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GAS PHASE REACTIONS

XXXXVI *. SILABENZENE: PHOTOELECTRON SPECTRUM FROM 1-SILA-2,5-HEXADIENE PYROLYSIS AND ASSIGNMENT OF VALENCE IONISATION ENERGIES **

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Summary

The pyrolysis of 1-sila-2,5-hexadiene has been optimized by photoelectron spectroscopic real-time gas analysis. At 1050 K the thermal dehydrogenation yields exclusively hydrogen and silabenzene, for which all valence ionization energies up to 21 eV are observed. The corresponding radical cation states of silabenzene are assigned by ab initio SCF calculations and compared to those for the isovalent benzene.

Silabenzene, a 6π-electron cyclic species involving SiC multiple bonds, long resisted attempts to demonstrate its existence conclusively by observation of any of its molecular state finger-prints. Its stability with respect to other isomers or some of its possible decomposition products was predicted as early as 1975 by Dewar et al. [3] using semiempirical methods and in 1978 by Schlegel et al. [4] from ab initio calculations. The low-energy ionization pattern was correctly predicted in 1977 by Bock [1,5] on the basis of perturbation arguments applied to the series of heterobenzenes $(HC)_5X$ [6].

The first unambiguous evidence was obtained for silatoluene: the thermal decomposition of 5-methyl-5-allyl-5-silacyclohexa-1,3-diene (**1** $R = CH_3$) reported by Barton and Burns [7] allowed Bock, Solouki et al. [8] to record the photoelectron

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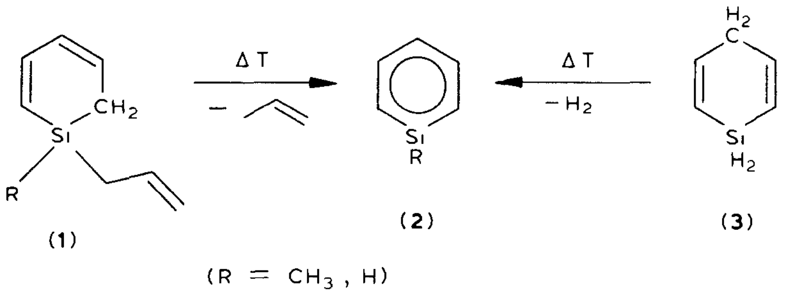
* For Part XXXXV see ref. 1. For an earlier communication on silabenzene see ref. 2.

** Dedicated to Professor M. Kumada.

spectrum of the silatoluene (overlapped by that of propene) in a flow system, and enabled Chapman et al. [9] to trap it in an argon matrix and so to identify it by IR and UV spectroscopy:



(1) (2) (3)

(R = CH_3, H)

(1)

Shortly afterwards, the pyrolysis of the unsubstituted precursor **1** (R = H), (synthesized, as reported by Maier, Mihm and Reisenauer [10]) was optimized by Solouki, Rosmus, Bock and Maier [2] using photoelectron spectroscopic real-time analysis [11]. Silabenzene was identified for the first time by its photoelectron ionization pattern in its mixture with propene obtained from the pyrolysis [2]. In their own investigations, Maier, Mihm and Reisenauer succeeded in trapping silabenzene **2** (R = H) in an Ar matrix and recording its UV and IR spectra [10].

Numerous investigations have contributed synthetic [12–14], spectroscopic [15] and theoretical [16,17] detail to the chemistry of silabenzene. Still lacking, however, was a photoelectron spectrum of silabenzene which allowed observation of all the valence ionization states within the He(I) measurement region combined with an ab initio SCF calculation, with at least a double ζ basis set for the assignments. Starting from the thermal dehydrogenation of 1-sila-2,5-cyclohexadiene-3, discovered by Maier et al. [12], such a spectrum has not been obtained for the short-lived species $(HC)_5SiH$.

Photoelectron spectra

The He(I) PE spectra for the dehydrogenation of 1-sila-2,5-cyclohexadiene are compared in Figure 1 with those for the silabenzene generated from 1-allyl-1-sila-2,4-cyclohexadiene.

In the PE spectrum of the 1-sila-2,5-cyclohexadiene precursor (Fig. 1, A), the first two bands, at 9.66 eV and 10.19 eV, are revealed by their shape to be π-ionizations, which have to be assigned to the bonding π_b (b_g) and antibonding π_b (b_g) and antibonding π_{ab} (a_u) ethene-π-combinations. Comparison with the carbon analogue of D_{2h} symmetry exhibiting π-ionizations at 8.82 and 9.88 eV [19] shows that both the "through space" interaction of the localized π(CC) units as well as the hyperconjugative shift [20] of the π_b (b_{1u}) combination are smaller; presumably due to the larger SiC bond distances.

On heating the decomposition tube to 1050 K (cf. Exp. Part), the ionization finger-prints of 1-sila-2,5-cyclohexadiene, e.g. the prominent bands at 10.19 or at 14.56 eV, vanish, and new peaks, e.g. at 8.12, 9.46 or 13.74 eV, appear (Fig. 1, C). Comparison with the PE spectrum (Fig. 1, D) of the pyrolysis mixture from 1-allyl-1-sila-2,4-cyclohexadiene (**1**) shows striking similarities: the peaks numbered from 1 to 7 are evidently, identical, and obviously belong to silabenzene. However,

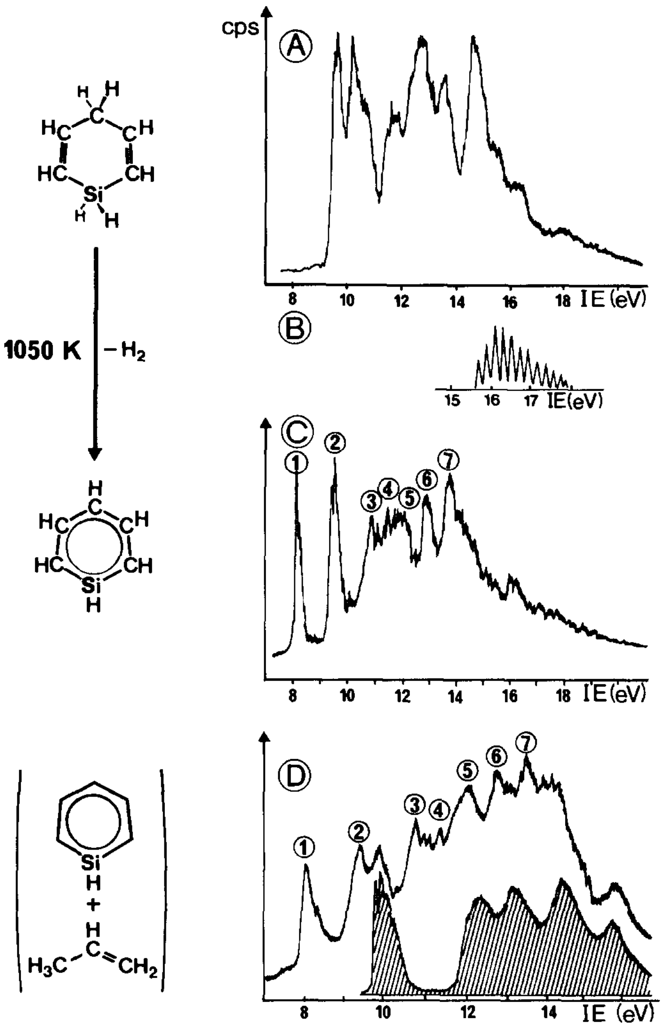


Fig. 1. He(I) PE spectra of (A) 1-sila-2,5-cyclohexadiene, (B) hydrogen [18], (C) a silabenzene/H_2 mixture at 1050 K, (D) a silabenzene/propene mixture at 1000 K (cf. [2]) and propene (hatched).

the PE spectroscopic contours of the latter are obscured to some extent by those of the "leaving molecule" propene (Fig. 1, D). The hydrogen molecule cannot be seen at all (Fig. 1, B and C), presumably due to its much smaller photoionization cross section, its PE spectrum being hidden under the noise from the high-energy bands of silabenzene. Thus, the thermal dehydrogenation of 1-sila-2,5-cyclohexadiene yields a silabenzene PE spectrum exhibiting the complete ionization pattern in the He(I) measurement region up to 21.21 eV.

PE spectroscopic assignment and correlation with the valence ionizations of benzene

The electronic states of benzene radical cation $C_6H_6^{+\cdot}$ are of considerable interest in connection with numerous aspects of its behaviour such as its fragmentation

[21,22] multiphoton-photodissociation processes [23], and ion molecule reactions [24], and its Rydberg spectra [25]. The $C_6H_6{}^+$ ion has been trapped in an argon matrix and its UV spectrum reported [26]. The PE spectrum of benzene has been studied many times, and the assignment of the ionization bands to individual radical cation states has been subject of much controversy [27,28], but experimental and theoretical evidence accumulated in recent years points to the assignment depicted in Fig. 2. The sophisticated calculations by Cederbaum et al. [29], in particular have convincingly demonstrated that the electronic doublet states (except for $\tilde{B}(^2A_u)$) resulting from ionization of benzene valence electrons up to 17 eV can be well described by the Koopmans approximation, $IE_n^v = -\epsilon_J^{SCF}$, and so the orbital eigenvalues $-\epsilon_J^{SCF}$ from Hartree–Fock calculations can be used to interpret the PE spectrum of benzene (Fig. 2, B).

In extension of the reasoning [29] from benzene to silabenzene, Hartree–Fock calculations (cf. Experimental) have been carried out to enable assignment of the PE spectrum (Fig. 2, A) by use of Koopmans' theorem (Table 1).

However, the Hartree–Fock eigenvalue sequence (Table 1) only provides the ordering of the orbitals from which the one-electron ionization processes occur. Accordingly, for the two regions of each of the three close-lying excited radical cation states of silabenzene only group assignments are given in Table 1 and Fig. 2.The Koopmans' assignment of the silabenzene PE spectrum can be substantiated and improved by comparison with that of the isovalent parent molecule benzene

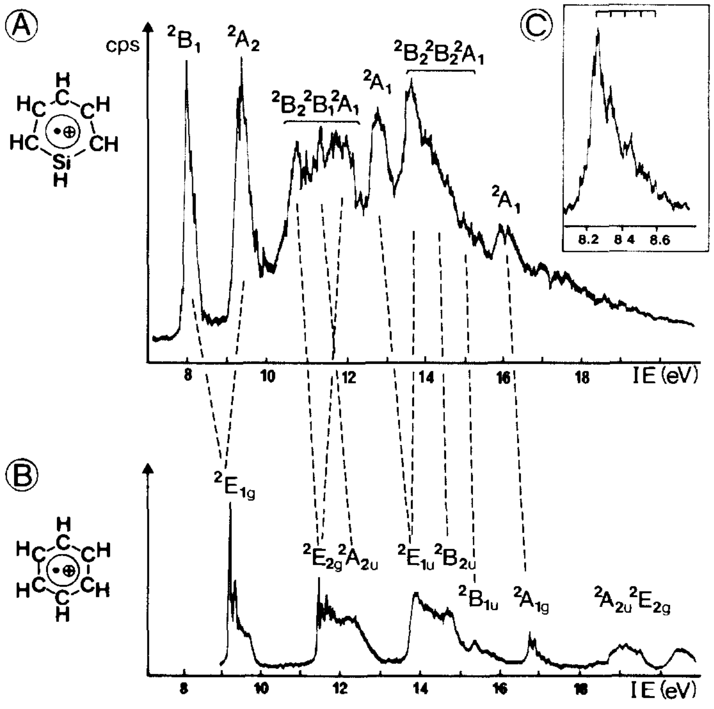


Fig. 2. Comparison of the He(I) PE spectra of silabenzene (A) and benzene (B) with assignments based on Hartree–Fock calculations. Insert: Expanded scale PE spectrum of the first ionization band of silabenzene (C) (see text).

TABLE 1

HARTREE-FOCK VALENCE ORBITAL SYMMETRIES (C_{2v}) AND ENERGIES FOR SILABENZENE CORRELATED VIA KOOPMANS' THEOREM WITH THE He(I) PE SPECTROSCOPIC IONIZATION ENERGIES

Symmetry	$-\epsilon_J^{\mathrm{SCF}}$ (eV)	IE_n^v (eV)	Symmetry	$-\epsilon_J^{\mathrm{SCF}}$ (eV)
$2\,B_1$	7.80	8.11	$3\,A_1$	20.71
$1\,A_2$	9.43	9.46	$2\,B_2$	21.80
$5\,B_2$	11.80	10.84	$2\,A_1$	25.54
$1\,B_1$	12.84	11.35	$1\,B_2$	27.68
$7\,A_1$	13.09	(12.0)[a]	$1\,A_1$	30.32
$6\,A_1$	14.33	12.86		
$4\,B_2$	15.72	13.74		
$3\,B_2$	16.11	(14.1)[a]		
$5\,A_1$	16.94	(14.7)[a]		
$4\,A_1$	18.52	16.1		

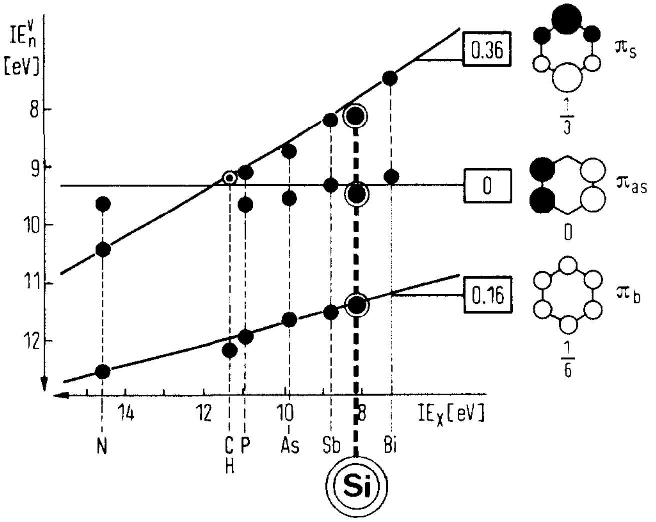
[a] Overlapping bands.

(Fig. 2). Due to $D_{6h} \rightarrow C_{2v}$ symmetry reduction, the degeneracies are removed, and thus the electronic ground state of the silabenzene radical cation, $\tilde{X}(^2B_1)$, is found, as expected, at lower ionization energy than that of benzene. The degenerate ground state of the latter, $\tilde{X}(^2E_{1g})$, also correlates with the first excited $M^{+\cdot}$ state, $\tilde{A}(^2A_2)$, of silabenzene, which is observed 1.4 eV above its $\tilde{X}(^2B_1)$ ground state (Fig. 2). In addition, it should be noted that the Jahn/Teller broadening in the first PES band of benzene is not present in the silabenzene spectrum. An expanded-scale record of the first PES band of silabenzene (Fig. 2, C) shows a progression of 800 ± 50 cm^{-1}, which is assigned to the vibrational excitation of one of the ring modes, and suggests structural changes between the electronic ground states of silabenzene and its radical cation. A more specific assignment is prevented by lack of information concerning the vibrational frequencies of the silabenzene ring modes, which are not yet well-established [10,13].

The PES bands of silabenzene at higher ionization energies are assigned according to the orbital symmetries from the Hartree–Fock calculations (Table 1). The statisfactory correlation with the corresponding benzene radical cation states (Fig. 2) provides additional support for the group assignments of close-lying electronic $M^{+\cdot}$ states of silabenzene as given in Table 1. As is obvious, the removal of degeneracy in the E states of benzene results in a rather high density of excited radical cation states of silabenzene in the region between 10.5 and 15 eV. Their symmetries are different from those of the minima caused by distortion of the Jahn/Teller states in benzene.

In contrast to those of benzene, no Rydberg states of silabenzene are known so far; the first PE band (Fig. 2, C) should be of particular help in identifying these. It is also likely that emission or adsorption spectra for the $\tilde{X}(^2B_2) \leftrightarrow \tilde{A}(^2A_2)$ transition at 1.4 eV $\triangleq$ 11300 cm^{-1} would reveal information about vibration-rotation states of the interesting silabenzene cation.

In conclusion we note that silabenzene is best considered as a symmetry-distorted 6π-electron ring. The electronic perturbation caused by replacing one carbon by a silicon is relatively small, as is obvious from the PE spectroscopic correlation presented in Fig. 2. Correspondingly, the Hartree–Fock calculations predict a rather



(2)

Fig. 3. Silabenzene ionizations/heterobenzene correlations (see ref. 6).

small dipole moment for silabenzene (cf. Experimental). Additional support is supplied by a comparison of the UV spectra of benzene and silabenzene [2,10–12], which reveals a 1/1 correspondence, with the ^1L_b, ^1L_a and B_{ab} bands of benzene shifted to longer wavelengths by 8100, 12200 and 7100 cm^{-1}, respectively. Probably the most striking is the perfect fit of the silabenzene ionizations (Table 1) into the heterobenzene correlation proposed by Heilbronner et al. [6] (Fig. 3). This correlation has been used as indicated in the introductory remarks [5], to predict correctly the π-ionization pattern of silabenzene, and thus has been of considerable help in the detection of this short-lived molecule in the gas mixture from flow pyrolysis [2].

Experimental

1-Sila-2,5-cyclohexadiene was synthesized as described in ref. 12 and its purity checked by MS and ^{1}H NMR (cf. [12]).

Photoelectron spectra were recorded on a Leybold Heraeus UPG 200 spectrometer [11]; the resolution was about 18 meV and the count rate 10^3 cps throughout the experiments. All PE spectra were calibrated using the argon double peak $^2P_{3/2,1/2}$ at 15.76 and 15.94 eV.

Pyrolysis was carried out using the electron-impact high-temperature oven, developed together with Leybold Heraeus and described in detail in ref. 30. The short-pathway arrangement permits a minimum distance of about 4 cm between the end of the heating zone and the target chamber of the PE spectrometer. After generation of a vapor pressure of about 10^{-1} mbar and recording of the PE spectrum of 1-sila-2,5-cyclohexadiene at room temperature, the oven-temperature was raised in 50 K steps and, finally, optimized to ±10 K. The high-frequency current was switched on above 800 K.

Calculations. The unknown structure of silabenzene has been estimated by MNDO geometry optimization calculation [31], which resulted in, e.g., d(CSi) 172 pm or angle CSiC 109°, in agreement with e.g., refs 4 and 17. For the ab initio calculations, the following Gaussian basis set [32] was chosen (in parentheses: each the numbers of contracted inner functions): $2 \times s$ for H, $7 \times s(4)$ and $3 \times p(2)$ for C as well as $9 \times s(6)$ and $5 \times p(3)$ for Si. This basis, consisting altogether of 76 groups of Gaussian orbitals for 50 electrons, yielded a SCF total energy of -481.1428 a.u., i.e. considerably better than the values (-476.0432 a.u. [4] or -479.2064 a.u. [17]) obtained with the rather unsaturated STO-3G [4] or 3-21G* [17] basis sets. Our Hartree–Fock calculations yielded a dipole moment of 0.3 Debye for silabenzene in its electronic ground state. The computations (cf. Tab. 1) were carried out in the IBM 360/168 Computer of the Rechenzentrum of the Technische Hochschule Darmstadt.

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