Re-examination of the Electrochemical Reduction of Halogeno-silanes and -germanes

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Summary The electrochemical reduction of halogeno-silanes and -germanes in aprotic solvents, to give principally the corresponding dimer, is shown to be an irreversible process taking place at low potentials [-2 to $-2{\cdot}5$ V *vs.* standard calomel electrode (S.C.E.)]; all reduction waves observed at $-0{\cdot}4$ V *vs.* S.C.E. corresponded to the reduction of HCl formed in the hydrolysis.

THE electrochemical reduction of chloro-silanes and -germanes has been studied[1–3] but the exact processes occurring are not yet clear. Dessy *et al.*[1] reported the formation of Si–H and Ge–H bonds in the reduction of Ph_3SiCl and Ph_3GeCl in 1,2-dimethoxyethane (DME) using a mercury cathode at $-3{\cdot}1$ and $-2{\cdot}8$ V respectively, *vs.* $AgClO_4$–Ag ($-2{\cdot}5$ and $-2{\cdot}2$ V *vs.* S.C.E.). Hengge *et al.*,[3] however, observed Si–Si bond formation in the electrolyses of Me_3SiCl under similar conditions but without control of the applied potential. Recently, Allred *et al.* have studied the electroreduction of Me_3SiCl[4] in MeCN. Platinum was used as the working, counter, and reference electrodes. The results were interpreted as a reversible electroreduction taking place at -1 V *vs.* the Pt reference electrode (which is assumed to be $+0{\cdot}6$ V more positive than S.C.E.[5]). The passivation of the electrode by Me_3SiO^- was demonstrated.[4]

Previously[6] we noted the important influence of water contained in the solvent, even at very low concentrations (10^{-3}—10^{-2} M); very fast hydrolysis of the halogenosilanes was found to occur when a nucleophilic agent such as hexamethylphosphoramide (HMPT) was added. We here

$$R_3SiCl + H_2O \xrightarrow{\text{HMPT}} R_3SiOH + HCl$$

report a re-examination of the electrochemical reduction of halogeno-silanes and -germanes in order to distinguish between the reduction and hydrolysis reactions.

The first experiment was carried out using Ph_3MCl (M = Si or Ge) which is less sensitive than Me_3SiCl towards hydrolysis. We determined the precise reduction potential of these halides and that of HCl (HCl is released by hydrolysis). In anhydrous solvents such as tetrahydrofuran (THF)

TABLE. Electrochemical results.[a]

Cathode	Solvent	Compound	$E_{1/2}$/V[b]	E/V applied	% Dimer[c]	% Hydride[c]
Hg	DME	HCl	−0·5			
Hg[d]	DME	Me_3SiCl	−0·5	75	28	
Hg	DME	Ph_3SiCl	−2·4	−2·6	42	1
Pt	MeCN	Ph_3SiCl		−0·5	0	
Hg	DME	Ph_3GeCl	−2·2	−2·4	86	3
Hg	DME	Ph_3GeBr	−2·0	−2·4	86	2
Pt	MeCN	Me_3SiCl		−0·5	0	
Hg	MeCN	Me_3SiCl		−0·5	0	

[a] Polarographic measurements were carried out in the 0·5—1·5 mM concentration range and controlled potential electrolyses in the 0·1—0·2 M concentration range. Water concentrations, determined by Karl Fischer titration, were in the 10^{-3}—10^{-2} M range. Controlled potential electrolyses were carried out in a Moinet's cell (C. Moinet and D. Peltier, *Bull. Soc. chim. France*, 1969, 690). All experiments were carried out under nitrogen in a glove box. The solvents THF and DME were refluxed and distilled over $LiAlH_4$, and MeCN over CaH_2, under nitrogen, before use. [b] The $E_{1/2}$ values were obtained *vs.* a THF saturated $Bu^n{}_4NI$, AgI–Ag reference electrode. They were corrected to S.C.E. by adding −0·4 V. [c] All products were isolated and chemically identified. [d] See ref. 3.

or DME, without a nucleophilic agent, the polarograms showed a single reduction wave. The $E_{1/2}$ results obtained are summarised in the Table. The use of linear sweep voltammetry to detect the presumed radical intermediate in this halide reduction was unsuccessful. The voltammograms showed a single cathodic peak at a potential corresponding to the $E_{1/2}$ value. A high degree of electrochemical irreversibility leads to an evaluation of the number of electrons used *via* coulometry. Controlled potential coulometric measurements were carried out at a potential value corresponding to the cathodic wave to give an average value of 1·2 mol. of electrons per mol. of initial halide. Exhaustive controlled potential electrolyses were carried out with a mercury pool cathode. The electrochemical results are given in the Table, the major product formed being the disilane or digermane.

However, the reduction peak potential reported for the reduction of Me_3SiCl in MeCN by Allred was more positive than ours. Furthermore, in DME, the voltammograms of Me_3SiCl (7×10^{-3} M) and HCl (4×10^{-3} M) were identical. We have repeated Allred's experiment using platinum electrodes and MeCN as solvent. Me_3SiCl gives, effectively, a reversible electroreduction voltammogram at the reported potential, but a solution of HCl in MeCN studied under the same conditions shows a similar voltammogram. Ph_3SiCl also exhibits a similar voltammogram, but the reduction peak at −0·4 V (*vs.* S.C.E.) increases with time and reaches a maximum when a nucleophilic agent such as HMPT is added. This behaviour corresponds to the reduction of HCl formed by hydrolysis. Ph_3GeBr, being difficult to hydrolyse, shows no peak in that potential range, but when HMPT is added the cathodic peak at −0·4 V appears with the corresponding anodic one. Thus the reversible voltammogram observed in the case of Me_3SiCl in MeCN corresponds to HCl reduction; Me_3SiCl is easily hydrolysed even with a very low concentration of water in the solvent.

Moreover, controlled potential electrolysis of Me_3SiCl in MeCN with platinum electrodes performed at −1 V *vs.* Pt (−0·4 *vs.* S.C.E.) shows gas evolution and the electrolysis current decreases rapidly to its residual value. Analysis by g.l.c. of the products obtained reveals no trace of $Me_3SiSiMe_3$. The same result was obtained on a mercury cathode. We note that $Me_3SiSiMe_3$ can be obtained[3] but only in low yields and with an uncontrolled potential.

We conclude that Me_3SiCl is a bad choice for electroreduction because of its great affinity for water. The peak at 1 V *vs.* Pt (−0·4 V *vs.* S.C.E.) corresponds to HCl reduction and the electrode passivation observed by Allred arises from the Me_3SiOH initially formed in the hydrolysis, and not from the $Me_3Si\cdot$ radical. Ph_3SiCl has a more obvious behaviour; its reduction takes place irreversibly at −2·4 V (*vs.* S.C.E.), very close to the solvent reduction value. This illustrates that halogenosilanes are poor one-electron acceptors; they are unsuitable substrates for reactions taking place by a one-electron transfer process.[7]

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