Acc. Chem. Res. **1982**, *15*, 9–17 **9**

Organosilicon Radical Cations[1,2]

HANS BOCK* and WOLFGANG KAIM

Department of Chemistry, Johann Wolfgang Goethe University Frankfurt, D-6000 Frankfurt, Niederurseler Hang, West Germany

Received November 4, 1980 (Revised Manuscript Received September 18, 1981)

The early tempestuous years of electron spin resonance (ESR) spectroscopy[3,4] were largely devoted to the development of methodology and to the recognition of major fundamental characteristics of ESR spectra. Today, in a more mature era, application of ESR spectroscopy to the study of chemical phenomena is the dominant theme.[5] There is now an opportunity for preparative chemists to participate[6a–z] and to make use of the ESR experience gathered during many years for purposes of designing and synthesizing novel persistent[7] radicals and radical ions.

In our laboratory, we have discovered how to generate a large number[6g–z,8] of novel organosilicon radical cations (Figure 1). Examination of their ESR spectra has provided a wealth of information about the structures and dynamic characteristics of these species. This includes the spin distribution in the radical cations, their rigidity or flexibility on the ESR time scale, and their structural characteristics relative to the parent neutral molecules. The often striking effects of silyl substituents, as determined by ESR, are parallel to effects seen in the reactivity of organosilicon compounds and are therefore of direct interest to preparative chemistry as well as to studies of reaction mechanisms.

Preparation of Organosilicon Radical Cations

Our studies have enabled us to develop a general procedure, indeed a recipe, for the discovery and generation of novel radical cations.[6i] One chooses a promising parent molecule and determines its photoelectron spectrum (PES); this takes about an hour. If the first ionization potential is less than 8 eV, one proceeds to generate the radical cation by adding $AlCl_3$ to a dichloromethane solution of the parent molecule in a capillary within the ESR cavity. The ESR spectrum is then recorded. All this takes approximately 1 h more.

In terms of this procedure, most of the problems usually involved in the search for novel radical cations are thus reduced to two questions: Will a chosen parent molecule be ionized at less than 8 eV? Will the radical cation persist[7] long enough for its ESR spectrum to be measured?

In choosing molecules as candidates for oxidation to persistent radical cations, one can be guided by some rather obvious general principles.[5] In general, ionization will occur most readily when the electron lost is either from an unshared pair or a bonding electron associated with an atom of low effective nuclear charge. A complementary consideration, which is of general validity but particularly applicable for π systems, is that delocalization of the positive charge produced on electron expulsion helps to stabilize a radical cation.

More quantitatively, estimates of first vertical ionization potentials can be derived from quantum mechanical eigenvalues via Koopman's theorem[5]

$$\mathrm{IE}_n = -\epsilon_J{}^{\mathrm{SCF}}$$

Hans Bock, Professor of Chemistry at the University of Frankfurt, is primarily interested in properties of individual molecular states and thus pursues research stretching from synthesis of heteroorganic (Si, P, S) model compounds to application of physical methods (PES, CT, UV, ESR) and interpretation (MO) of the data measured. He received his Ph.D. from the University of Munich and lectured there until 1968. He is recipient of the Chemistry Award of the Academy of Sciences (Göttingen 1968) and the ACS Kipping Award (1975). In 1977 he was appointed External Scientific Member of the Max Planck Society, in 1979 he was elected Corresponding Member of the Academy of Sciences (Mainz), and in 1981 he was appointed Adjunct Professor at the University of Michigan, Ann Arbor.

Wolfgang Kaim studied chemistry at the Universities of Konstanz and Frankfurt, where he received his Ph.D in 1978. As recipient of a Liebig stipend from the Verband der Chemischen Industrie, he spent the subsequent year with F. A. Cotton at Texas A&M University.

---

(1) Presented in part as an invited lecture at the Second Chemical Congress of the North American Continent, Las Vegas, NV, Aug 28, 1980.

(2) Part 50 of the series on radical ions; for part 49, see H. Bock, W. Kaim, M. Kira, and H.-G. Viehe, *Tetrahedron*, in press. For the preceding 8th Essay on Molecular Properties and Models, see H. Bock and B. Solouki, *Angew. Chem.*, **93**, 425 (1981); *Angew. Chem., Int. Ed. Engl.*, **20**, 427 (1981).

(3) Cf., eg., K. Scheffler and H. B. Stegmann, "Elektronenspinresonanz", Springer-Verlag, Heidelberg 1970; J. E. Wertz and J. R. Bolton, "Electron Spin Resonance", McGraw-Hill, New York 1972.

(4) Cf., e.g., the Annual Specialist Periodical Reports of the Chemical Society, "Electron Spin Resonance", Vol. 1 (1973), and following volumes.

(5) Cf., e.g., the lecture in honor of Erich Hückel's 80th birthday; H. Bock, *Angew. Chem.*, **89**, 631 (1977); *Angew. Chem. Int. Ed. Engl.*, **16**, 613 (1977), and the literature quoted therein.

(6) Publications on organosilicon radical ions: (a) H. Alt, H. Bock, F. Gerson, and J. Heinzer, *Angew. Chem.*, **79**, 933 (1967); *Angew. Chem. Int. Ed. Engl.*, **6**, 941 (1967). (b) F. Gerson, J. Heinzer, H. Bock, H. Alt, and H. Seidl, *Helv.* Chim. *Acta*, **51**, 707 (1968). (c) H. Alt, E. R. Franke, and H. Bock, *Angew. Chem.*, 81, 538 (1969); *Angew Chem., Int. Ed. Engl.*, **8**, 525 (1969). (d) F. Gerson, U. Krynitz, and H. Bock, *Angew. Chem.*, **81**, 786 (1969). (e) F. Gerson, U. Krynitz, and H. Bock, *Helv. Chim. Acta*, **52**, 2512 (1969). (f) F. Gerson, J. Heinzer, and H. Bock, *J. Mol. Phys.*, 18, 461 (1970). (g) H. Bock, G. Brähler, G. Fritz, and E. Matern, *Angew. Chem.*, **88**, 765 (1976); *Angew Chem., Int. Ed. Engl.*, **15**, 669 (1976). (h) H. Bock, W. Kaim, and J. Connolly, *Angew. Chem.*, **88**, 766 (1976); *Angew. Chem. Int. Ed. Engl.*, **15**, 700 (1976). (i) H. Bock and W. Kaim, *Tetrahedron Lett.*, 2343 (1977). (j) H. Bock, W. Kaim, and H. E. Rohwer, *J. Organomet. Chem.*, **135**, C14 (1977). (k) H. Bock and W. Kaim, *Nachr. Chem. Techn. Lab.*, **25**, 306 (1977). (l) G. Fritz, E. Matern, H. Bock, and G. Brähler, *Z. Anorg. Allg. Chem.*, **439**, 173 (1978). (m) H. Bock, W. Kaim, N. Wilberg, and G. Ziegleder, *Chem. Ber.*, 111, 3150 (1978). (n) H. Bock, W. Kaim, A. M. Semkow, and H. Nöth, *Angew. Chem.*, **90**, 308 (1978); *Angew. Chem., Int. Ed. Engl.*, 17, 286 (1978). (o) H. Bock and W. Kaim, *Chem. Ber.*, 111, 3552 (1978). (p) H. Bock, W. Kaim, and H.-E. Rhower, *ibid.*, 111, 3573 (1978). (q) W. Kaim and H. Bock, *ibid.*, 111, 3585 (1978). (r) M. Kira, E. Hengge, and H. Bock, *J. Organomet. Chem.*, **164**, 277 (1979). (s) W. Kaim and H. Bock, *ibid.* **164**, 281 (1979). (t) H. Bock, W. Kaim, M. Kira, H. Osawa, and H. Sakurai, *ibid.*, **164**, 295 (1979). (u) H. Bock and W. Kaim, *Z. Anorg. Allg. Chem.*, **459**, 103 (1979). (v) H. Bock, W. Kaim, M. Kira, and R. West, *J. Am. Chem. Soc.*, **101**, 7667 (1979). (w) H. Bock, W. Kaim, H. Nöth, and A. Semkow, *ibid.* **102**, 4421 (1980). (x) H. Bock and W. Kaim, *ibid.*, **102**, 4429 (1980). (y) H. Bock, G. Brähler, W. Kaim, M. Kira, B. Roth, A. Semkow, U. Stein, and A. Tabatabai in "Compoutational Methods in Chemistry", Plenum Press, New York, 1980, p 103. (z) W. Kaim, H. Tesmann, and H. Bock, *Chem. Ber.*, **113**, 3221 (1980).

(7) D. Griller and K. U. Ingold, *Acc. Chem. Res.*, **9**, 13 (1976).

(8) Cation radicals containing R_3Si groups were reported earlier, viz., bis[(trimethylsilyl)benzene]chromium cation radical by C. Elschenbroich (*J. Organomet. Chem.*, **22**, 677 (1970)) and *p*-(trimethylsilyl)-*N*,*N*-dimethylaniline cation radical by M. J. Drews, P. S. Wong, and P. R. Jones (*J. Am. Chem.* Soc., **94**, 9122 (1972). However, these radical cations do not owe their stability to the presence of SiR_3 substituents, and neither ^{29}Si nor silylmethyl proton coupling constants were observed in the ESR spectra.

0001-4842/82/0115-0009$01.25/0

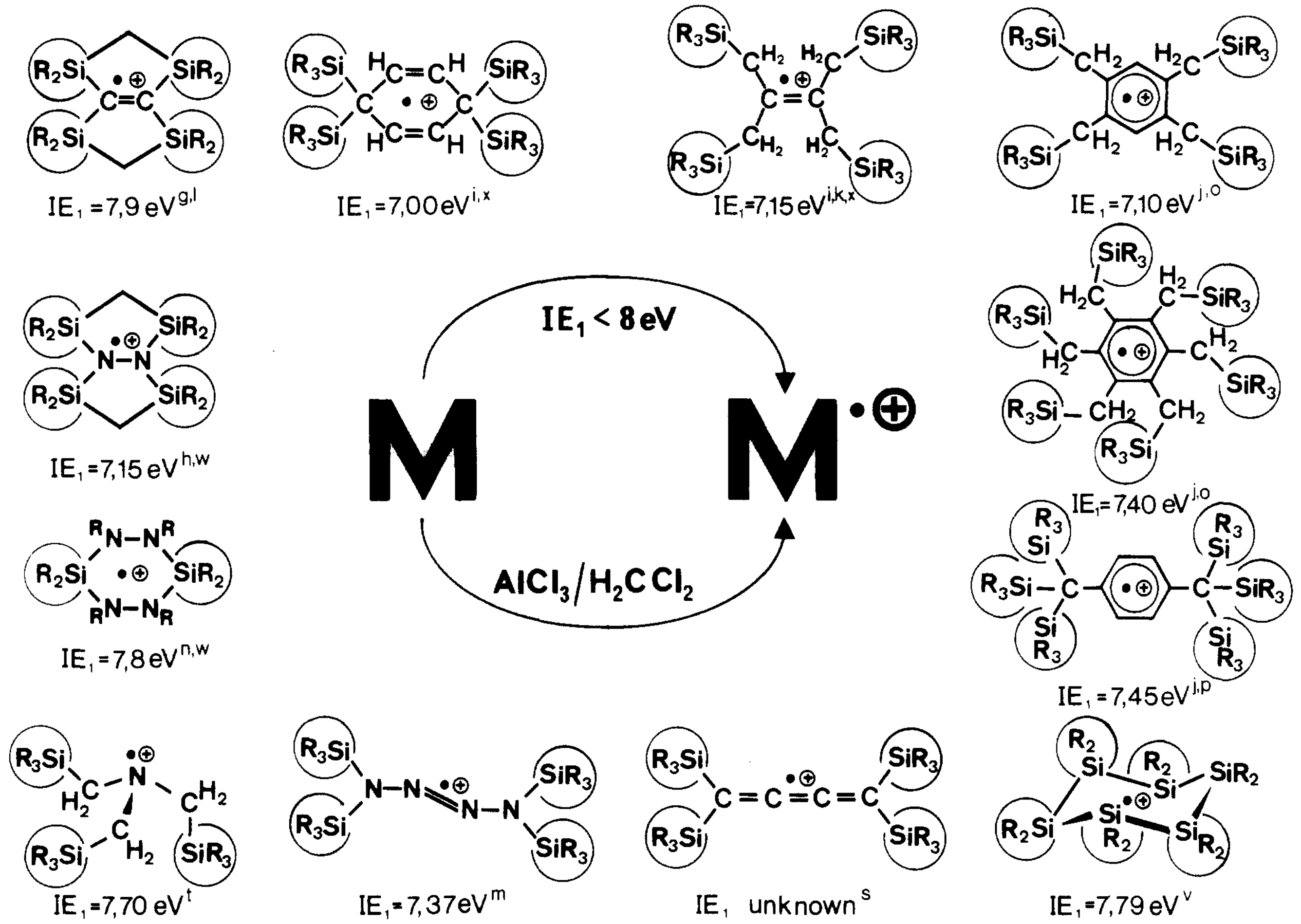
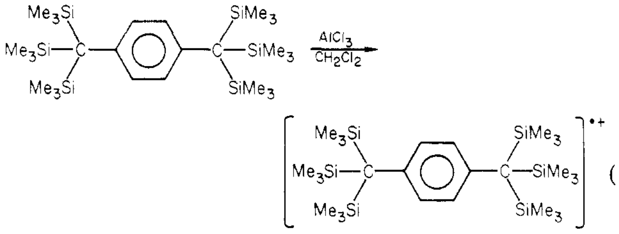


Figure 1. Prototypes of organosilicon radical cations, derived from neutral parent compounds exhibiting vertical first ionization potentials below 8 eV. All were generated by using the oxidizing system $AlCl_3/CH_2Cl_2$ and characterized by their ESR spectra.[6g–z] Tetrakis(trimethylsilyl)butatriene is still unknown; its radical cation[6e] is formed on $AlCl_3/CH_2Cl_2$ oxidation of the butyne $(Me_3Si)_3CC{\equiv}CC(SiMe_3)_3$.

For larger molecules (cf. Figure 1), an advantageous approximation can be based on radical cation state comparison of molecules closely related chemically, applying first-[6o] and/or second-order[6p] perturbation models.[5]

$AlCl_3$ in nitromethane has been commonly used by other workers[9] for oxidation of molecules to radical cations. However, we sought an oxygen-free solvent and found that "solutions" of $AlCl_3$ in dichloromethane[10]—a solvent with low melting point, low viscosity, and a sufficiently high dielectric constant to solvate ions—provided to be both effective and selective for our oxidizing purposes.[6i,j,11] From our experience with application of this oxidizing system to numerous compounds, we have been able to recognize that the "oxidizing potential" of $AlCl_3/H_2CCl_2$ corresponds approximately to a first vertical ionization potential of 7.8 eV for the substrate. Occasionally, molecules with higher oxidation potentials, up to 8.2 eV, can be oxidized by using this system if adiabatic electron removal is accompanied by significant structural changes toward stabilization of the resulting radical cation.[6n,w,12,13]

A representative oxidation process is shown in eq 1.



(1)

No reduction products have so far been isolated.[11]

Persistency of Organosilicon Radical Cations.

A number of novel organosilicon radical cations generated by the procedure outlined are shown in Figure 1. They vary from organosilicon derivatives of ethene[6g,2,k,l,x] and benzene[6j,o,p] and other molecules with π-type systems[6q,s,z] through organosilicon derivatives of amines[6t] and hydrazines[6h,n,w] to σ systems like dodecamethylcyclohexasilane, Si_6Me_{12},[6v] which no longer contain π bonds or lone pairs.

The species shown in Figure 1 are all sufficiently persistent to be observable by ESR spectroscopy. A major factor contributing to their kinetic stability, by

---

(9) W. F. Forbes, P. D. Sullivan and H. M. Wang, *J. Am. Chem. Soc.*, 89, 2705 (1967).

(10) D. W. Grattan and P. H. Plesch, *J. Chem. Soc., Dalton Trans.* 1734 (1977).

(11) The combination $AlCl_3/CH_2Cl_2$ was previously used for the generation of cation radicals from (methylthio)ethenes by D. H. Geske and M. W. Merrit (*J. Am. Chem. Soc.*, 91, 6921 (1969). The mechanism of the redox reaction is not yet fully understood; cf. A. J. Bard, A. Ledwith, and H. J. Shine, *Adv. Phys. Org. Chem.*, 13, 156 (1976).

(12) S. F. Nelsen, G. R. Weisman, P. J. Hintz, D. Olp, and M. R. Fahey, *J. Am. Chem. Soc.*, 96, 2916 (1974).

(13) H. Bock and U. Stein, *Chem. Ber.*, 113, 3194 (1980). Cf. also *Angew. Chem.*, 92, 863 (1980); Angew. *Chem., Int. Ed. Engl.*, 19, 834 (1980).

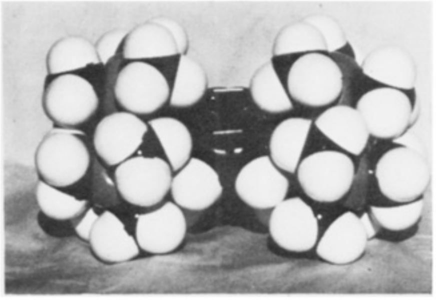


Figure 2. Space-filling model of $\alpha,\alpha,\alpha,\alpha',\alpha',\alpha'$-hexakis(trimethylsilyl)-*p*-xylene.

analogy to factors affecting the persistence of organosilicon radicals,[7] is extensive shielding by bulky substituents. The concept is illustrated by the picture of a space-filling model of hexakis(trimethylsilyl)-*p*-xylene (cf. eq 1), shown as Figure 2. Examination of models of this type shows that many organosilicon compounds approach either "bivalve"- or "ball"-like shapes with hydrogen covered surfaces. Furthermore, trimethylsilyl substituents in positions α or β to π systems or to unshared electron pairs help to stabilize the radical cations by charge delocalization.[14,15]

ESR Investigation of Organosilicon Radical Cations

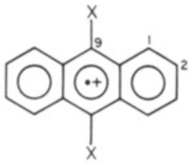
General Characteristics of ESR Spectra. All ESR spectra of organosilicon radical cations (cf. Figure 3) display pronounced hyperfine structure with line widths often smaller than 0.01 mT (0.1 G). They not only reflect the coupling of α and β hydrogens, H_α and H_β, but also the characteristic coupling with the ^{29}Si isotope (4.7% natural abundance, $I = {}^1/_2$). A frequent feature is methylsilyl proton splitting (H_δ). High multiplicities result on multiple introduction of $(H_3C)_3Si$ groups, leading to extreme intensity ratios. Thus, for the 54 equivalent protons in hexakis(trimethylsilyl)-*p*-xylene radical cation[6p] (cf. eq 1 and Figure 2) the intensity ratio between the outermost and the center line of that multiplet amounts to 1:1 946 939 425 648 112![6o]

The *g* values of most of the radical cations generated range from 2.0025 to 2.0035; remarkably high values of *g*, about 2.01, are determined for permethylcyclopolysilane radical cations.[6v]

Analysis of the unusally line-rich ESR spectra (Figure 3) has been accomplished by two complementary means: meticulous simulation of the experimental ESR spectra was carried out by means of a specially designed computer program capable of handling high multiplicities,[6o,p] isotope combinations,[6s] and large numbers of theoretical lines.[6o,x] In some instances the results of the ESR analysis were reexamined and confirmed by ENDOR measurements;[16] it turned out that the $AlCl_3/CH_2Cl_2$ mixture is a very suitable system for this rapidly developing spectroscopy.[4]

Chart I

π Spin Populations ρ_π in Substituted Anthracene Radical Cations As Derived from ESR Coupling Constants

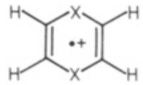


X	$\rho_\pi(1)$	$\rho_\pi(2)$	$\rho_\pi(9)$
H[a]	0.087	0.039	0.187
CH_3[b]	0.073	0.034	0.235
CH_2SiMe_3[c]	0.052	0.030	0.321

[a] J. R. Bolton and G. K. Fraenkel, *J. Chem. Phys.*, **40**, 3307 (1964). [b] J. R. Bolton, A. Carrington, and A. D. McLachlan, *Mol. Phys.* **5**, 31 (1963). [c] Reference 6q.

Chart II

Ring Proton Coupling Constants a_H (mT) of Silylated 1,4-Cyclohexadienes and Related Heterocyclic Radical Cations



X	$CHSiMe_3$	$C(SiMe_3)_2$	NH[a]	NMe[b]	S[c]
a_H	0.32	0.303	0.316	0.290	0.282

[a] B. L. Barton and G. K. Fraenkel, *J. Chem. Phys.*, **41**, 1455 (1964). [b] M. K. Ahn and C. S. Johnson, Jr., *ibid.*, **50**, 632 (1969). [c] P. D. Sullivan, *J. Am. Chem. Soc.*, **90**, 3618 (1968).

Spin Distribution. The most valuable information obtained from high-resolution ESR spectroscopy concerns the distribution of the unpaired electron in the paramagnetic molecule as sensed by electron/nuclear spin–spin coupling. For π–type radicals two useful equations relate the π spin populations ρ_π with experimental coupling constants a_H; these are the McConnell[17] (eq 2) and the Heller–McConnell[18] (eq 3) equations:

$$a_{H_\alpha} = Q^H \rho_\pi \tag{2}$$

$$a_{H_\beta} = (B_0{}^H + B_2{}^H \cos^2 \theta_{CH}) \rho_\pi \tag{3}$$

where θ_{CH} is the torsion angle between the C–H σ bond and the axis of the π orbital at the substitution center.[18] Constants Q^H ($\simeq$3.5 mT[19]) and $B_0{}^H$ ($B_0{}^H << B_2$[18]) describe the spin transfer by the σ–π spin polarization mechanism, whereas $B_2{}^H$ ($\simeq$7.5 mT[20]) is the constant for the angle-dependent σ–π hyperconjugation. We have discovered that these relations are also valid for ^{29}Si coupling constants a_{Si_α}[6f] and $a_{Si\beta}$[6o,p,x]:

$$a_{Si_\alpha} = Q^{Si} \rho_\pi \qquad Q^{Si}(M^{-}\cdot) = 2.3\ mT^{6f} \tag{4}$$

$$a_{Si_\beta} = B_2{}^{Si} \cos^2 \theta_{CSi}\, \rho_\pi \qquad B_2{}^{Si}(M^{+}\cdot) = 3.2\ mT^{6o,p} \tag{5}$$

The value of these relations with respect to organosilicon radical cations is demonstrated by examples now to be considered.

Substituent effects of (trimethylsilyl)methyl groups in radical cations, in comparison with other electron donor substituents,[6p] are illustrated in Figure 4. The delocalizing strength of the $CH_n(SiR_3)_{3-n}$ groups, as sensed by the reduction of the aromatic proton coupling constant $a_H{}^{Ph}$, is surpassed only by that of methylthio

---

(14) Cf., e.g., H. Bock and H. Seidl, *J. Am. Chem. Soc.*, **90**, 5694 (1968), or H. Bock and H. Alt, *ibid.*, **92**, 1569 (1970), and literature quoted.

(15) Cf., e.g., C. G. Pitt, *J. Organomet. Chem.*, **61**, 49 (1973), and literature summarized therein.

(16) The ENDOR measurements were kindly performed by Dr. Ch. Wydler and Professor F. Gerson at the University of Basel.

(17) H. McConnell, *J. Chem. Phys.*, **24**, 632 (1956).

(18) C. Heller and H. McConnell, *J. Chem. Phys.*, **32**, 1535 (1960).

(19) I. C. Lewis and L. S. Singer, *J. Chem. Phys.*, **43**, 2712 (1965).

(20) M. Brustolon, C. Corvaja, and G. Giacometti, *Theor. Chim. Acta*, **22**, 90 (1971).

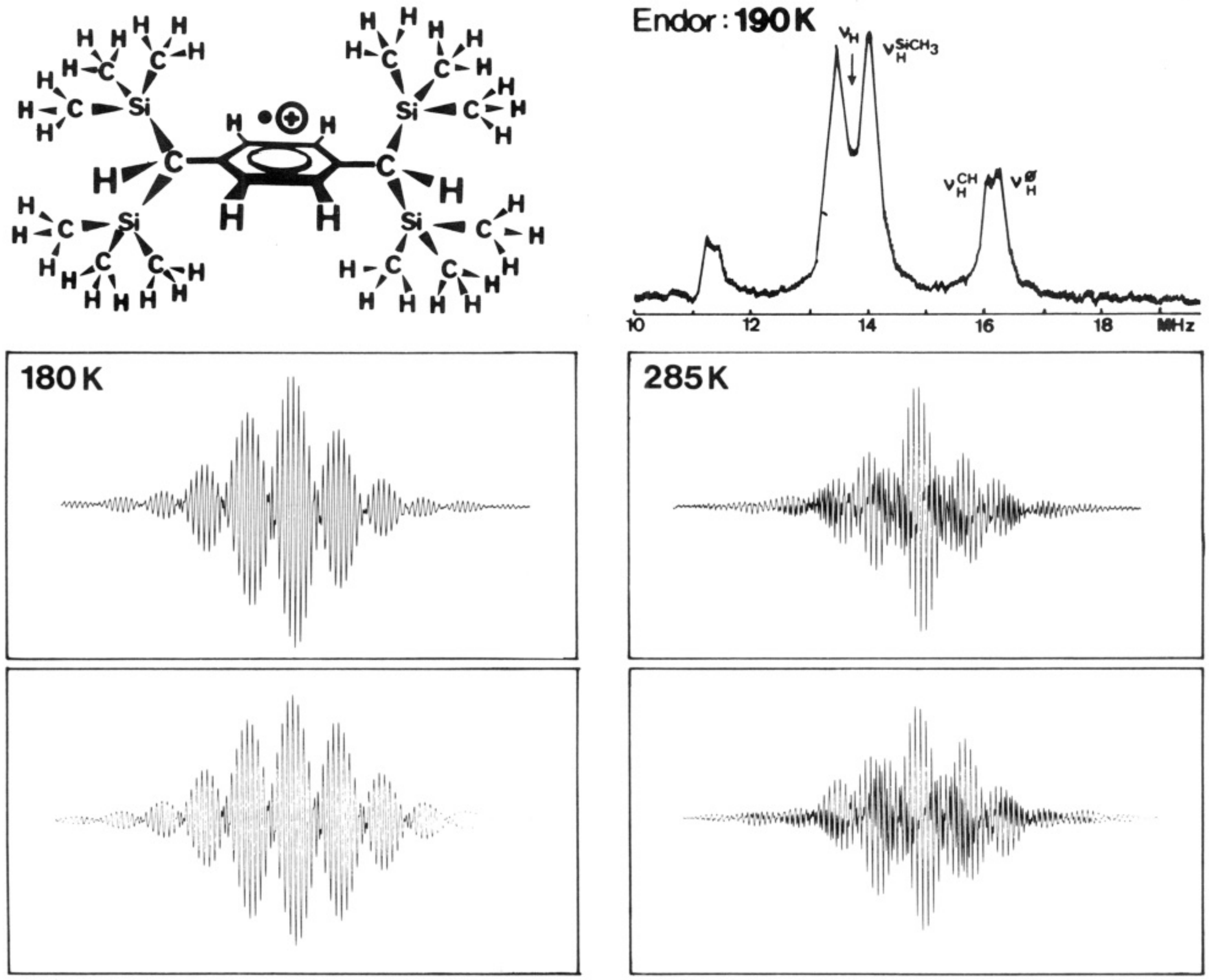


Figure 3. ESR spectra analysis for the radical cation of $\alpha,\alpha,\alpha',\alpha'$-tetrakis(trimethylsilyl)-*p*-xylene. The ENDOR spectrum (electron-nuclear double resonance) at 190 K shows three ^1H coupling constants, two of which are of almost equal magnitude at that temperature. The ESR spectrum (cf. 180 and 285 K) is temperature dependent due to variation of the $^1H_\beta$ and $^{29}Si_\beta$ coupling. Scrupulous computer simulation of the 1665 line spectrum serves to establish the splitting parameters at each particular temperature.[6p]

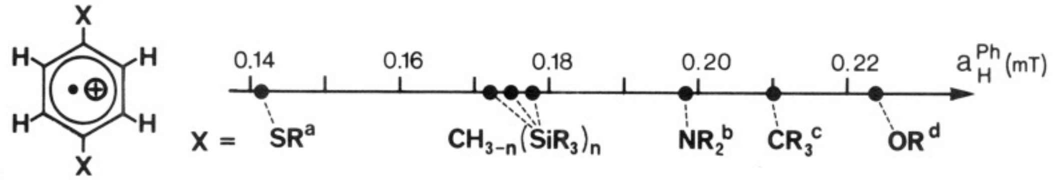


Figure 4. Ring proton coupling constants a_H^{Ph} of 1,4-disubstituted benzene radical cations. (a) W. F. Forbes and P. D. Sullivan, *Can. J. Chem.* **46**, 317 (1968); average for isomers. (b) Cf. J. E. Wertz and J. R. Bolton, "Electron Spin Resonance", McGraw-Hill, New York, 1972, p 446. (c) R. M. Dessau, S. Shih, and E. I. Heiba, *J. Am. Chem. Soc.*, **92**, 412 (1970). (d) W. F. Forbes, P. D. Sullivan, and H. M. Wang, *J. Am. Chem. Soc.*, **89**, 2705 (1967); average for isomers.

substituents. Strong delocalization of spin toward the Me_3SiH_2C-substituted π centers is also observed in more extended π systems like anthracene[6q] (Chart I).

Me_3SiH_2C-substituted compounds show low first ionization potentials (Figure 1). This stabilization of the radical cation ground state in turn corresponds to a shift of unpaired electron density to the substituted π centers (Chart I) and, to some extent, also into the substituents. A remarkable example is found on comparing silylated 1,4-cyclohexadiene derivatives[6i,x] with electron-rich heterocycles (Chart II). In this series, the organosilicon group is about equivalent to nitrogen and nearly as good as sulfur in reducing the spin density on the ring carbon atoms. Application of eq 2 leads to a π spin population of only $\rho_\pi \simeq 0.1$ at each of the olefinic π centers; the remaining spin population $\rho^\pi \simeq 0.6$ has then to be attributed to the "saturated" $>CH_n(SiMe_3)_{2-n}$ groups!

This ability of Si–C σ bonds to carry a considerable amount of spin density led us to attempt the one-electron oxidation of systems which are totally devoid of π bonds or lone pairs. Indeed, treatment of electron-rich[21] permethylcyclopolysilanes with $AlCl_3/CH_2Cl_2$ at low temperatures gave ESR signals of the corresponding radical cations.[6v]

[21] H. Bock and W. Ensslin, *Angew. Chem.*, **83**, 435 (1971); *Angew. Chem., Int. Ed. Engl.*, **10**, 404 (1971).

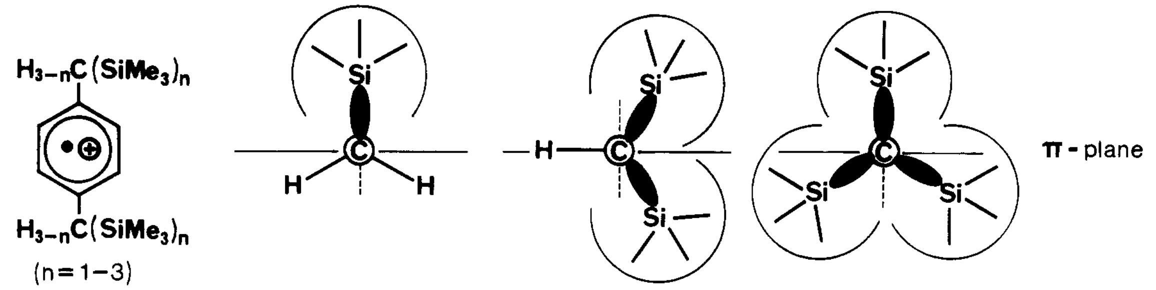


Figure 5. Sterically preferred conformations of substituents $CH_{3-n}(SiMe_3)_n$, $n = 1, 2, 3$, relative to the plane of a π system, e.g., in *p*-xylene derivatives.

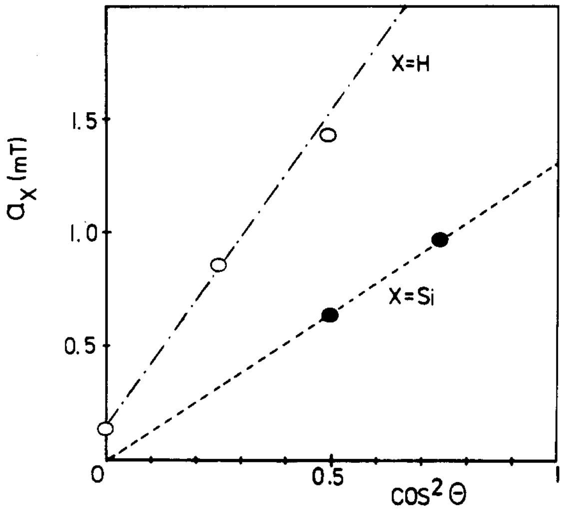
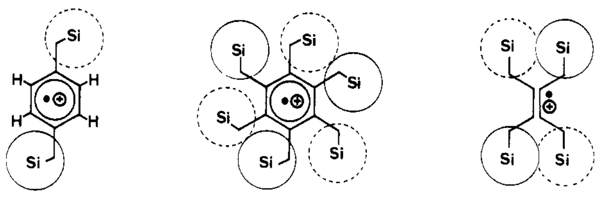


Figure 6. Angular dependence of β coupling constants a_H and a_{Si} in *p*-xylene derivatives.

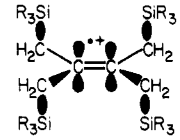


$R = \frac{0.84}{1.41^a} = 0.60$ $\frac{0.353}{0.645^b} = 0.55$ $\frac{0.783}{1.66^c} = 0.47$

Figure 7. Values of R (eq 6) for Me_3SiH_2C-substituted radical cations. Data for methyl derivatives: (a) Ref 22; (b) R. M. Dessau, S. Shih, and E. I. Heiba, *J. Am. Chem. Soc.*, **92**, 412 (1970); (c) R. M. Dessau, *ibid.*, **92**, 6356 (1970).

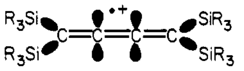
Hyperconjugation models are advantageously used to correlate ESR parameters with radical geometry. A particularly instructive example is given by *p*-xylene derivatives[6j,p] (Figure 5). The ESR parameters show a distinct sequence of β coupling constants a_β (Figure 6): assuming an unchanged spin distribution in the benzene ring as proven by the almost constant values a_H^{Ph}, the β splittings vary according to the sterically preferred conformations of the substituents toward the benzene π system (Figure 5). Together with toluene radical cation,[22] a graphic correlation of a_β vs. $\cos^2 \theta$ using the conformations from Figure 5 exhibits two straight lines, from which the parameters for eq 3 and 5 can be derived[6p] (Figure 6). Whereas the constant $B_2^H = 6.75$ mT corresponds to the literature value of $B_2^H(M^{+\cdot}) \simeq 7.5$ mT,[20] it is possible here to determine also the small and usually neglected[18] parameter $B_0^H = 0.38$ mT.[23] Moreover, the Heller–McConnell relation seems to hold also for Si_β nuclei (eq 5). The values $B_0^{Si} = 0$ and $B_2^{Si} = 3.2$ mT taken from Figure 6 were confirmed by other benzene radical cations.[6o]

A striking example of the dominating hyperconjugative effect in organosilicon radical cations is given by two olefinic derivatives. Both species 1 and 2 have one central double bond interacting hyperconjugatively with four Si–C σ bonds which are parallel to the C=C π system. Consequently, both radical cations exhibit almost identical coupling constants a_{Si} and $a_H^{SiCH_3}$; moreover, both the ethene 1 and the butatriene 2 cation radicals are exceptionally persistent at room temperature.[6s,x]



1

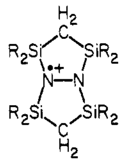
$a_{^{29}Si} = 1.23$ mT[6x]
$a_H^{SiCH_3} = 0.031$ mT



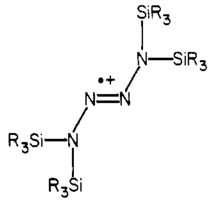
2

1.210 mT[6s]
0.033 mT

^{29}Si coupling constants have also proven to be a useful source of information when silicon is bonded to nitrogen. Contrasting the radical cation of a planar tetrasilylhydrazine 3[6h,w] with that of planar[24] tetrakis(trimethylsilyl)-2-tetrazene (4)[6m] reveals that the central N=N unit causes a reduction of a_{Si} from 0.50 mT (3) to 0.39 mT for 4. Thus, one can immediately obtain spin populations of 0.39 for the N-1 and N-4 and of 0.11 for the N-2 and N-3 centers of the tetrazene radical. This spin distribution may then be compared with that of other 4-center/5-electron π systems like butadiene radical anions.[6m]



3



4

R = CH_3

Configurations of organosilicon radical cations containing a six-membered "boat"-ring like 5[25] and 6[26]

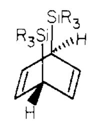
---

(22) J. K. Kochi, R. T. Tang, and T. Bernath, *J. Am. Chem. Soc.*, **95**, 7114 (1973).

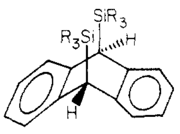
(23) Cf. N. L. Bauld, C. E. Hudson, and J. S. Hyde, *J. Chem. Phys.*, **54**, 1834 (1971).

(24) M. Veith, *Acta Crystallogr., Sect. B*, **31**, 678 (1975).

(25) C. Eaborn, R. A. Jackson and R. Pearce, *J. Chem. Soc., Perkin Trans. 1*, 2055 (1974).



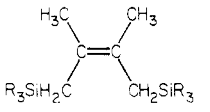
5



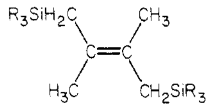
6

can be deduced from the ESR splitting pattern; equivalence of the coupling constants shows that the species observed exist in cis configurations (cf. 5 and 6), which also ensure optimum hyperconjugative interaction.[6q,x] Obviously the trans isomers, although present in excess in the starting materials,[6q,x] do not yield sufficiently persistent radical cations.

Oxidation of the isomeric *Z* and *E* olefins, 7 and 8, gives but one radical cation,[6i] which is held to be the *E* isomer.[6x]



7



8

It seems likely here that the reduced C=C π bond order in the cation radical as well as the catalytic property of $AlCl_3$[27] cause an easy isomerization. Similar observations were made for stilbene radical anions.[28]

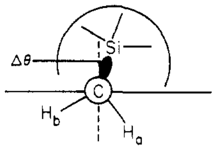
Restricted rotation of XH_2C substituents in radicals is assessed qualitatively by the "*R* values" of McKinney and Geske:[29] Comparison with corresponding methyl-substituted radicals and use of eq 3 for each radical enable—under certain assumptions[29]—values of *R* to be reckoned by use of eq 6.

$$R = \frac{a_H^{CH_2X}}{a_H^{CH_3}} = \frac{\langle \cos^2 \theta \rangle}{0.5} \qquad (6)$$

Whereas *R* should be 1 for free rotation of the XH_2C group, a completely blocked conformation of the kind shown in Figure 5 yields $R = 0.5$.[29] In the intermediate range, the *R* values serve as an indicator of freedom of internal rotation. From several values of *R* determined,[6q,t,x] three examples have been selected to demonstrate the mobility of Me_3SiH_2C substituents in π radical cations (Figure 7).

The 1,4-disubstituted benzene exhibits a moderately restricted Me_3SiH_2C rotation according to $R = 0.60$. The fully substituted benzene, on the other hand, is almost totally "blocked" in its substituent mobility. The "impossible" low value *R* of 0.47 for the ethene derivative indicates—besides total blocking—some distortion of the substituents (Figure 7).

Nonequivalent methylene protons in $(H_3C)_3SiH_2C$-substituted radical cations were observed in several instances.[6i,k,o,t,x] This inequivalence is largely a result of unequal steric interaction of the substituent with the remaining part of the molecule, changing the ideal conformation as shown in Figure 5 to an unsymmetrical arrangement 9. Some mean deviation parameters $\Delta\theta$, as derived from a modified eq 3,[6o] are shown in Chart III. Obviously, steric crowding leads to closer

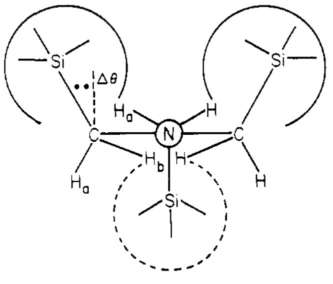


9

packed substituents and hence to smaller values of $\Delta\theta$.[6o,x,t]

Steric crowding and inequivalence of CH_2 protons have also been observed for *neutral* tetrakis(trimethylsilylmethyl)ethene.[6k,x] The coalescence temperature of 0 °C and the corresponding barrier of rotation stand in distinct contrast to the data for the carbon analogue,[30] where the shorter C–X bond causes an even more diminished substituent mobility.

Dynamic processes in radicals can be analyzed by ESR if they occur within the ESR time scale of 10^{-6} to 10^{-8} s. This "time window" is too narrow for most of the sterically crowded organosilicon radical cations. However, two examples of equilibration processes were observed. One of these concerns ring inversion in an octahydronaphthalene derivative.[6x] The other one concerns the temperature-dependent selective ESR line broadening of the tris(trimethylsilylmethyl)amine radical cation.[6t] The low-temperature spectrum shows three different CH_2 proton coupling constants which correspond to the "frozen"conformation 10. Raising the temperature results in selective line broadening due to rotational interconversion among conformations, which at 310 K is almost complete with six equivalent methylene hydrogens.[6t] This is most intriguing, inasmuch as the isoelectronic methyl radical $\cdot C(CH_2SiMe_3)_3$ does not show any temperature dependence.[6t] The different behavior of $(Me_3SiCH_2)_3N^{+}\cdot$ must result from strong hyperconjugative interaction between the cationic nitrogen and the C–Si σ bonds.



10

Structural changes in molecules on addition or removal of an electron are a general phenomenon.[5] Mostly these are changes of degree, but there are a few cases in which the molecular symmetry is totally altered. An instructive example is the hydrazine system: neutral N_2H_4 in the gas phase adopts a gauche conformation with C_2 symmetry and a lone pair dihedral angle of ~90°.[31] The radical cation $N_2H_4^{+}\cdot$, however, appears to be essentially planar.[6n,w,32] The INDO-calculated open-shell hypersurface (Figure 8) indicates a total energy minimum for a planar structure with the considerably shortened N–N bond length of only 128 pm (1.28 Å).[6n,w,12]

---

(26) R. M. G. Roberts, *J. Organomet. Chem.*, **110**, 281 (1976).

(27) H. Pines and N. E. Hoffmann in "Friedel-Crafts and Related Reactions, G. A. Olah, Ed., Vol. II/2, Interscience Publishers, New York, 1964, p 121 ff.

(28) R. Chang and C. S. Johnson, Jr., *J. Chem. Phys.*, **46**, 2314 (1967).

(29) T. M. McKinney and D. H. Geske, *J. Am. Chem. Soc.*, **89**, 2806 (1967).

(30) G. A. Olah and G. K. Surya Prakash, *J. Org. Chem.*, **42**, 580 (1977).

(31) Y. Morino, T. Iijima, and Y. Murata, *Bull. Chem. Soc. Jpn.*, **33**, 46 (1960).

(32) J. Q. Adams and J. R. Thomas, *J. Chem. Phys.*, **39**, 1904 (1963).

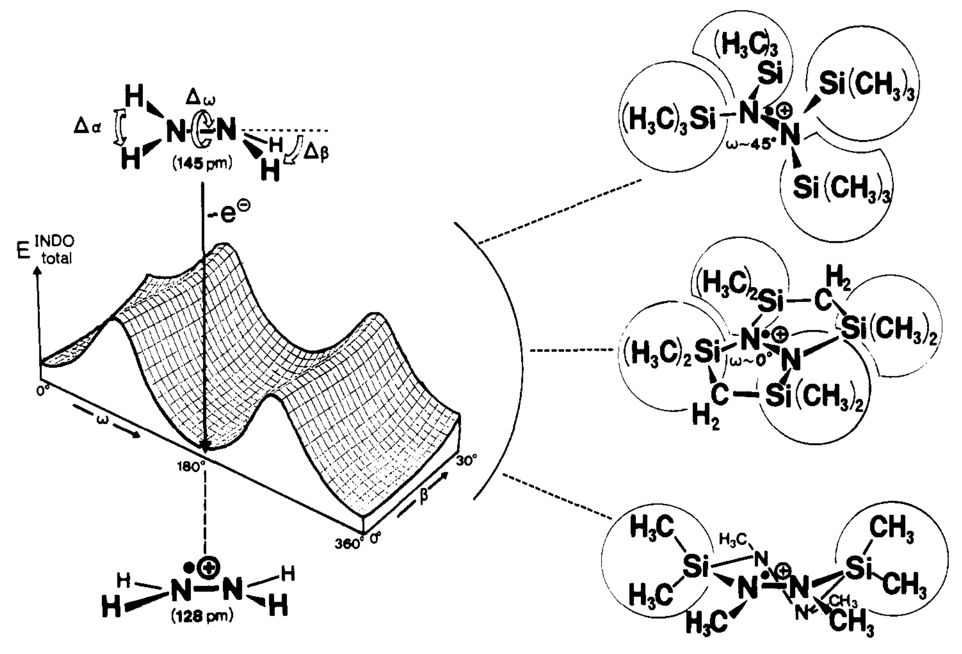
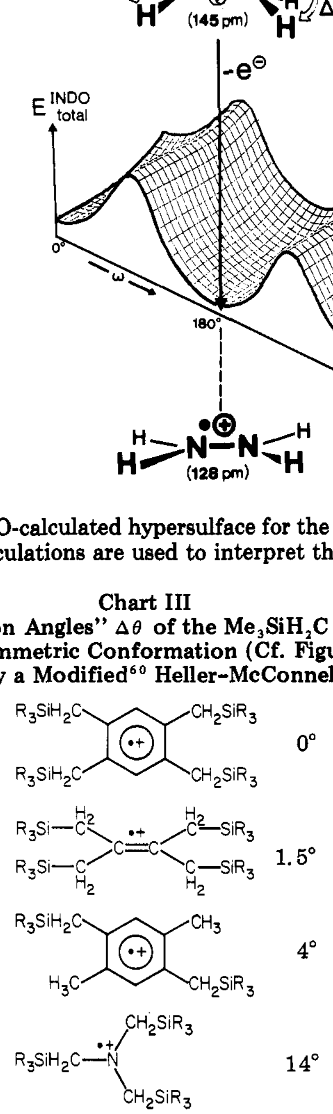
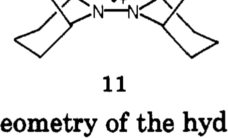


Figure 8. INDO-calculated hypersulface for the total energy of hydrazine radical cation $N_2H_4^{+\cdot}$, depending on angles β and ω. Data from INDO calculations are used to interpret the structural changes on oxidation of the silylhydrazines shown.

Chart III
Mean "Deviation Angles" $\Delta\theta$ of the Me_3SiH_2C Substituent from the Symmetric Conformation (Cf. Figure 5) As Determined by a Modified[60] Heller-McConnell Equation



This prediction has been confirmed by an X-ray structure determination of an exceptionally persistent tetraalkylhydrazine radical cation 11; it exhibited essentially planar geometry of the hydrazine unit and a N-N bond length of 126.9 pm.[33] Additionally INDO-calculated coupling constants for $N_2H_4^{+\cdot}$ depend predominantly on the dihedral angle and have been used to interprete the ESR results for open-chain and cyclic silylhydrazine radical cations.



11

The bicyclic tetrasilylhydrazine in Figure 8 possesses an essentially fixed geometry because of steric constraints; the virtually planar conformation in the molecular as well as in the cation radical ground state leads ot a large n_N/n_N lone pair splitting as determined by photoelectron spectroscopy.[6n,w]

The neutral open-chain derivative $(Me_3Si)_2NN(SiMe_3)_2$ possesses most probably a conformation with perpendicular molecular halves; a dihedral angle of ~ 90°[34] is confirmed by minimal n_N/n_N splitting. On oxidation, the system tends to achieve the planar conformation, but steric requirements force it to adopt an intermediate structure (Figure 8). ESR parameters reflect this behavior: the ^{29}Si coupling constant is reduced to one-third of the value for the planar, bicyclic derivative, a diffeence which is nicely explained by graphic results from extended INDO calculations on $N_2H_4^{+\cdot}$.[6n,w]

The six-membered-ring derivative (Figure 8) exhibits spin localization to only one hydrazine unit on oxidation. One understands that the radical cation adopts a half-chair conformation and that the intramolecular electron-transfer rate is slow on the ESR time scale.[6w,35]

Reactions of Organosilicon Radical Ions

Oxidation of reduction of molecules may lead not only to extensive structural changes but also to secondary radical ions with different constitutions, i.e., to chemical reactions.

Hexakis(trimethylsilyl)-2-butyne has an ionization potential of only 7.60 eV[6s] and should therefore lose one electron in $AlCl_3/CH_2Cl_2$ solution. The actual experiment does not yield the corresponding cation radical, but—after appearance of a paramagnetic intermediate at low temperature—one observes the ESR spectrum of a new radical ion (Figure 9).[6s] Careful comparison with computer-simulated spectra reveals the presence of only four equivalent Me_3Si substituents; two silyl groups were apparently lost during the reaction.

The most reasonable structure for the new radical ion is that of a tetrakis(trimethylsilyl)butatriene radical

---

[33] S. F. Nelsen, W. C. Hollinsed, C. R. Kessel, and J. C. Calabrese, *J. Am. Chem. Soc.*, **100**, 7876 (1978).

[34] C. Güdewell, D. W. H. Rankin, A. G. Robiette, and G. M. Sheldrick, *J. Chem. Soc. A*, 318 (1970).

[35] Cf. S. F. Nelsen, *Acc. Chem. Res.*, 14, 131 (1981), and literature cited therein.

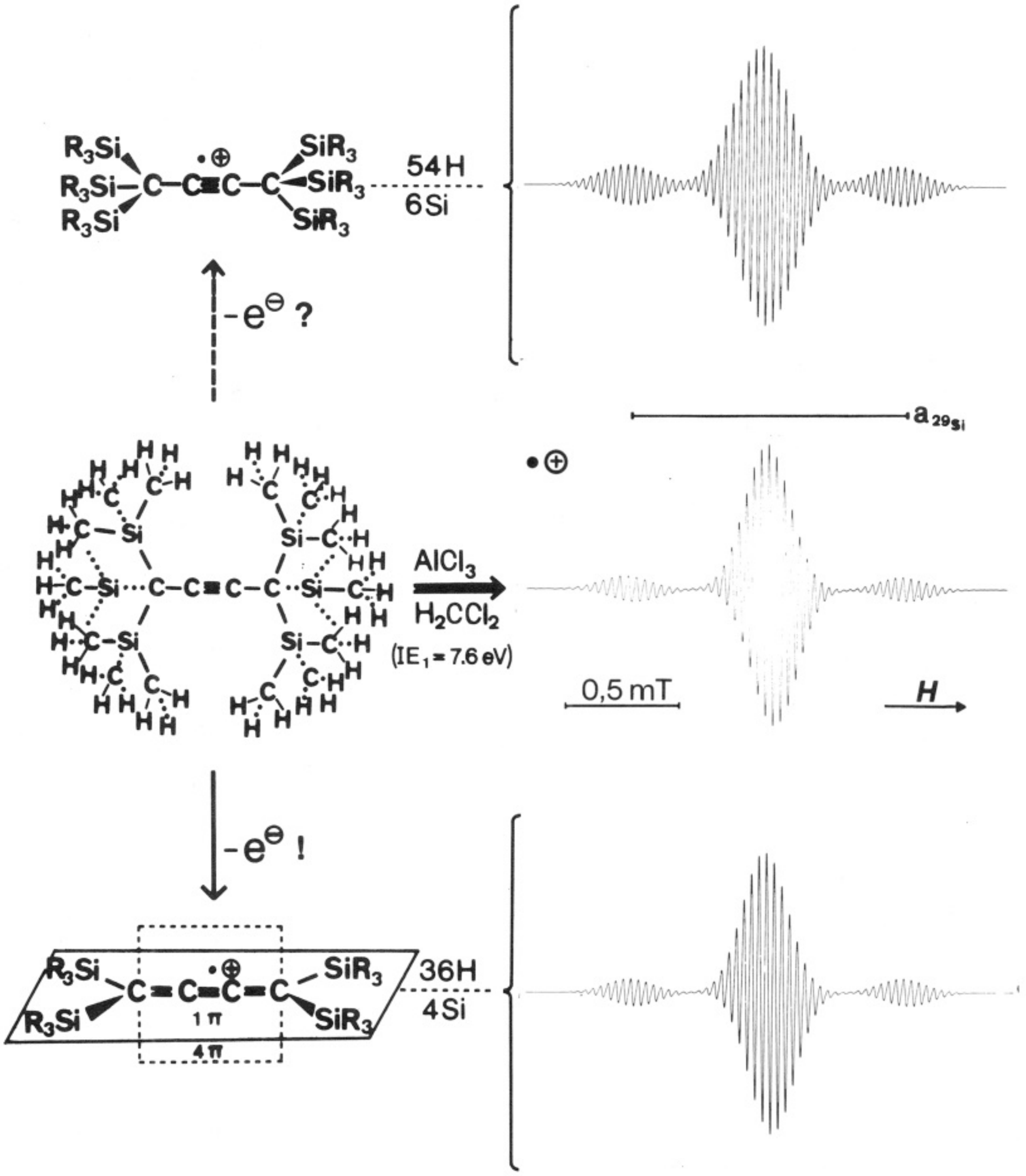
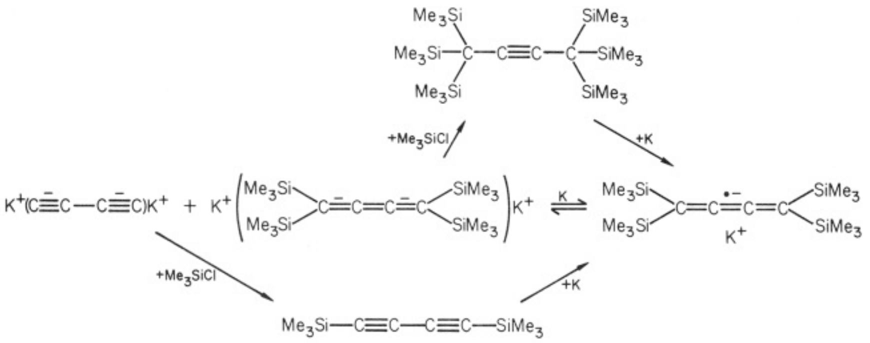


Figure 9. ESR spectrum of the radical cation generated by $AlCl_3/CH_2Cl_2$ oxidation of hexakis(trimethylsilyl)-2-butyne (center) and computer simulations assuming either six $(H_3C)_3Si$ groups (above, dissimilar) or four substituents with 36 H and 4 Si nuclei (below, perfect reproduction).

Scheme I



cation; various arguments can be made for this assignment.[6s,36] Incidentally, on reaction of the butyne with alkali metals one obtains the radical anion of $(Me_3Si)_2C{=}C{=}C{=}C(SiMe_3)_2$. Moreover, this same species is formed by reduction of bis(trimethylsilyl)-1,3-butadiyne;[6s] see Scheme I. This overall reaction scheme, which includes a remarkable disproportionation sequence, is supported by synthetic studies: on reductive silylation of bis(trimethylsilyl)-1,3-butadiyne

---

(36) Tetrakis(trimethylsilyl)ethene radical cation, recently generated by H. Sakurai, Y. Nakadeira, M. Kira, and H. Tobita, *Tetrahedron Lett.*, 3077 (1980), can be excluded as oxidation product.

with K/Me_3SiCl *both* the butadiyne and the butyne can be isolated.[6s] Summarizing, although the neutral compound, $(Me_3Si)_2C{=}C{=}C{=}C(SiMe_3)_2$, is not yet known, its radical ions are (therefore?) favored reaction products.

Outlook

"During the past decade, electron paramagnetic resonance spectroscopy has been developed into a remarkably powerful tool for the physical-organic chemist".[37] The very same statement holds for the synthetic chemist with interest in the design of novel persistent radicals[13,38] and the study of their properties. ESR studies are also attractive to the physical organic chemist with interest in the structural changes accompanying the redox reactions used for the generation of persistent radicals, in substituent effects on ESR spectra and in their reactions[39-41] and in attempts to isolate them.[33,42] It is hoped that this Account of research on novel organosilicon radical cations by a group who resumed ESR research only in 1976[6y] will demonstrate the usefulness of this technique, illustrate the wealth of general information accessible, and stimulate its application to numerous other compounds also capable of forming radical ions.

Our research on radical ions has been and is supported very generously by the Land Hessen, by the Deutsche Forschungsgemeinschaft, and by the Fonds der Chemischen Industrie. To the organosilicon part reported here, valuable contributions have been made by Dr. G. Brähler and by Dr. M. Kira. It is also a pleasure to acknowledge the cooperation of colleagues from other universities, especially G. Fritz (Karlsruhe), E. Hengge (Graz), G. Maier (Giessen), H. Nöth (Munich), H. Sakurai (Sendai), D. Seebach (Zürich), P. L. Timms (Bristol), R. West (Madison), and N. Wiberg (Munich).

---

(37) D. Griller and K. U. Ingold, *Acc. Chem. Res.*, **13**, 193 (1980).

(38) Cf., e.g., H. Bock, G. Brähler, A. Tabatabai, A. M. Semkow, and R. Gleiter, *Angew. Chem.*, **89**, 745 (1977); *Angew. Chem., Int. Ed. Engl.*, **16**, 724 (1977).

(39) Cf., e.g., W. Kaim, H. Bock, P. Hawker, and P. L. Timms, *J. Chem. Soc., Chem. Commun.*, 577 (1980), and H. Bock, W. Kaim, P. L. Timms, and P. Hawker, *Chem. Ber.*, **113**, 3194 (1980).

(40) Cf., e.g., H. Bock, B. Roth and G. Maier, *Angew. Chem.*, **92**, 214 (1980); *Angew. Chem., Int. Ed. Engl.*, **19**, 209 (1980).

(41) Cf., e.g., H. Bock and U. Stein, unpublished results. Cf. U. Stein, Thesis, University of Frankfurt, 1980, and *Chem. Eng. News*, *Sept.* 15, 34 (1980).

(42) Cf., e.g., H. Bock, G. Brähler, U. Henkel, R. Schlecker, and D. Seebach, *Chem. Ber.*, **112**, 289 (1979).