, which were carried out in THF with Bu$_4$NClO$_4$ as an electrolyte, show a one-electron quasi-reversible[6] reduction couple at $E^{1/2}{}_{\text{red}} = -1.80$ V (vs Ag/AgCl) and a broad, ill-defined oxidation wave, centered at ∼0.4 V. The redox couple did not disappear even after seven consecutive scans. This behavior indicates that, although the anion radical $\mathbf{1}^{\bullet -}$ is stable during the time scale of the voltammogram measurement in this medium, the cation radical is not. When the voltammogram was measured in CH$_2$Cl$_2$−Bu$_4$NClO$_4$, an oxidation couple corresponding to the cation radical $\mathbf{1}^{\bullet +}$ was detected at $E^{1/2}{}_{\text{ox}} = +0.28$ V, but no reduction wave was found up to −2 V. However, the quasi-reversible[6] couple disappears quite rapidly upon consecutive scans (only a trace of it remained at the third cycle), indicating that **1** is relatively short-lived (seconds) and undergoes decomposition in this solvent−electrolyte system.[6,7] In any case, this is the first reported observation by CV at room temperature of both the anion radical and the cation radical of the same organosilicon compound.[8−10]

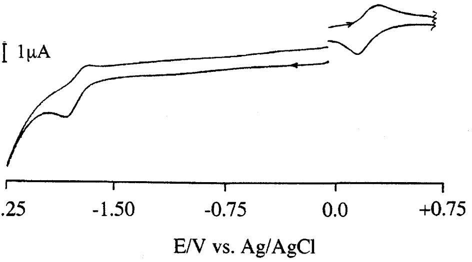

Figure 1. Cyclic voltammograms of silene **1** (2−3 mM) at a Pt working electrode (Fc/Fc$^+$ = 0.50 V vs Ag/AgCl), in CH$_2$Cl$_2$−0.1 M Bu$_4$NClO$_4$ (positive scan) and in THF−0.1 M Bu$_4$NClO$_4$ (negative scan). The sweep rate was 100 mV/s.

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(1) Gusel'nikov, L. E.; Flowers, M. C. *Chem. Commun.* **1967**, 864.

(2) For the most recent comprehensive review on silenes see: Müller, T.; Ziche, W.; Auner, N. In *The Chemistry of Organic Silicon Compounds*; Rappoport, Z., Apeloig, Y., Eds.; Wiley: Chichester, U.K., 1998; Vol. 2, Chapter 16.

(3) For previous reviews see: (a) Raabe, G.; Michl, J. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: Chichester, U.K., 1989; Chapter 17. (b) Brook, A. G.; Brook, M. A. *Adv. Organomet. Chem.* **1996**, *39*, 71. (c) Raabe, G.; Michl, J. *Chem. Rev.* **1985**, *85*, 419.

(4) (a) Buffy, J. J.; West, R.; Bendikov, M.; Apeloig, Y. *J. Am. Chem. Soc.* **2001**, *123*, 978. (b) Bendikov, M.; Solouki, B.; Auner, N.; Apeloig, Y. *Organometallics* **2002**, *21*, 1349. (c) Bendikov, M.; Apeloig, Y.; Bukalov, S.; Garbuzova, I.; Leites, L. *J. Phys. Chem. A* **2002**, *106*, 4880.

(5) Apeloig, Y.; Bendikov, M.; Yuzefovich, M.; Nakash, M.; Bravo-Zhivotovskii, D.; Bläser, D.; Boese, R. *J. Am. Chem. Soc.* **1996**, *118*, 12228.

(6) Peak separations (ΔE_p) of ∼120 mV were found in both solvents. This value is greater than the theoretical 58 mV, which is the reason for calling the electron-transfer process "quasi-reversible". However, it is quite common to obtain peak separations larger than 58 mV in solvents with small dielectric constants, such as THF and CH$_2$Cl$_2$. Since the silene is relatively stable in THF, the current function ($i_p/(C\nu^{1/2})$) of the reduction peak could be evaluated and was found to be constant over the range of 50−500 mV/s, indicating that the limiting current is diffusion controlled. Also, a comparison with Fc$^+$/Fc as external standard (diffusion controlled) indicates that the electron-transfer process involves one electron.

(7) Control experiments show that silene **1** is indefinitely stable only in nonpolar solvents such as hexane or toluene but slowly decomposes in more polar solvents such as THF and CH$_2$Cl$_2$. Since we found that on the time scale of the CV measurements the decomposition is considerably faster in CH$_2$Cl$_2$, it is probable that only a fraction of silene **1** survives during the measurements.

(8) (a) We disregard cases in which the organosilicon compound is oxidized or reduced not at the silicon atom but at different atoms. (b) Reversible chemical oxidation and reduction of cyclotetrasilenyl radical were reported recently; Matsuno, T.; Ichinohe, M.; Sekiguchi, A. *Angew. Chem., Int. Ed.* **2002**, *41*, 1575.

(9) A two-electron redox process leading to a dication or dianion is highly unlikely (HOMO-1 and LUMO+1 separated from FMO by at least 1.4 eV, at MP2/6-31G*//B3LYP/6-31G* and B3LYP/6-31G*//B3LYP/6-31G*).

(10) Fuchigami, T. In *The Chemistry of Organosilicon Compounds*; Rappoport, Z., Apeloig, Y., Eds.; Wiley: Chichester, U.K., 1998; Vol. 2, Chapter 23.

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The most remarkable result of this study is the very low oxidation potential (+0.28 V) of silene **1**, especially upon considering the fact that the $Si{=}C$ bond in **1** is nonconjugated and is substituted only with moderate electron donor substituents.[11] **1** is one of the best known closed-shell neutral organic electron donors (e.g., the oxidation potential of tetrathiafulvalene (TTF) is 0.34 V[12]). Taken together with the relatively low reduction potential, this results in an unusually small electrochemical HOMO−LUMO gap of ~2.1 eV,[13] unprecedented for nonconjugated double bonds.

It is of interest to compare the redox potentials of **1** with those of alkenes and disilenes. As expected, the $Si{=}C$ double bond, which is weaker than the $C{=}C$ bond,[2] is both oxidized and reduced more easily than a $C{=}C$ bond. Thus, the oxidation potentials (corrected for Ag/AgCl) of ethylene (over 3 V),[14,15] 2,3-dimethyl-1,3-butadiene (~2.3 V),[15] and tetramethylethene (~1.6 V)[14,16] are all significantly higher than that of **1**. Even in the cases of the electron-rich alkenes tetraethoxyethene and $(p\text{-Anis})_2C{=}C(p\text{-Anis})_2$ (p-Anis ≡ $p\text{-}CH_3OC_6H_4{-}$), the oxidation potentials of ~0.7 V[16] and ~0.8 V,[17] respectively, are higher than those of **1**. Only in extreme cases, as for the very electron rich compound $(Me_2N)_2C{=}C(NMe_2)_2$, the oxidation potential (−0.73 V) is lower than for **1** (+0.28 V).[18]

Our data suggest that the oxidation and reduction potentials of silene **1** are both lower than those of disilenes, $R_2Si{=}SiR_2$;[19−21] i.e., it is easier to oxidize and reduce **1** in comparison to disilenes. Thus, CV measurements of substituted disilenes show irreversible oxidation waves at 0.4−0.6 V (vs Ag/AgCl) and irreversible reduction waves at −2 to −2.6 V (vs Ag/AgCl).[13,19,20,22] This is surprising, because the $Si{=}Si$ double bond is estimated to be weaker than the $Si{=}C$ double bond.[23]

The electrochemical measurements are in line with the picture of the electronic structure of silenes, which emerges from physical measurements[2,4] and from quantum-mechanical calculations.[2,3] Thus, the low oxidation potential of **1** is in line with its very low first ionization potential of 6.9 eV,[4b] similar to that of TTF (6.7−6.9 eV).[24] This low potential is partially due to the unique characteristics of the $Si{=}C$ double bond (the ionization potential of ethylene is 10.51 eV)[24] and partially to the effect of the particular substituents in **1** (compare to 8.9 eV for $H_2Si{=}CH_2$ (**2**)). In agreement, the calculated[25] HOMO energy in **1** is much higher than in the parent silene **2** (Table 1), whereas the HOMO energy of ethylene is much lower (more negative) than in **2**. It is noteworthy that the ionization potential of the disilene $Mes_2Si{=}SiMes_2$ (7.53 eV)[26] is also higher than that for **1**, in good agreement with electrochemical measurements (E^p_{ox} for $Mes_2Si{=}SiMes_2$ is 0.43 V vs Ag/AgCl[19]).[27] Again, this reflects the effect of the substituents, as the HOMO of $H_2Si{=}SiH_2$ is higher than that of **2**.

Table 1. Calculated HOMO and LUMO Energies (eV) of 1, $H_2Si{=}CH_2$, $H_2Si{=}SiH_2$, and Ethylene[a]

	HOMO	LUMO
$H_2C{=}CH_2$	−10.11 (−7.26)	4.91 (0.51)
$H_2Si{=}CH_2$ (**2**)	−8.41 (−6.19)	2.46 (−1.01)
$H_2Si{=}SiH_2$	−7.64 (−5.92)	0.62 (−2.35)
$(tBuMe_2Si)(Me_3Si)Si{=}2\text{-Ad}$ (**1**)	−7.07 (−5.03)	2.31 (−0.92)

[a] At the MP2/6-31G*//B3LYP/6-31G* and B3LYP/6-31G*//B3LYP/6-31G* (in parentheses) levels.

The electron affinity of $H_2Si{=}CH_2$ (0.29 eV at B3LYP/aug-cc-pVTZ[28]) is calculated to be much smaller than that of $H_2Si{=}SiH_2$ (1.34 eV at B3LYP/DZP++ [29]). In agreement, the LUMO of $H_2Si{=}CH_2$ is calculated to be higher than that of $H_2Si{=}SiH_2$ (Table 1), and thus $H_2Si{=}SiH_2$ should be easier to reduce than **2**. The LUMO energies of **1** and **2** are similar.

On the basis of the calculations and the experimental data, we conclude that the fact that silene **1** is oxidized and reduced electrochemically more easily than $Mes_2Si{=}SiMes_2$ and other known disilenes is related to the special substitution pattern of **1** and this does not necessarily imply that silenes are inherently oxidized or reduced in solutions more easily than disilenes.[22]

The first electronic transition for silene **1** occurs at λ_{max} 322 nm (3.85 eV),[4c] indicating that the spectral HOMO−LUMO gap is much larger than the electrochemically determined value of 2.1 V.[30] It is well established that, in the case of redox-active compounds

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[11] $\sigma_p(SiMe_3) = -0.07$: Hansch, C.; Leo, A.; Taft, R. W. *Chem. Rev.* **1991**, *91*, 165.

[12] 0.34 V vs Ag/AgCl, on a Pt electrode in CH_2Cl_2: Moore, A. J.; Bryce, M. R.; Ando, D. A.; Hursthouse, M. B. *J. Chem. Soc., Chem. Commun.* **1991**, 320. Bryce, M. R.; Marshallsay, G. J.; Moore, A. J. *J. Org. Chem.* **1992**, *57*, 4859.

[13] The oxidation and reduction potentials were measured in different solvents. This may change the gap by 0.1−0.2 V.

[14] This kind of comparison has to be made with great care and reservation because the oxidation of ethylene and tetramethylethylene is irreversible, whereas that for **1** is reversible.

[15] *Encyclopedia of Electrochemistry of the Elements*; Bard, A. J., Ed.; Marcel Dekker: New York, 1978; Vol. XI, Chapter 1.

[16] Gersdorf, J.; Mattay, J.; Goerner, H. *J. Am. Chem. Soc.* **1987**, *109*, 1203.

[17] Most (if not all) electrochemical reductions of olefins are confined to olefins activated by electron-withdrawing substituents. $CH_2{=}CH_2$ exhibits no reduction wave (in dioxane), and $PhCH{=}CH_2$, $Ph_2C{=}CH_2$, and $Ph_2C{=}CPh_2$ in DMF are reduced at −2.4, −2.25, and ~−2 V, respectively (Ag/AgCl corrected); see: Technique of Electroorganic Synthesis. In *Techniques of Chemistry*; Weisberger, A., Ed.; Wiley: New York, 1975; Vol. V (Weinberg, N., Vol. Ed.), Part II, pp 679−685.

[18] Burkholder, C.; Dolbier, W. R., Jr.; Médebielle, M. *J. Org. Chem.* **1998**, *63*, 5385.

[19] Shepherd, B. D.; West, R. *Chem. Lett.* **1988**, *2*, 183.

[20] Kira, M.; Ishima, T.; Iwamoto, T.; Ichinohe, M. *J. Am. Chem. Soc.* **2001**, *123*, 1676.

[21] $Mes_2Si{=}SiMes_2$ was electrolyzed preparatively: Zhang, Z.-R.; Becker, J. Y.; West, R. *Chem. Commun.* **1998**, 2719.

[22] All reductions and oxidations of disilenes were found to be irreversible. Therefore, see footnote 14.

[23] π-bond energy: $Si{=}Si$, 24 kcal mol^{-1}; $Si{=}C$, 36 kcal mol^{-1}. Schleyer, P. v. R.; Kost, D. *J. Am. Chem. Soc.* **1988**, *110*, 2105.

[24] Lias, S. G. In *Ionization Energy Evaluation*; Mallard, W. G., Linstrom, P. J., Eds.; NIST Chemistry WebBook, NIST Standard Reference Database Number 69, July 2001; National Institute of Standards and Technology: Gaithersburg, MD 20899 (http://webbook.nist.gov).

[25] All calculations used the GAUSSIAN 98 series of programs: Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Rega, N.; Salvador, P.; Dannenberg, J. J.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Baboul, A. G.; Stefanov, B. B.; Liu, G. Liashenko, A. Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, Revision A.11.4; Gaussian, Inc., Pittsburgh, PA, 2002.

[26] Okazaki, R.; West, R. *Adv. Organomet. Chem.* **1996**, *39*, 231.

[27] For a detailed discussion of substituent effects on the HOMO energy of silene **1**, see ref 4b.

[28] Wenthold, P. G. *Chem. Phys. Lett.* **1998**, *297*, 445.

[29] Pak, C.; Rienstra-Kiracofe, J. C.; Schaefer, H. F., III. *J. Phys. Chem. A* **2000**, *104*, 11232.

which afford very delocalized radical-ion species (e.g., conjugated polymers[31] or oligoacenes), the electrochemical and spectral HOMO−LUMO gaps are usually similar. The significant discrepancy found for **1** probably stems from the high reorganization energy[32] of the solvation shells of the localized ion radicals of **1** in comparison to the lower solvation reorganization energy for π-extended ion radicals.[33]

The very low oxidation potential and the small electrochemical gap of silene **1** make it an interesting candidate for various redox chemistry applications, which are being studied in our laboratory.

Experimental Section

A drybox (M. Braun Co., Model Labmaster 130) was used to obtain strict anhydrous and inert conditions for CV measurements. The amounts of both oxygen and water throughout measurements were less than 1 ppm. HPLC grade CH_2Cl_2 (BioLab; distilled from CaH_2) and THF (BioLab; distilled from CaH_2) were used freshly distilled. Tetrabutylammonium perchlorate (Bu_4NClO_4, purissimum grade, Fluka) was dried in a vacuum oven for 24 h at 70 °C. Silene **1** was synthesized as reported previously and recrystallized from pentane.[5] Cyclic voltammetric (CV) experiments were performed using a conventional three-electrode cell. A platinum disk (ca. 1 mm diameter), a cylindrical Pt gauze, and Ag/AgCl (Bioanalytical Systems) were used as working, counter, and reference electrodes, respectively. The concentration of the silene was 2−3 mM, and that of the supporting electrolyte was 0.1 M. The CV measurements were carried out with a Princeton Applied Research (PAR) Model 173 potentiostat/galvanostat, PAR Model 175 universal programmer, and a Yokogawa Model 3068 XY recorder.

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(30) $Mes_2Si{=}SiMes_2$ absorbs at 420 nm (2.95 eV) (West, R.; Fink, M. J.; Michl, J. *Science* **1981**, *214*, 1343), and its electrochemical HOMO−LUMO gap is 2.50 V.[19]

(31) Roncali, J. *Chem. Rev.* **1997**, *97*, 173.

(32) The reorganization energy is the energy released on relaxation of a cation radical in an adiabatic transition.

(33) Eberson, L. *Electron-Transfer Reactions in Organic Chemistry*; Springer-Verlag: Berlin, 1987.