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EXPERIMENTAL AND THEORETICAL STUDY OF ELECTROCHEMICAL REDUCTION OF HALOSILANES *

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Summary

The reduction peak CV potentials in a series of methylchlorosilanes $Me_{4-n}SiCl_n$, trimethylhalosilanes Me_3SiX and the corresponding carbon analogues have been measured using anisole and DMF as solvents. The observed trends in reduction potentials are discussed and interpreted on the basis of correlations with theoretical quantum chemical calculations.

Introduction

Although the electrochemistry of organic halides is relatively well established much less is known about the electrochemical behaviour of halogen derivatives of Si, Ge, Sn and Pb [1,2].

As far as we know the first ** polarographic study of halosilanes was published by Russian authors in 1971 [4]. Since that time a number of papers have been published dealing not only with the mechanism of electrochemical reduction of these compounds but also with the effect of systematic structural variations [5–12]. Because of the extreme sensitivity of halosilanes to traces of residual water in nonaqueous solvents the reliability of some of these results was however questioned [13,14]. As was demonstrated, the CV reduction peaks of halosilanes may be interfered with by the reduction peak of the hydrogen chloride which results from their hydrolysis by traces of water in the solvent, especially in the presence of a strong nucleophile of the HMPT type. Moreover, in some nucleophilic solvents the formation of intermediate complexes between halosilanes and solvents have also been described [15,16].

The aim of the present paper is to contribute to the systematic study of the

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* This paper is dedicated to Professor M. Kumada on the occasion of his retirement.

** The study reported by Abrahamson [3] was performed in a 25/75 vol./vol. water-pyridine mixture and the results were distorted by the solvolysis of Si–Cl bonds.

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electrochemical behaviour of halosilanes by attempting to eliminate the interfering influence of the solvent from the effect of intrinsic structural variations. For this purpose the values of peak CV reduction potentials in a series of halosilanes of the type Me_3SiX ($X = F, Cl, Br, I$) and $Me_{4-n}SiCl_n$ ($n = 1, 2, 3$), systematically investigated in DMF and anisole as solvents, have been correlated with quantum chemical calculations. For comparison the same procedure was applied to the series of aliphatic carbon analogues $Me_{4-n}CCl_n$ ($n = 1, 2, 3$).

The philosophy underlying the use of these theoretical methods is based on a generally accepted model, according to which radical anions appear as intermediates during the electrochemical reduction. The formation of these species can be described, in the framework of the orbital approximation, by a process in which the incoming electron enters into the lowest unoccupied molecular orbital (LUMO). The ability of the compound to undergo the reduction is then governed, above all, by the energy of this orbital. In a series of structurally-related compounds one may thus expect a correlation between the experimental reduction potentials and the corresponding LUMO energies. Since these quantities are readily accessible by quantum chemical calculations on an arbitrary level of approximation, they can be used to rationalise the observed experimental data.

Experimental

DMF (Lachema Brno) was purified by keeping it over anhydrous cupric sulphate for some days, followed by distillation in argon under reduced pressure, and treated with reactivated neutral alumina immediately before use [17].

Anisole (Lachema Brno) was dried over sodium and distilled under an argon atmosphere immediately before use.

Tetraethylammonium perchlorate (TEAP) and tetrabutylammonium perchlorate (TBAP), both "FLUKA AG purum", were crystallized from water and dried in vacuo at 60 °C.

Trimethylhalosilanes Me_3SiX ($X = F, Br, I$) were prepared by standard procedures [18–20]. All methylhalosilanes were purified by distillation under argon before use.

Electrochemical measurements

Voltammograms were recorded using a PAR-175 instrument. All experiments were performed at room temperature (Me_3SiF at 6°C) under an atmosphere of argon. Platinum wire microelectrodes were used as working and counter electrodes. For measurements in DMF, the reference electrode was $Cd(Hg)_x/CdCl_2$ with a potential shifted relative to the SCE * potential by −0.75 V [21]. In anisole, the $Ag/AgNO_3$ reference electrode was used (its potential being higher than that of the SCE by +0.63 V) [22]. The voltammograms were determined using 1.5 mmol of methylhalosilanes in 10 ml of a solution of 0.1 *M* TEAP in DMF or in 10 ml of a solution of 0.2 *M* TBAP in anisole. The scan rate used in all experiments was 100 mV/s.

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* SCE = saturated calomel electrode.

TABLE 1

CALCULATED VALUES OF LUMO ENERGIES (in a.u.) IN THE SERIES OF COMPOUNDS STUDIED

Compound	ϵ_{LUMO}	
	sp	*spd*
Me_3SiCl	0.072	0.085 [a]
Me_2SiCl_2	0.048	0.053 [a]
$MeSiCl_3$	0.018	0.032 [a]
Me_3SiF	0.076	0.099
Me_3SiBr	0.067	0.042 [a]
Me_3CCl	0.136	0.097 [b]
Me_2CCl_2	0.100	0.058 [b]
$MeCCl_3$	0.054	0.026 [b]

[a] *d*-Orbitals on both Si and halogen atoms are included. [b] The *d*-orbitals only on the halogen atoms are included.

Calculations

The quantum chemical calculations for all the series of compounds studied were performed by the standard semi empirical CNDO/2 method [23] modified for the inclusion of a bromine atom [24]. The geometry of all the molecules was derived from the idealised tetrahedral arrangement with either standard or experimental bond lengths [25], i.e. r(C–H) 0.109, r(C–Si) 0.187, r(Si–Cl) 0.205, r(C–Cl) 0.178, r(Si–Br) 0.211 nm. Since for the silicon derivatives the calculations may be sensitive to the eventual inclusion of low-lying *d*-orbitals, the calculations were performed both with their inclusion (basis set *spd*) and without them (basis set *sp*).

The calculated values of the LUMO energies for all of the compounds under study are summarised in Table 1. For comparison the data for the aliphatic carbon analogues are also included in the same Table.

Results and discussion

The crucial problem in the voltammetric study of halosilanes is the proper choice of solvent system. In choosing from the range of potential solvents one has to take into consideration two fundamental factors, the first one being the required resistance of the solvent to the reduction, dictated by the necessity of working at relatively high negative potentials. The other factor is connected with the extreme solvolytic sensitivity of halosilanes, which excludes the use of protic solvents. The sensitivity of halosilanes to moisture is in fact so extreme that it was used by Corriu et al. as the basis for the polarographic method for the determination of residual traces of water in nonaqueous solvents [14].

The above requirements are best satisfied by carefully dried anisole [26]. That is why we have used it with TBAP as supporting electrolyte (cathodic limit -2.9 V vs. Ag/Ag^+ reference electrode) [22]. The values of the reduction CV potentials for the whole series of compounds studied (including the carbon analogues) are collected in Table 2. Let us proceed now to the detailed discussion of observed results.

The data in Table 2 demonstrate that the ease of reduction increases with increasing number of chlorine atoms in the series of methylchlorosilanes $Me_{4-n}SiCl_n$

TABLE 2

EXPERIMENTAL VALUES OF REDUCTION POTENTIALS E_P^K OBTAINED BY CYCLIC VOLTAMMETRY MEASUREMENTS ON A SERIES OF HALOSILANES AND THE CORRESPONDING CARBON ANALOGUES [a]

Compound	E_P^K	
	DMF	Anisole
Me_3SiCl	−0.50	−1.11
Me_2SiCl_2	−0.60	−0.93
$MeSiCl_3$	−0.68	−0.81
Me_3SiF	[b]	[b]
Me_3SiBr	−0.41	−0.20
Me_3SiI	[c]	[c]
Me_3CCl	[b]	[b]
Me_2CCl_2	[b]	−2.13
$MeCCl_3$	−2.26	−1.81

[a] Values in volts vs. SCE. [b] Outside of the cathodic decomposition limit of the system. [c] Non-interpretable complex voltammograms obtained.

($n = 1-3$) as well as on going from the fluoro to bromo derivative in trimethylhalosilanes Me_3SiX (X = F, Cl, Br) *. (The reduction potential of Me_3SiF is so negative that it lies outside the decomposition limit of the solvent-supporting electrolyte system.) The same trends are also observed in the series of carbon analogues (in this case, even regardless of the solvent [27,28]). This order is identical with that which could be expected on the basis of classical chemical experience, and it is also shown by the values of the corresponding LUMO energies. The agreement is not only qualitative but, as Fig. 1 demonstrates there is even a satisfactory correlation between the experimental and theoretical quantities (irrespective of the basis set used). The most substantial difference between the silicon and carbon analogues is the considerably easier reduction in the former series.

This result, despite being the complete reversal of that predicted by Corriu et al. [14], is again correctly reproduced by the theoretical LUMO energies. The quantum chemical calculations thus provide important support for the reliability of our experimental data. There is, however, yet another aspect of the correlations with quantum chemical quantities, arising from the fact that the calculations are performed on the isolated molecule approximation. Consequently one may consider them as a standard which reflects the pure structural effects, undistorted by interactions with the solvent. The comparison of theoretical and experimental quantities thus provides a specific means of extracting from the complex experimental data the interfering influence of the solvent effects. In the case of the experimental data from anisole such a comparison confirms the relatively inert behaviour of this solvent, as demonstrated by the fact that is does not alter the intrinsic trends in reduction potential of the studied compounds.

For the purposes of comparison we have also performed all the measurements in dimethylformamide using TEAP as supporting electrolyte (cathodic limit −2.05 V vs. the $Cd(Hg)_x/CdCl_2$ reference electrode). The corresponding values of the

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* Non-interpretable complex voltammograms were obtained in the case of Me_3SiI.

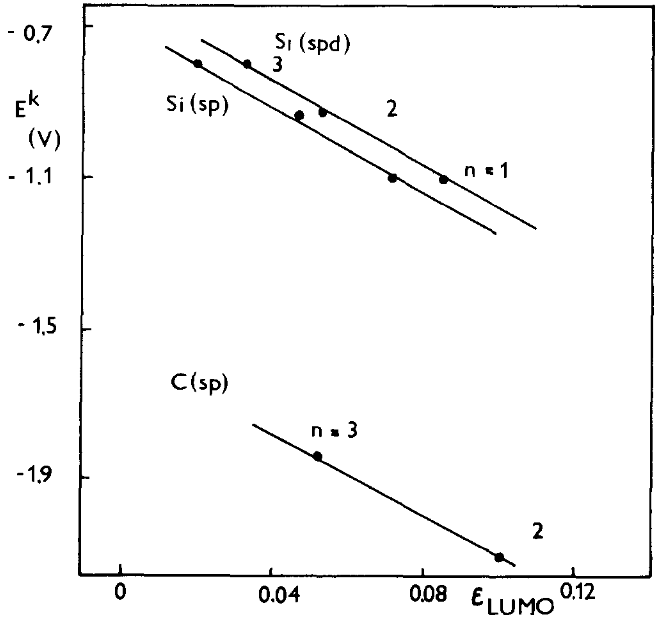

Fig. 1. Correlation of experimental reduction potentials (in anisole, SCE) with calculated LUMO energies of methylchloro derivatives of the type $Me_{4-n}MCl_n$.

reduction potentials are also collected in Table 2. Despite being frequently used as a solvent for electrochemical reductions, DMF does not seem to be the best suited for the systematic study of structural effects, because of the reported complex formation [15,16] with halosilanes and also because of much higher residual water content. Both of these factors have thus to be taken into consideration in discussing the values of reduction potentials in DMF. We are of course aware of the fact that it is frequently not possible to estimate the relative importance of these individual factors but, in our case, we believe that the contaminating influence of hydrogen chloride is not sufficient to outweigh the effects of complex formation. The trends in the values of the reduction potentials can then probably be attributed to the complexation of halosilanes in DMF. Nevertheless, as will be shown below, such a simplification is not sufficient to enable the elucidation of the observed irregularities.

The formation of halosilane ··· DMF complexes has been investigated experimentally by several authors but the conclusions concerning e.g. the structural effects on the complex stability, are frequently contradictory (e.g. [15] vs. [16]). This of course makes it difficult to discuss the observed trends in terms of simple qualitative concepts (substituent electronegativity vs. steric effect). The complete lack of reliable experimental data on the structure of possible complexes renders it also impossible to apply, for this purpose, the theoretical quantum chemical approach based on the calculation of the LUMO energies of the complexes. Under these circumstances we can only conclude that the process of electrochemical reduction in DMF is so complicated that it is not so far possible to characterise it unambiguously in terms of simple specific effects.

Unlike anisole, DMF thus appears to be a completely inconvenient solvent for systematic electroanalytical measurements.

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