A RE-EXAMINATION OF THE ELECTROCHEMICAL REDUCTION OF HALOSILANES AND HALOGERMANES *

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(Received July 23rd, 1979)

Summary

The electrochemical reduction peaks previously observed at about —0.4 V vs. SCE in the case of chloro- or bromo-silanes and -germanes actually refer to reduction of HCl or HBr formed by hydrolysis arising from traces of water in the solvent. This hydrolysis is catalysed by nucleophilic solvents. The electrochemical reduction of halo-silanes and -germanes in aprotic solvents giving the corresponding disilanes and digermanes is shown to be an irreversible process taking place at a low potential (—2 to —2.5 V vs. SCE).

Introduction

The electrochemical reduction of chloro- or bromo-silanes and -germanes has been studied [1—4], but the results are not concordant and processes occurring are not clear. Dessy et al. [1] reported the formation of Si—H and Ge—H bonds by reduction of Ph_3SiCl and Ph_3GeCl in 1,2-dimethoxyethane (DME) using a dropping mercury cathode at —3.1 and —2.8 V, respectively, vs. $AgClO_4/Ag$ ($\sim$ —2.5 and —2.2 V vs. SCE); however, the products were not isolated, and were identified only by UV spectra. On the other hand, Hengge et al. [3], reported Si—Si bond formation in electrolysis of Me_3SiCl under similar conditions but without control of the applied potential.

Recently, Allred et al. studied the electroreduction of Me_3SiCl [4] in MeCN. Platinum was used as the working, counter, and reference electrode. Their results were interpreted as a reversible electroreduction taking place at —1 V vs. Pt reference electrode, (which is assumed to be +0.6 V more positive than SCE [4]). Passivation of the electrode by Me_3SiO^- was observed.

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* No reprints available.

Previously [5,6] we carried out polarography of halosilanes and we noted the important influence of water contained in all the solvents even at very low concentrations (1—10 mM). Thus very fast hydrolysis of halosilanes was found to occur when a nucleophile such as hexamethylphosphoramide (HMPT) was added to the solution:

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

As the solvents used for electrochemical studies (CH_3CN, DMF, MeOH, etc.) act as nucleophiles towards halo-silanes and -germanes [7,8], we have re-examined their electrochemical reductions in order to distinguish between reduction and hydrolysis.

Experimental

Chemicals

Most of the organosilicon and germanium compounds were synthesized by standard procedures, e.g. triphenylchlorosilane [12], and triphenylbromogermane [13]. Others were commercial products such as tripethylchlorosilane "Fluka purum", which was purified by distillation immediately before use. "Merck" acetonitrile was stirred with K_2CO_3, refluxed one day over CaH_2 and distilled under nitrogen immediately before use. DME and THF were of "Backer Analysed" Reagent" grade and were refluxed one day over $LiAlH_4$ and distilled under nitrogen immediately before use. The water concentration were determined by the Karl Fischer method, and found to be in the range 5—10 mM. Tetrabutyl-ammonium perchlorate (TBAP) was of "Fluka A.G. purum" grade, and was recrystallized from water and dried for one week over P_2O_5 in vacuum.

Electrochemical measurements

(a) Polarographic measurements. Data were obtained using conventional three electrode equipment. The reference electrode was n-Bu$_4$NI, AgI/Ag; a silver wire coated with silver iodide (produced by electrolysis) was placed in a tube closed by a sintered glass disk and filled with a saturated solution of n-Bu$_4$NI. A platinum wire anode and a dropping mercury cathode were used.

Polarograms were recorded using a Tacussel PRT 10-05 L potentiostat and a Tacussel UAP 3 polarograph with mechanical control of the drop time. All experiments were performed at room temperatures under nitrogen. The polaro-grams were determined using 4 mM of R$_3$MX in 20 ml of 0.1 M TBAP in 1,2-dimethoxyethane or 0.1 M TBAP in CH_3CN.

(b) Linear sweep voltammetry. Platinum wire anode and hanging mercury drop or platinum disk cathodes were used. The reference electrode was n-Bu$_4$NI$_{sat}$, AgI/Ag or a single Pt wire as used by Allred. Voltammograms were recorded using a GSTP 3 Tacussel instrument and recorded with a Tektronix oscilloscope R 5103 N single beam storage D 11.

(c) Controlled potential electrolysis. A Tacussel PRT 100-1X potentiostat with an associated Tacussel IG5-LN integrator was used. All experiments were performed at room temperature in a glove box under nitrogen. Mass electrolysis products were isolated from solution by extracting the residue
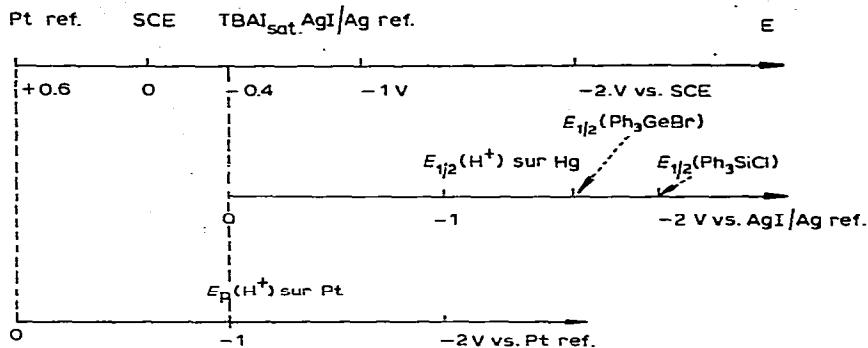
Fig. 1.

with diethyl ether (in which TBAP is insoluble); after removal of the ether, GLC and spectroscopic examination was carried out.

(d) Reference electrodes potential comparison. In order to compare our results with others, it was necessary to list the various reference electrode potentials used in a single diagram and this is done in Fig. 1. Some half wave potential values are also shown in Fig. 1. Additional potential values vs. SCE are given below.

Results

(a) Polarography

The first experiment was carried out using Ph_3MX compounds (M = Si or Ge; X = Cl or Br) which are less sensitive than Me_3SiCl towards hydrolysis. In

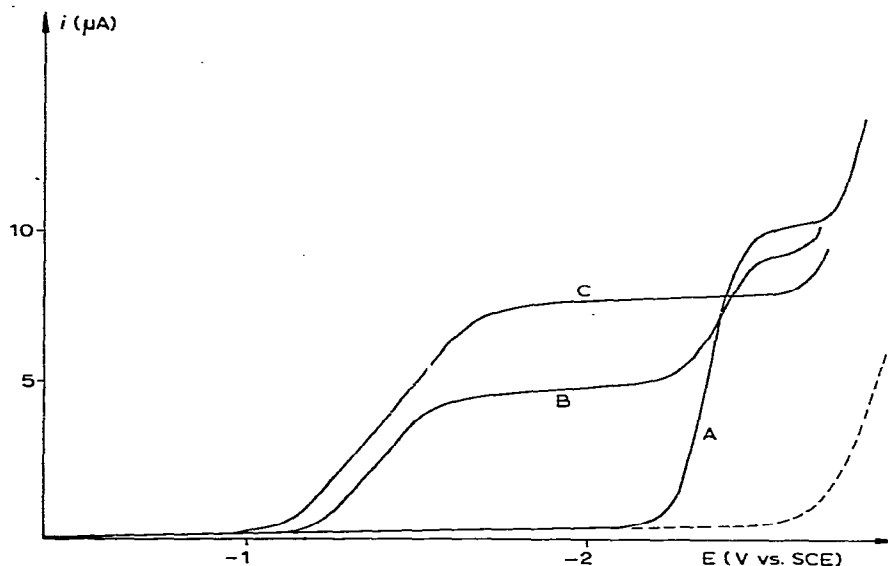Fig. 2. Polarograms of (— — — —) 0.1 *M* TBAP in DME; (A) 5 m*M* Ph_3SiCl in 0.1 *M* TBAP, DME solution; (B) 5 m*M* Ph_3SiCl and 1 m*M* HMPT in 0.1 TBAP, DME solution; (C) ~4 m*M* HCl in 0.1 TBAP, DME solution;

anhydrous solvents such as THF or DME without added nucleophiles, the polarogram shown in Fig. 2, consits of a single reduction wave in the low cathodic range (-2 to -2.5 V). But when a nucleophile such as HMPT is added an additional wave appears at -1.4 V in the polarographic curves for Ph_3SiCl and Ph_3SiBr. This second wave increases in height with time while the initial wave decreases. The polarograms for a solution of HCl and the same medium give the same reduction wave at -1.4 V; and this wave increases in height with the HCl concentration. The height of this wave reaches a maximum with an excess of Ph_3SiCl, and corresponds with an HCl concentration equivalent to that of the residual water in the solvent as a measured by Karl Fischer titration. The electrochemical results are summarized in Table 1.

(b) Linear sweep voltammetry

The voltammograms showed single cathodic peaks at potential corresponding to $E_{1/2}$ value with hanging mercury cathode. Fig. 3A shows the irreversible curves obtained.

The reduction peak potential at a platinum cathode reported for the reduction of Me_3SiCl in CH_3CN by Allred had a higher positive value than ours of a mercury cathode. But in DME, the voltammograms for Me_3SiCl (7 mM) and HCl (4 mM) were identical (Fig. 3B). Thus we repeated Allred's experiment with platinum electrodes and CH_3CN as solvent. Me_3SiCl does in fact give, a reversible electroreduction voltammogram at the reported potential (Fig. 3C) but HCl in CH_3CN under the same conditions shows a similar voltammogram (Fig. 3C). Ph_3SiCl also exhibits a similar voltammogram, but the reduction at -0.4 V (vs. SCE) increases with time and reaches a maximum when a nucleophile such as HMPT is added. This corresponds to the reduction of HCl formed by hydrolysis. Since Ph_3GeBr is less readily hydrolysable, it gives no peak in this potential range; but when HMPT is added the cathodic peak at -0.4 V appears along with the corresponding anodic one (Fig. 3D).

TABLE 1

ELECTROCHEMICAL RESULTS

Cathode	Solvent	Compound	$E_{1/2}$ (V) [b]	1 E_p (V) [c]	E [d]	Dimer [e] (%)
Pt	DME	HCl		-0.4		
Pt	DME	Me_3SiCl		-0.4		
Hg	DME	HCl	-1.4			
Hg	DME	Me_3SiCl	-1.4		75 [f]	28 [f]
Pt	CH_3CN	Me_3SiCl		-0.4	-0.5	0
Hg	CH_3CN	Me_3SiCl			-1.5	0
Hg	DME	Ph_3SiCl	-2.4		-2.6	42
Hg	DME	Ph_3GeCl	-2		-2.4	86

[a] Polarographic measurements were carried out in the 0.5—1.5 mM concentration range and controlled potential electrolysis in the 0.1—0.2 M concentration range. [b] The $E_{1/2}$ values were measured vs. n-Bu_4NI_{sat}, IAg/Ag reference electrode and corrected to SCE by adding -0.4 V (after ohmic drop correction). [c] The peak potentials were obtained vs. Pt reference and corrected to SCE by adding 0.6 V. [d] Controlled potential applied during electrolysis carried out in a Moinet cell [9] with the anodic and cathodic compartment separated by a sintered glass disk. [e] Ph_3Si—$SiPh_3$ and Ph_3Ge—$GePh_3$ precipitate out of the solution. [f] Value issue of ref. [3].
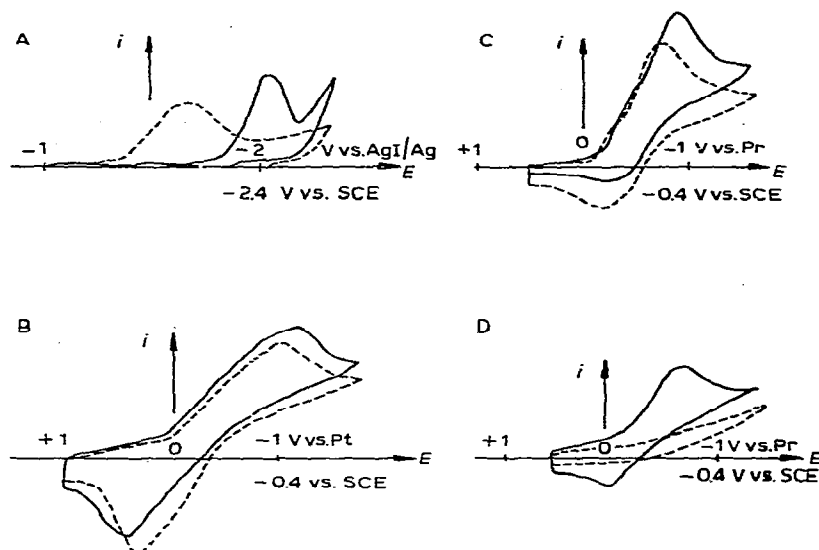
Fig. 3. A. Cyclic voltammograms of (————) Ph$_3$SiCl, (— — — —) Ph$_3$GeBr in 0.1 M TBAP in DME with a hanging mercury drop electrode and TBAI, AgI/Ag reference electrode. Scan rate 400 mV s^{-1}. B. Cyclic voltammograms of (————) Me$_3$SiCl, (— — — —) HCl in 0.1 M TBAP in DME, with platinum reference electrode. Scan rate 3 V s^{-1}. C. Cyclic voltammograms of (————) Me$_3$SiCl, (— — — —) HCl in 0.1 M TBAP in CH$_3$CN, with platinum working electrode and platinum reference electrode. Scan rate 2 V s^{-1}. D. Cyclic voltammograms of (— — — —) Ph$_3$GeBr and (————) Ph$_3$GeBr + HMPT in 0.1 M TBAP in CH$_3$CN solution, with platinum working electrode and platinum reference electrode. Scan rate 1.5 V s^{-1}.

(c) Controlled potential electrolysis

Gas is evolved during the controlled potential electrolysis of Me$_3$SiCl in CH$_3$CN with platinum electrodes performed at -1 V vs. Pt (-0.4 V vs. SCE) and the electrolysis current falls rapidly to its residual value. GLC analysis of the products only reveals traces of Me$_3$Si—SiMe$_3$. The same result was obtained with a mercury cathode. The mass spectrum showed a peak at 146, but exactly the same peak is given by Me$_3$SiCl alone. Thus Me$_3$Si—SiMe$_3$ is not formed when the electrolysis is performed with a controlled potential of -0.4 V. We note that Me$_3$Si—SiMe$_3$ can be formed [3], but only with an uncontrolled potential, and undoubtedly at a high cathodic potential.

Discussion

From the results it is clear that the reversible voltammograms observed in every case correspond to reduction of HCl. Me$_3$SiCl is very easily hydrolysed and even the trace of water contained in the solvent the Me$_3$SiOH and HCl are produced.

The reversible observed reduction by Allred was in fact the reversible reduction of HCl [15]. There is always a slight amount of water in solvents used for electrochemistry even after purification, and its concentration is in the same range as that of the halides used in polarographic or voltammetric measurements. The hydrolysis of the halides causes an increase in conductivity [10] and can

give rise to formation of hydrogen in electrochemical reduction [11].

We conclude that Me_3SiCl is a bad choice for electroreduction studies because of its great ease of hydrolysis. Ph_3SiCl or Ph_3GeBr are better and in the absence of added nucleophiles their reduction take place irreversibly at about —2 V vs. SCE.

The radical $Me_3Si^{\cdot}$ was not formed at low cathodic potential (−0.4 V vs. SCE) since no $Me_3Si–SiMe_3$ was obtained. The passivation of the electrode by Me_3SiO^-, reported by Allred [4], probably arises from the reaction of Me_3SiOH (formed by hydrolysis of Me_3SiCl) with the electrode. The $Me_3Si–SiMe_3$ observed by Henge must be produced at a high cathodic potential [3] by an irreversible process. Work is currently in progress to establish the mechanism and the yields of products formed in the electrochemical reduction of halo-silanes and -germanes under anhydrous conditions.

Our findings show that halosilanes have a low ability to accept electron and confirms the observation made by Felkin et al. [14] that chlorosilanes are unsuitable substrates for reactions taking place by a one electron transfer process.

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