Notes

A Simple Correlation of Anodic Peak Potentials of Silylarenes and Their Vertical Ionization Energies

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Received September 23, 2003

Summary: The anodic oxidation potentials of a series of 16 silylarenes have been determined by cyclic voltammetry in acetonitrile. All oxidation steps have been found to be irreversible. The effect of substituents and substitution patterns on the oxidation potentials can be presented as a linear correlation between the experimental oxidation potentials and the calculated vertical ionization energies of the silylarenes, using correlated ab initio methods at the MP2 level of theory. This correlation is useful to predict oxidation and ionization potentials of other silylarenes.

Introduction

The oxidative electrochemical properties of *methyl*benzenes have been studied extensively by both voltammetry and preparative-scale electrolysis.[1−4] As expected, the higher the number of methyl substituents attached to the benzene ring, the lower the oxidation potential, due to the inductive effect exerted by the *methyl* groups. With this background, it is of interest to compare the electrochemical properties of methylbenzenes with those of their silicon analogues: viz., the *silyl*arenes, Ar(SiH_3)$_n$. The synthesis of a variety of aromatic hydrocarbons with *silyl* substituents (SiH_3) has been described recently.[5,6] These hydrogen-rich silylarenes are important precursors for arylpolysilanes, which are potentially useful for applications in optoelectronic devices.[7−10]

Experimental Section

Figure 1 shows the 16 silyl-arene compounds (**I**−**XVI**) which have been studied electrochemically in this work. The compounds were synthesized and purified according to procedures described in refs 5 and 6.

All cyclic voltammetry (CV) measurements were carried out in a glovebox under a nitrogen atmosphere strictly excluding moisture and oxygen (both less than 1 ppm). A conventional three-electrode cell has been used with a glassy-carbon disk (ca. 3 mm diameter) as the working electrode and a Pt wire as the counter electrode. The concentration of the substrate was 1−2 mM in acetonitrile and 0.1 M in lithium perchlorate. The solvent was distilled twice over CaH_2 under nitrogen, and the electrolyte was dried under vacuum (~30 mmHg) at 85 °C for 24 h before use. Potentials are quoted vs the Ag/AgCl reference electrode, at a scan rate of 100 mV/s (first cycle). Quantum-mechanical calculations[11] have been performed initially at the hybrid density functional B3LYP level.[12] The structures of the neutral silyl-arenes **I**−**XVI** have been optimized using the 6-31G(d) basis set, and the structures have been verified to be minima on the potential energy surface by a subsequent frequency calculation. Refined energies were obtained using single-point calculations at the MP2 level employing the extended 6-311+G(d,p) basis set. The vertical IPs were calculated by subtracting the absolute energy of the radical cation with the structure of the neutral silylarene from the absolute energy of the neutral compound. Solvent effects have been introduced using a self-consistent reaction field on the basis of the Onsager model at the B3LYP/6-311+G(d,p)//B3LYP/6-31G(d) level.[13]

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10.1021/om030609j CCC: $27.50
Publication on Web 02/25/2004

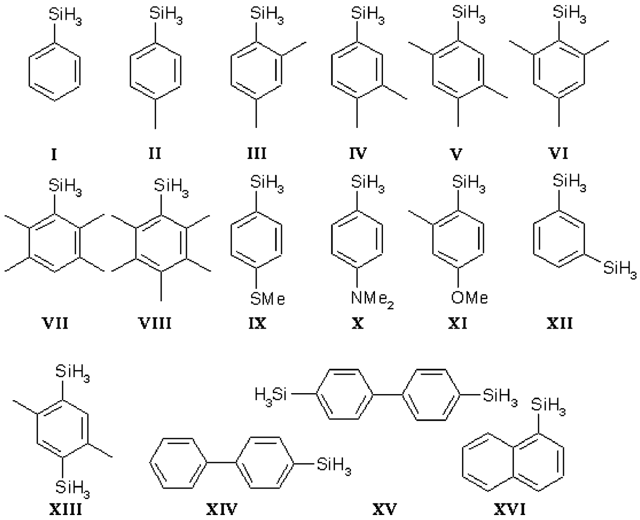

Figure 1. Structural formulas of the silylarenes investigated.

Table 1. Anodic Peak Potentials (E_{p}, V) of Silylarenes Measured by Cyclic Voltammetry and Vertical Ionization Energies (I_{P}, eV) Calculated at the MP2/6-311+G(d,p)//B3LYP/6-31G(d) Level

substrate	E_{p}^{1}(ox)	E_{p}^{2}(ox)	E_{p}^{3}(ox)	$E_{\mathrm{p/2}}$(ox)	I_{P}
I	2.26			2.12	9.398
II	2.12			2.00	9.131
III	2.06			1.93	8.852
IV	2.01			1.90	8.822
V	2.04			1.87	8.563
VI	2.00	2.16		1.90	9.014
VII	1.80	2.13	2.32	1.69	8.339
VIII	1.69	2.10	2.26	1.60	8.236
IX	1.44	1.80	2.11	1.32	8.019
X	0.86	2.40		0.80	7.341
XI	1.84	2.05[b]	2.30[b]	1.68	8.404
XII	2.21[a]			2.14	9.374
XIII	2.04			1.92	8.732
XIV	1.94			1.83	8.381
XV	2.01	2.26[b]		1.88	8.606
XVI	2.10			1.80	8.229

[a] A shoulder was observed at 1.98 V due to toluene impurity. [b] An ill-defined wave.

Results and Discussion

Table 1 lists the anodic peak potentials of **I**−**XVI**, as measured by CV, on a glassy-carbon (GC) working electrode in acetonitrile. CV measurements were also conducted on Pt, but the peaks appeared to be less sharp than those obtained by GC. Also, in general, they appear at 0.1−0.2 V less positive potentials. All peaks have been found to be irreversible on both working electrodes. Some derivatives exhibited a second (and sometimes a third) oxidation wave, but generally with current amplitudes considerably lower compared with that of the first wave. No reduction peak was found for any of the derivatives studied upon scanning to −2.5 V (vs Ag/AgCl) in acetonitrile.

Tri*alkylsilyl* groups, R_3Si, are known to have a positive inductive effect as electron-donating moieties and, therefore, tend to decrease oxidation potentials, when attached to hydrocarbon molecules.[14] To study the effect of the SiH_3 group in comparison to the CH_3 group, we measured the oxidation potential of toluene and benzene under the same experimental conditions as for **I**. The anodic peak potential, E_{p}, of **I** is found to be 2.26 V (vs Ag/AgCl): higher than that of toluene (1.96 V) but lower than that of benzene (2.4 V). These results are supported by photoelectron spectroscopy measurements[15] carried out for benzene, toluene, and **I**. The measurements of the first vertical ionization potentials gave 9.24, 8.80, and 9.18 eV, respectively. Obviously, the SiH_3 group is less capable of electron donation than the methyl group, but the Si−C bond is still slightly more polar than the C_{ar}−H bond. Therefore, the SiH_3 group raises the oxidation potential of **I** relative to toluene and lowers it, though to a lesser extent, relative to benzene.

As to the role of inductive, hyperconjugative, and d-orbital effects in organosilicon compounds, contradictory models have been advanced in the literature. Early computations suggested[16] that orbitals of Si atoms connected to an aromatic system give only poor overlap with the aromatic π system due to the large Si−C distance and energy difference, ruling out any hyperconjugative effect toward the ring. Nevertheless, the positive inductive effect, caused by the inherent polarity of the Si−C bond, was expected to make the aromatic ring slightly more electron-rich. This conclusion is in accordance with Pauling's electronegativity scale for carbon and silicon atoms, with values of 2.5 and 1.8, respectively.

As a result of later computations by Veszpremi and Nagy,[17] it was suggested that all three effects play an important role and that the relative importance of the effects depends on the individual system. For $PhSiH_3$ hyperconjugation appears to be the main effect. However, from the photoelectron spectrum of $PhSiH_3$ it was concluded that the stabilization of its HOMO must also include $p\pi$−$d\pi$ interactions.[15,18] More recent advanced calculations have yielded bonding models with greatly reduced d-orbital participation, important only for silicon moieties attached to strongly electronegative groups,[19,20] but the contributions are certainly not to be ignored altogether.

The present study has shown that upon introduction of a *methyl* group into phenylsilane **I** in the para position, as in **II**, or of two methyl groups, as in **III** and **IV**, the oxidation potentials become lower (Table 1) compared to that of **I** due to the inductive effect exerted by the methyl groups. In general, as it was found for poly*methyl* benzenes, the larger the number of methyl groups, the lower the oxidation peak potential of the $(Me)_nAr$−SiH_3 compounds. Indeed, the derivative with five methyl groups (**VIII**) has the lowest oxidation potential. A thiomethyl group or a methoxy group has an even stronger impact, as is observed for **IX** (vs **II**) and similarly for **XI** (vs **III**).

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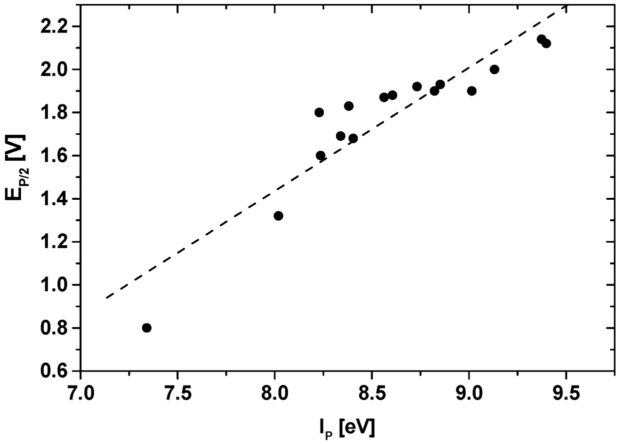

Figure 2. Plot of $E_{p/2}$ vs computed I_P energy.

Correlations of anodic oxidation potentials ($E_{1/2}$) and ionization potentials (IP) of organic compounds have been established.[15] However, measurements of ionization potentials of silylarenes have been scarce and confined only to $PhSiX_3$ type silanes.[21] In the absence of experimental data for ionization potentials of silylarenes, the vertical ionization energies (I_P) for the compounds **I**−**XVI** have been calculated at the MP2/6-311+G(d,p)//B3LYP/6-31G(d) level of theory.[11,12] In Table 1, the anodic half-peak potentials ($E_{p/2}$) of the first oxidation waves of derivatives **I**−**XVI** and their I_P's are presented. The preference of using $E_{p/2}$ rather than E_p values stems from the fact that the results are more accurate for irreversible electrochemical processes, because they take into account both peak amplitude and wave width. Indeed, this advantage is evident when comparing the two derivatives, both of which are tetrasubstituted at the same positions, **XIII** (with two SiH_3 groups and two methyl groups) and **V** (with one SiH_3 group and three methyl groups). While there is no difference in their E_p values (both show 2.04 V; Table 1), they differ in their $E_{p/2}$ values, at 1.92 and 1.87 V, respectively. As anticipated (e.g. **I** vs **II**), the former is more difficult to oxidize due to the presence of two silyl groups, compared with one silyl and one methyl group, at the 1- and 4-positions, respectively.

A linear correlation is obtained upon plotting $E_{p/2}$ vs. I_P for 16 compounds involving all the substituted benzene rings, the two biphenyl derivatives **XIV** and **XV**, and the naphthalene derivative **XVI**, with a correlation coefficient of 0.92 (Figure 2). The plot fits the equation $E_{p/2} = (-3.15 \pm 0.55\ \mathrm{V}) + (0.573 \pm 0.064\ \mathrm{V\ eV^{-1}})I_P$. The fit is reasonably good, considering that, on one hand, vertical ionization energies have been used and, on the other hand, the fact that all measured oxidation potentials are electrochemically irreversible, with no surface, solvation, adsorption, or kinetic effects taken into account. Inclusion of solvent effects in the calculation of the I_P values on the basis of the Onsager model[13] shows only negligible improvement (see the Supporting Information) compared with calculations confined to the gas phase.[22,23]

The fact that a satisfactory straight line is observed for the silylbenzenes indicates that the change in free energy of solvation of the substrate as it is oxidized to its respective cation radical is fairly constant for the whole series of substituted phenylsilanes. This result means that the solvation effects associated with the delocalization of the charge on the cation radical are not significant. The new simple least-squares equations above could therefore be useful in predicting both oxidation and ionization potentials of silylarenes.

The outcome of electrolysis of poly*methyl*benzenes with controlled potential was found to be dependent on solvent. In strongly polar solvents, oxidation of hexamethylbenzene and durene led to the formation of benzylic type cations, followed by nucleophilic attack of the solvent (acetonitrile or acetic acid).[2] However, in the presence of a less polar solvent, such as dichloromethane, a biphenyl derivative was formed from mesitylene[3] and a diarylmethane derivative from durene.[4] To the best of our knowledge, there are only a limited number of publications that describe the electrochemical oxidation of phenylsilanes in organic media.[24−26] Ph_4Si, $Ph_2Si(OH)_2$, $PhSiH_3$, and $PhSiMe_3$ were oxidized in acetonitrile−$LiClO_4$ and on dichloromethane−$AlCl_3$−Bu_4NClO_4-activated alumina. In the latter dry medium, the cation radicals of the substrates were generally shown to be stable. With residual water, the electrolyses led to black deposits on the anode (Pt), consisting mainly of conductive conjugated aromatic polymers.[24] From substituted monosilanes, such as $MePhSiH_2$ and $PhSiH_3$, polysilanes were also formed electrochemically at Pt electrodes in 1,2-dimethoxyethane (DME).[25] Electrochemical oxidation of Me_2PhSiH in DME in the presence of $CuCl_x$ and BF_4^- salts affords substitution products, mainly $Me_2PhSiCl$ and Me_2PhSiF, respectively.[26] When a mixture of $MePh_2SiH$ and $MePh_2SiCl$ was electrolyzed in DME, using a Cu anode and a Pt cathode, the disilane $MePh_2Si{-}SiPh_2Me$ was obtained in good yield.[26] Electrochemical oxidation of various silylarenes by controlled-potential electrolysis, under different experimental conditions and under a strictly inert atmosphere, are underway in our laboratory.

Supporting Information Available: A table giving absolute energies of compounds **I**−**XVI** at different levels of theory and a figure giving a comparison between gas-phase and SCRF calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

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(22) Self-consistent reaction field calculations at the B3LYP/6-311+G(d, p)//B3LYP/6-31G(d) level of theory for acetonitrile as solvent gave the following correlation between $E_{p/2}$ and I_P: $E_{p/2} = (-2.98 \pm 0.67\ \mathrm{V}) + (0.578 \pm 0.082\ \mathrm{V\ eV^{-1}})I_P$ ($R = 0.88$), which must be compared to the results of gas-phase computations: $E_{p/2} = (-3.08 \pm 0.73\ \mathrm{V}) + (0.588 \pm 0.089\ \mathrm{V\ eV^{-1}})I_P$ ($R = 0.87$). See the Supporting Information for details.

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