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Preliminary communication

RADICAL IONS

XI [*]. ONE-ELECTRON OXIDATION OF ALKYLSILYL BENZENES IN THE GAS PHASE AND IN SOLUTION

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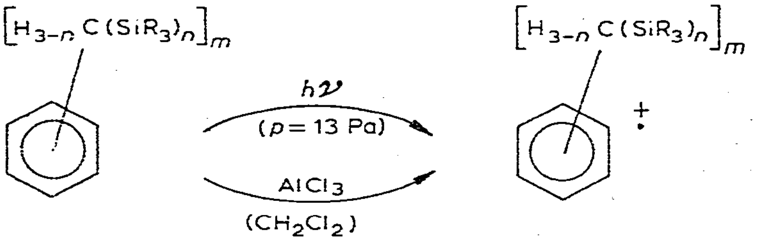
Summary

Compounds which exhibit first ionization potentials below ~8 eV in their photoelectron spectra can in general be oxidized to their corresponding radical cations. This new criterion for predicting the existence of the less frequent $M^{+\cdot}$ species has been successfully applied to poly(trimethylsilylalkyl)-substituted benzene derivatives. The key to the generation of their cation radicals is a selective one-electron oxidation, involving solid $AlCl_3$ in H_2CCl_2.

The PE and ESR spectra yield information not only on the charge delocalization but also on the conformations of the radical cations generated.

Numerous novel radical cations [1—3] can be generated with $AlCl_3$ [3,4][**] in H_2CCl_2 solution from parent molecules which exhibit vertical first ionization potentials lower than ~7.8 eV (eq. 1).



(1)

($R = CH_3$; n = 1,2,3 ;
m = 2,4,6)

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[*] cf. ref. 1. For part IX and X see ref. 2. Part of the thesis of W. Kaim [3].

[**] For other uses of $AlCl_3$ as oxidizing agent cf. e.g. the recent review in ref. 4.

To detect and to characterize the species $M^{\dot{+}}$. photoelectron (PE) spectroscopy has been used for the gas phase and electron spin resonance (ESR) technique for solution (Fig. 1 and Table 1).

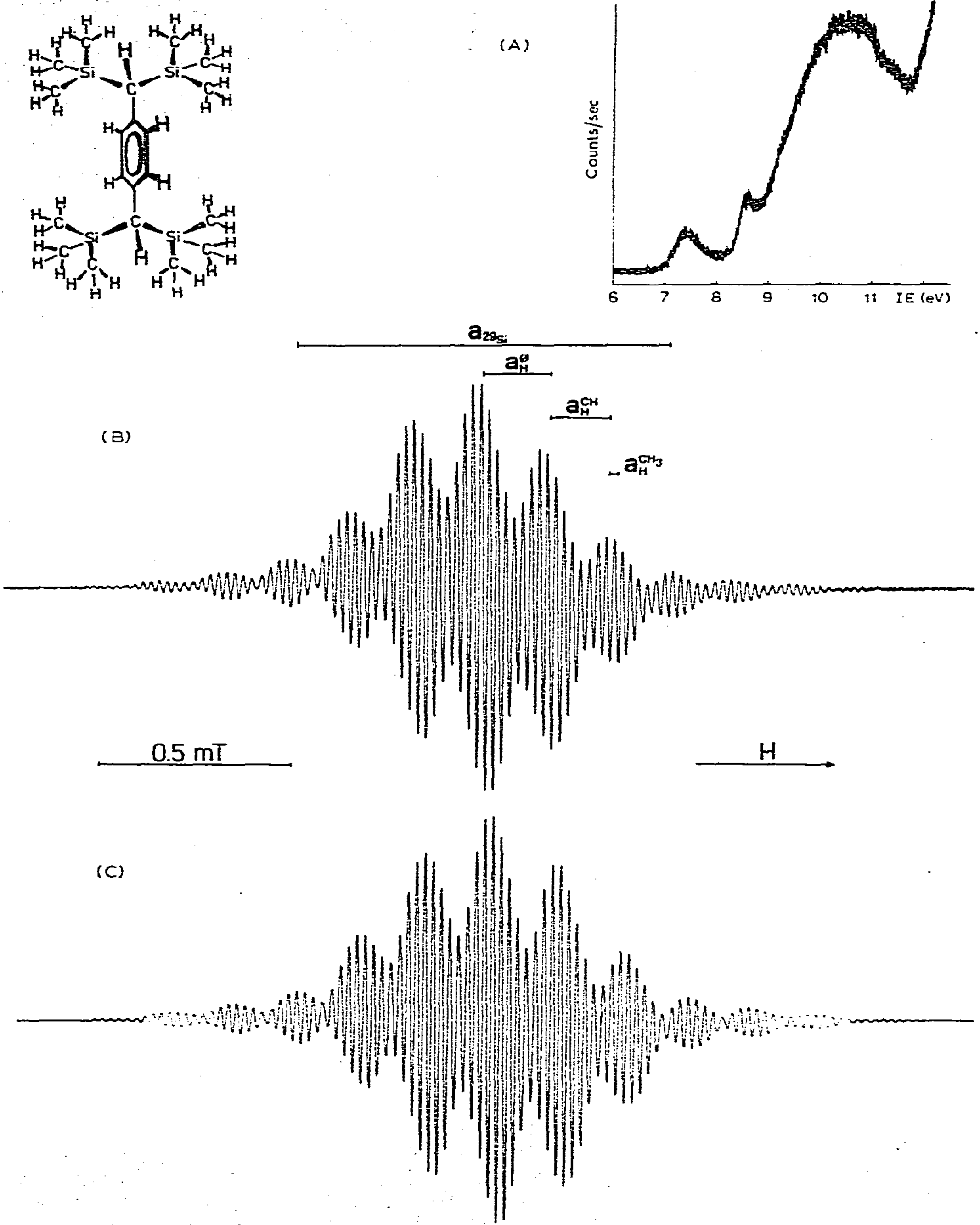
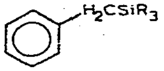
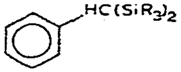
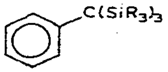
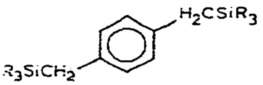
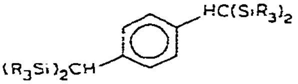
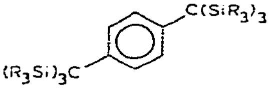
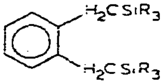
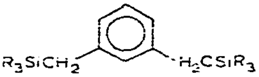
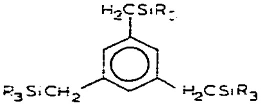
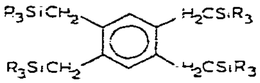
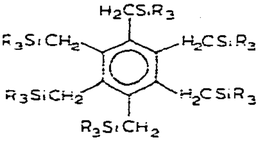
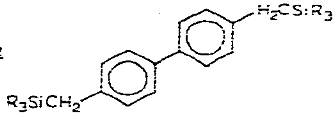


Fig. 1. Radical cation of α, α, α', α'-tetrakis(trimethylsilyl)-*p*-xylene: PE spectrum (A), ESR spectrum (B) and the computer simulation (C).

TABLE 1

RADICAL CATIONS OF ALKYLSILYLBENZENES[a]: VERTICAL FIRST IONIZATION POTENTIALS IE_1, ESR COUPLING CONSTANTS, a_X AND TEMPERATURE, T, AT WHICH ESR SPECTRA WERE RECORDED

Compound ($R = CH_3$)		IE_1 (eV)[b]	$a_H^{CH_3}$	$a_{^{29}Si}$	$a_H^{CH_n}$	a_H^{Ph} (mT)	T(K)[d,c]
I		8.35[6]	*e*				180
II		8.10	*e*				180
III		8.10	*e*				180
IV		7.75	0.029	*f*	0.84	0.177	190
V		7.40	0.021	0.97	0.154[g] 0.138	0.175	225 300
VI		7.45	0.013	0.63		0.171	250
VII		8.05	*e*				180
VIII		8.10	*e*				180
IX		7.85	*e*				180
X		7.10	0.018	0.83	0.579	0.060	275
XI		7.40	0.013	0.54	0.353		300
XII		7.60	0.012	*f*	0.554	0.201 0.053	200

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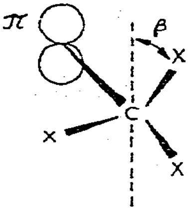
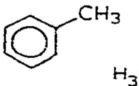
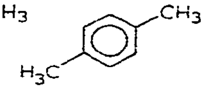
[a] All compounds are prepared by standard methods [5]; the synthesis of the new derivatives X and XI will be reported in detail elsewhere [3]. [b] Vertical, calibrated with Xe 12.13 eV. [c] Confirmed by computer simulation. [d] Calibrated with $ON(SO_3K)_2$: $2\,a_N = 2.618$ mT. [e] No signals observed. [f] Not observed due to low ^{29}Si content and low signal to noise ratio. [g] Temperature dependent (Fig. 1: 225 K).

The PES data (Table 1) demonstrate that trimethylsilylmethyl substituents drastically lower the first ionization potential of benzene IE_1 9.24 eV, e.g. 1,4-disubstitution (IV) by ΔIE_1 1.5 eV and for 1,2,4,5-tetrasubstitution down to IE_1 7.10 eV (X). This very large donor effect can be parametrized in terms of a hyperconjugation model [7], e.g. subdividing the total perturbation D^M for toluene and xylene derivatives ($c_{J\mu}^2 = 1/3 =$ constant) into conformationally dependent π-CX bond contributions d_{CX}^M (eq. 2).



$$D^M = \sum_{CX} d^M \langle \cos^2\beta \rangle \qquad (2)$$

		
IE_1	8.85	8.45 eV
d_{CH}	0.27	0.27 eV

	III	VI
IE_1	8.10	7.45 eV
d_{CSi}	0.77	0.62 eV

For the (non-additive) π-CSi interaction (eq. 2), preferred conformations with the bulky $(H_3C)_3Si$ groups perpendicular to the benzene molecular plane ($\cos^2 0° = 1$) have been assumed for steric reasons. Analogously, in V (Fig. 1) the two $Si(CH_3)_3$ groups are presumably arranged above and below the ring ($\cos^2 30° = 0.75$), for which eq. 2 yields $D^{xylene} = 1.86$ eV and $IE_1 = 9.24-1.86 = 7.38$ eV in perfect agreement with the experimental value (Fig. 1 and Table 1: 7.40 eV). Larger perturbations of the benzene π system, especially in polysubstituted derivatives such as the sterically overcrowded 102-atom molecule XI, are better rationalized in molecular state terms with the resulting radical cation $M^{+\cdot}$ being considerably stabilized due to optimal charge delocalization.

One-electron oxidation in solution carried out subsequently yielded well-resolved ESR spectra. Thus for $V^{+\cdot}$ (Fig. 1), besides the phenyl-proton quintet, the methine-proton triplet and the doublet due to ^{29}Si (natural abundance 4.7%, $I = 1/2$) one recognizes in the hyperfine splitting pattern the heptatriacontet for the 36 methyl protons (predicted intensity ratio between outermost and center signal 1/9075135300). A coupling with the up to 54 hydrogens in δ-position to the benzene π system is observed for all [3] radical cations generated (Table 1: $a_H^{CH_3}$) and manifests an extensive spin distribution over the alkylsilyl substituents. This effect, which is to be expected according to the above PES arguments, is further illustrated by the unusually small and nearly constant coupling constants for the ring protons * in *p*-disubstituted derivatives (Table 1: a_H^{Ph}) and the decreasing values for $a_H^{CH_3}$, $a_{^{29}Si}$ and $a_H^{CH_n}$ with increasing substituent size in IV → V → VI.

The hyperconjugation model 2 introduced to rationalize the low first ionization energies in the preferred gas phase conformation can be extended [9,10] to discuss the angular dependence of the coupling constants for the π-CH_n protons and π-$C^{29}Si$ silicon.

Under the reasonable assumptions, that the constant B_0 in the Heller—McConnell equation [9] $a_X^\beta = \rho_C^\beta(B_0 + B_2 \langle\cos^2\beta\rangle)$ can be neglected relative to B_2

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* For the *p*-di-t-butylbenzene radical cation a_H^{Ph} 0.21 mT has been reported [8].

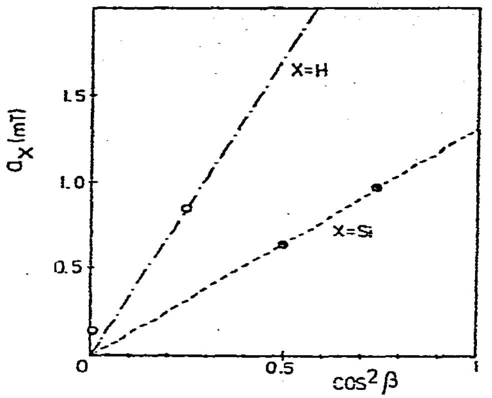
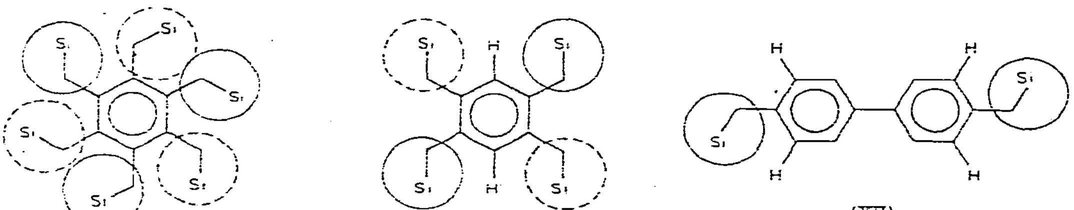


Fig. 2. Angular dependance of the coupling constants a_H for the CH_2-protons and $a_{^{29}Si}$ in compounds IV, V and VI (cf. Table 1).

[10], and that the spin populations ρ^π in the 1,4 positions of the benzene ring for IV, V and VI are nearly constant and can be approximated by HMO i.e. $\rho^\pi = c^2_{J\mu} = 1/3$, linear regressions (Fig. 2) through the origin result. The values B_2 obtained from their slope $B_2 \cdot \rho$ are in good agreement with literature data, e.g. $B_2^H(M^{+\cdot}) \sim 8$ mT [11] or $B_2^{Si}(M^\cdot) \sim 4$ mT *.

In connection with the overall coconut shape of most of the radical cations reported, PES shows that the tetra- and the hexa-substituted derivatives V and VI or X and XI exhibit similar vertical first ionization energies. For steric overcrowding, in ESR spectra, so-called values $R \equiv a_H^{CH_2X}/a_H^{CH_3}$ have been defined [13] with $R = 0.5$ indicating complete "blocking" and $R = 1$. "unhindered" rotation. From the known $a_H^{CH_3}$ values for the corresponding methyl substituted derivatives [11,14] 3 R-values can be derived (Fig. 3). Accordingly, X and XI are severely "blocked", but XII is also not"freely rotating".



(XI)

$R = \frac{3.53}{6.45} = 0.55$

(X)

$R = \frac{5.79}{10.70} = 0.54$

(XII)

$R = \frac{5.54}{8.79} = 0.63$

Fig. 3. Steric overcrowding in poly(trimethylsilylmethyl)-substituted benzene derivatives as demonstrated by ratios R of ESR coupling constants relative to the methyl compounds.

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* Estimated analogous to Fig. 2 with $\rho = 1$ from $a_{^{29}Si}$ values for radicals $M^\cdot$ reported by Griller and gold Ingold [12].

Combined PES and ESR analysis together with $AlCl_3$ oxidation establishes the existence of novel radical cations also from numerous other systems, e.g. R_3SiCH_2 or R_3Si substituted olefins [3,15] or compounds with lone pairs of e.g. the elements N [1,3,16], P [17] or S [18].

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