ELECTROCHEMICAL REDUCTION OF TRIORGANOHALO-SILANES AND -GERMANES *

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Summary

The electrochemical reduction of triorganohalo-silanes and -germanes in 1,2-dimethoxyethane has been investigated by polarography, cyclic voltammetry, controlled potential coulometry, and macroscale electrolysis. The reduction of the silicon compounds exhibits a single irreversible wave. The polarograms for the germanium compounds exhibit two irreversible waves. The second wave shifts to more anodic potentials with addition of phenol or acetic acid. Dimer (i.e. disilanes or digermanes) are the main product of macroscale electrolysis in aprotic solvent but the hydrides are the principal products in protic solution.

The results are interpreted in terms of the coexistence of two separate processes. The first involves a one electron reduction followed by dimerization of the radical. At higher cathodic potential a two electron charge transfer step occurs to form an anion, which in aprotic solvents reacts with the starting halogeno compound to form dimer, and in protic solutions gives the hydride.

Introduction

Studies of the electrochemical reduction of chloro-silanes and -germanes have been described [1—3], but the products and reduction mechanism were not clearly established.

We previously noted the important influence of the presence of water in the solvents, even at very low concentrations [5,6]: a very fast hydrolysis of halogenosilanes occurs when a nucleophilic agent is added to the solution, and the reversible reduction peak observed at —0.4 V vs. SCE is actually due to HCl

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* No reprints available.

formed by hydrolysis of the halides [7]. We also found that electrochemical reduction of these halides is irreversible and that the dimer yields are greater than hydride yields. Thus all studies must be carried out in anhydrous solvents, and without nucleophilic solvents which accelerate the hydrolysis.

In the case of organogermanium compounds the most comprehensive study was reported by Bottei et al. [4]. The compounds studied were Ph_3GeF, Ph_3GeCl, Ph_3GeBr and Ph_3GeI in 0.1 M TBAP/1,2-dimethoxyethane. The major product isolated and identified by infrared spectroscopy was hexaphenyldigermoxane with traces of other compounds (triphenylgermanium hydroxide triphenylgermanium hydride and hexaphenyldigermanium). In order to obtain more information about the electroreduction mechanism of those halogeno compounds, we have reexamined this work. The study described below of the electrochemical behaviour of some halogeno-silanes and -germanes has indicated the existence of an anionic process and established reduction yields of the main products formed by mass electrolysis in protic or aprotic solutions.

Experimental

Chemicals

DME and THF, Baker Analysed reagent, were refluxed for one day over $LiAlH_4$ and distilled under nitrogen immediately before use. The water concentration, determined by the Karl Fisher method was in the range 5—10 mM.

Tetrabutylammonium perchlorate (TBAP) "Fluka A.G. purum" was crystallized from water and dried under vacuum over P_2O_5.

Most of the organo silicon and germanium compounds were synthesized by standard procedures [8—10], and purified by recrystallization.

Electrochemical measurements

The reference electrode, a n-Bu$_4$NI$_{sat.}$, AgI/Ag system is a silver wire coated by silver iodide obtained by electrolysis. This wire is placed in a tube closed by a sintered glass disk and filled with a saturated solution of n-Bu$_4$NI in THF (or DME). It is connected to the polarographic cell through a salt bridge filled with 0.1 M n-Bu$_4$NClO$_4$ solution and closed with another sintered glass disc. Its potential is lower than the SCE potential by —0.44 Volts. A platinum wire anode and dropping mercury electrode, or hanging mercury drop, or mercury pool cathode were used. Controlled potential coulometry and electrolysis were carried out in a Moinet's cell [11] with anode and cathode compartments separated by a sintered glass disc.

Polarograms were recorded using a Tacussel PRT 10-0.5 L potentiostat and a Tacussel UAP 3 with mechanical control of drop time.

Voltammograms were generated using a GSTP 3 Tacussel and recorded with a Tektronix oscilloscope R 5103 N single beam storage D11.

A Tacusell PRT 100-1X potentiostat with an associated Tacussel IG5-LN integrator was used in controlled potential electrolyses. All experiments were performed at room temperature under nitrogen in a glove box.

A large uncompensated resistance (20000 ohm) was present in all the measurements. Correction for ohmic potential losses was made mathematically.

After precipitates had been filtered off, the mass electrolysis products were

isolated from solution by removing the DME on a rotary evaporator, extracting the residue with diethyl ether (in which TBAP is insoluble), and evaporating off the solvent. Separation was by thin layer chromatography and identification by mixed melting point, IR and NMR and Mass spectra, which were identical to the spectra of authentic samples. The yields observed are relative to the initial concentration of depolarizer.

Results

a) Polarography of halosilanes

In anhydrous solvents such as THF or DME, the polarograms show a single reduction wave at low cathodic range (~ -2 V). The shape of the polarogram depends on the depolarizer concentration, and a maximum is observed when $Co \geqslant 5$ mM.

Table 1 summarises the $E_{1/2}$ potentials for various halogeno-silanes. To study the effect of protic media upon the polarographic wave, a large amount of phenol was added to a polarographic solution (concentration ratio $PhOH/Ph_3SiX = 10$), no change of the height of the diffusion current was observed. The narrowness of the half wave potential range as X is varied is noteworthy.

b) Polarography of halogermanes

Table 1 lists the $E_{1/2}$ potentials for various halogeno-germanes. The polarograms of halogermanes present two cathodic waves. The second wave is very close to the solvent reduction value; its height is in the same range as that of the first. Fig. 1 shows the effect of adding phenol (or acetic acid) to a Ph_3GeBr solution; the new wave does not change with increase in the phenol concentration but its position depends on the acidity of the proton donor. Similar results were obtained with Ph_3GeCl.

The polarogram of hexaphenyl digermane shows a single reduction wave at -2.3 V, and addition of acetic acid does not change its position.

TABLE 1

POLAROGRAPHIC DATA

Silicon compounds	$E_{1/2}$ (V)	Germanium compounds	$E_{1/2}^1$ (V)	$E_{1/2}^2$ (V)
Ph_3SiF	-2.15	Ph_3GeF	-1.85	-2.3
Ph_3SiCl	-1.95	Ph_3GeCl	-1.75	-2.3
Ph_3SiBr	-1.93	Ph_3GeBr	-1.60	-2.3
$Ph_2MeSiCl$	-2.06	$(pCF_3Ph)_3GeCl$	-1.82	
Ph_2HSiCl	b	$(nBu)_3GeCl$	-1.50	
$PhMeHSiCl$	b	$Ph_2MeGeBr$	-1.35	
Me_3SiCl	b	1-$NpPhMeGeBr$	-1.40	-1.85 [a]
		$Ph_3GeGePh_3$	-2.30	

Polarographic measurements were carried out in the 0.5—1.5 mM concentration range. The $E_{1/2}$ value were measured versus $nBu_4NI_{sat.}$. AgI/Ag reference electrode and are corrected for ohmic loss.
[a] Reduction potential of naphthalene. [b] The small amount of water present in the polarographic solvent causes too rapid hydrolysis of this chlorosilane.
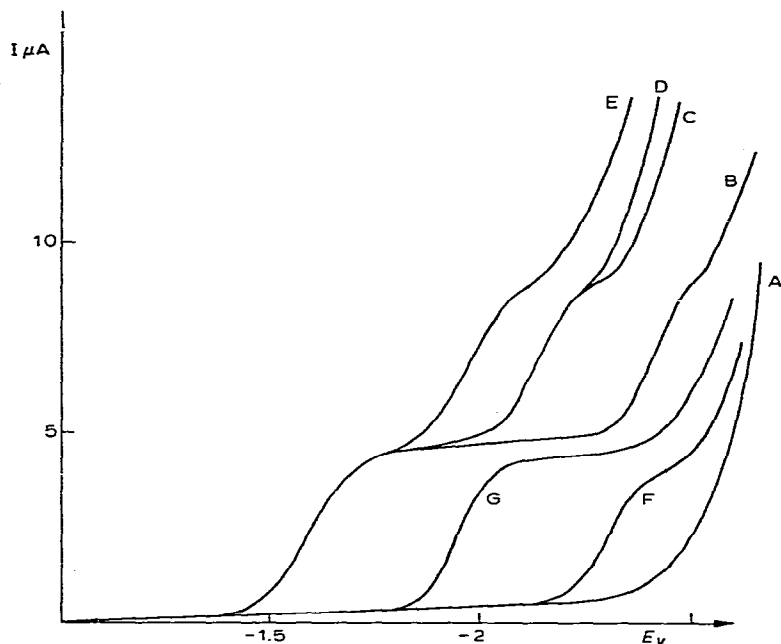
Fig. 1. Polarograms of: A 0.1 M TBAP, DME solution; B, 3.7 mM Ph$_3$GeBr; C, 3.7 mM Ph$_3$GeBr + 15 mM PhOH; D, 3.7 mM Ph$_3$GeBr + 66 mM PhOH; E, 3.7 mM Ph$_3$GeBr + 16 mM CH$_3$COOH; F, Ph$_3$Ge—GePh$_3$ (Sat.); G, 3 mM Ph$_3$SiCl. (B—G in 0.1 M TBAP, DME solution).

Controlled potential coulometry

The high degree of electrochemical irreversibility enables evaluation of the number of electrons used at each polarographic step (n_e) via coulometry. Controlled potential coulometric measurements on the plateau portion of the first wave give an average value of $n = 1.2 \pm 0.2$ Faraday/mol in aprotic solution. (The unprecision in this value is the result of the large background current contribution in electrolysis at high cathodic potential with a large mercury pool working electrode).

When phenol is added the number of electrons per mole rises to ~1.8 ± 0.3 F/mol for the halogermanes but remains around 1.2 ± 0.3 F/mol for halo-silanes.

Voltammetry

Although the anion radicals of phenylsilanes containing both hydrogen atoms and methyl groups attached to silicon have been characterized by electron spin resonance [12] or cyclic voltammetry [13], use of linear sweep voltammetry, to detect the presumed radical intermediate in the reduction of halo-silanes and -germanes was unsuccessful.

Ph$_3$SiX (with X = Cl, Br) exhibits a single voltammetry peak at ~—2 V. This cathodic peak is not coupled to a corresponding anodic peak even at the fastest scanning rates employed (400 mV/s).

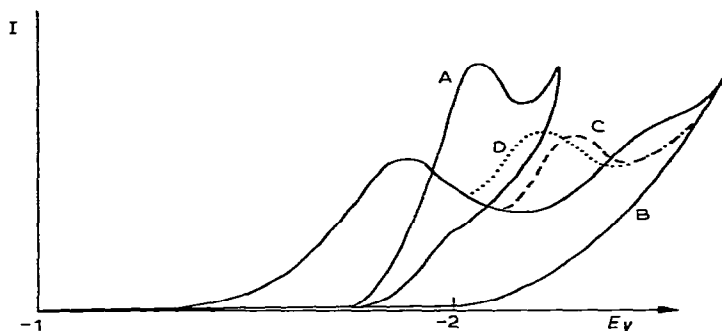Fig. 2 shows a typical cyclic voltammogram of Ph$_3$GeBr. Two irreversible

Fig. 2. Cyclic voltammograms of A (————), Ph₃SiCl; B (————), Ph₃GeBr; C (- - - - - -), Ph₃GeBr + PhOH; D (· · · · · ·) Ph₃GeBr + CH₃COOH in 0.1 M TBAP, DME solution with hanging mercury drop cathode and n-Bu₄NI, AgI/Ag reference electrode. Scan rate 400 mV s⁻¹.

cathodic peaks appear, at $\sim$—1.7 V and $\sim$—2.4 V, repectively, which correspond to the observed polarographic cathodic process. Addition of phenol (or acetic acid) to that solution causes a shift of the second cathodic peak which appears at $\sim$—2.1 V, (or $\sim$—2 V with acetic acid). The same result is observed with Ph₃GeCl.

Exhaustive electrolysis

The determination of the yields of dimer and hydride in this electrochemical reaction was one of our principal objectives. Exhaustive controlled potential electrolysis were carried out with a mercury pool cathode. The results are given in Table 2.

In the case of halosilanes, a large amount of disiloxane was always found ($R^t \geqslant 50\%$) and this is easily explained by the great affinity of silicon for oxygen. Except for this compound, in the absence of a proton donor the major product is the dimer (disilane). To help in establishing the electrode reaction mechanism, large scale electrolytic reductions were carried out in the presence of phenol. Experiment 2 (in Table 2) shows that it completely changes the products: the hydride (silane) is the primary product (25%), and secondary products such as Ph₃SiOPh (25%) appear as well as the disiloxane previously observed (experiment 2). Ph₃SiOPh must be formed during the electrolysis since no reaction occurs when Ph₃SiCl and PhOH are stirred for one day at room temperature.

In the case of halogermanes, the digermanoxane yields are lower than 15%, and the main product in aprotic solvents is the digermane. When phenol (or acetic acid) is added to the mixture, the change noted above is again observed, and germane is the main product. Moreover use of a PhOD/PhOH mixture in experiment 11 (Table 2) gives rise to Ph₃GeH and Ph₃GeD, characterised by their IR spectra.

The addition of a radical hydrogen donor such as Ph₃CH and dihydroanthracene (DHA) does not cause a large increase of hydride yields.

The electrolysis of a Ph₃GeBr/Me₃SiCl mixture at —1.6 V leads to substantial formation of Ph₃Ge—SiMe₃, but at —1.3 V only Ph₃Ge—GePh₃ is obtained
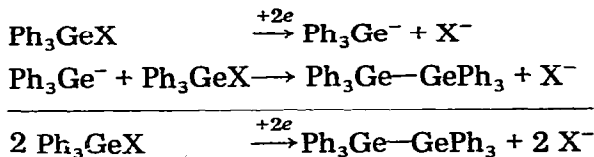
TABLE 2

ELECTROLYSIS DATA

| Experiment number	Compound	E^a (V)	Compound[b] added	Yield[c] dimer(%)	Yield[c] hydride(%)	Other compounds
1	Ph$_3$SiCl	−2.2		42	1	(Ph$_3$Si)$_2$O
2	Ph$_3$SiCl	−2.2	PhOH	0	25	Ph$_3$SiOPh (25%) / {(Ph$_3$Si)$_2$O
3	Ph$_3$SiCl	−2.2	Ph$_3$ClH	35	6	(Ph$_3$Si)$_2$O
4	Ph$_3$SiBr	−2.2	Ph$_3$ClH	29	1	(Ph$_3$Si)$_2$O
5	Ph$_3$GeF	−2.2	Ph$_3$ClH	50	5	{(Ph$_3$Ge)$_2$O (12%) / Ph$_3$GeOH (25%)
6	Ph$_3$GeF	−2.2	PhOH	0	33	{(Ph$_3$Ge)$_2$O / Ph$_3$GeOH
7	Ph$_3$GeCl	−2.0		86	3	(Ph$_3$Ge)$_2$O[d]
8	Ph$_3$GeCl	−2.0	PhOH	0	60	(Ph$_3$Ge)$_2$O[d]
9	Ph$_3$GeBr	−2.0		86	1	(Ph$_3$Ge)$_2$O[d]
10	Ph$_3$GeBr	−2.0	PhOH	0	36	(Ph$_3$Ge)$_2$O[d]
11	Ph$_3$GeBr	−2.0	PhOH/PhOD	0	23	Ph$_3$GeD (10%)
12	Ph$_3$GeBr	−2.0	CH$_3$COOH	0	35	(Ph$_3$Ge)$_2$O
13	Ph$_3$GeBr	−2.0	Ph$_3$CH	85	2	(Ph$_3$Ge)$_2$O
14	Ph$_3$GeBr	−2.0	DHA	not isolated.	6	(Ph$_3$Ge)$_2$O
15	Ph$_3$GeBr	−1.6	Me$_3$SiCl	19	d	Ph$_3$GeSiMe$_3$ / (Ph$_3$Ge)$_2$O[d]
16	Ph$_3$GeBr	−1.3	Me$_3$SiCl	30	d	(Ph$_3$Ge)$_2$O[d]
17	1-NpPhMeGeCl	−1.7		68	1	(1-NpPhMeGe)$_2$O[d]
18	1-NpPhMeGeCl	−1.7	PhOH	0	67	(1-NpPhMeGe)$_2$O[d]
19	(pCF$_3$Ph)$_3$GeCl	−2.0		71	6	(pCF$_3$Ph)$_3$Ge$_2$O (2%)
20	(pCF$_3$Ph)$_3$GeCl	−2.0	PhOH	0	34	(pCF$_3$Ph)$_3$Ge$_2$O (2%)
21	(nBu)$_3$GeBr	−1.8		50	2	(nBu)$_3$Ge$_2$O[d]
22	(nBu)$_3$GeBr	−1.8	PhOH	0	25	(nBu)$_3$Ge$_2$O[d]
23	Ph$_2$MeGeBr	−1.5		83	1	(Ph$_2$MeGe)$_2$O[d]
24	Ph$_2$MeGeBr	−1.5	PhOH	0	32	(Ph$_2$MeGe)$_2$O[d]

Controlled potential electrolyses were carried out in the 0.1—0.2 M conc. range. ^{a} Applied potential during electrolyses versus n-Bu$_4$NI, AgI/Ag reference electrode. ^{b} Additional compound at 0.5 M concentration. (DHA = 0.10-dihydroanthracene). ^{c} Products isolated and chemically identified. ^{d} Trace.

(experiments 16 and 17). Furthermore an attempt to reduce Ph_3Ge—$GePh_3$ at high cathodic potential gave only a very small yield of Ph_3GeH (~5%).

Discussion

In the light of the results we make the following comments:
a) The half wave potential values do not vary much with the nature of the halogen. They fall in the narrow potential range of —1.9 to —2.2 V for triphenyl halosilanes, and —1.6 to —1.85 V for triphenyl halogermanes.
b) All the electrochemical processes are irreversible [7].
c) The effect of addition of proton donor is very clear; it produces the Si—H or Ge—H bond. This good evidence for the existence of an anionic intermediate. The effect of addition of Me_3SiCl leads to the same conclusion, which is also confirmed by the shift to a more anodic value of the second wave observed in the polarographic reduction of Ph_3GeX when PhOH (or CH_3COOH) was added.
d) The electrochemical behaviour of the halo-silanes and -germanes are very similar: the only difference is the second wave, very close to the solvent reduction, observed in the case of the halogermanes. We assume that the same wave exists with halosilanes, but is masked by the solvent reduction.

From the above observations we propose the following mechanism. Two

SCHEME 1

FIRST WAVE

processes forming dimers are in competition with each other in aprotic solvents, viz. radical dimerization and nucleophilic attack of the anion on the initial halide. The electron number used per mole (~1.2 F/mol), the dimer formation and the narrowness of the polarographic potential reduction range for these compounds suggest a mechanism involving radical anion formation during the determining step, followed by breaking of the M—X bond in the radical dimerization. This intermediate radical, formed irreversibly, is not detectable by linear sweep voltammetry and has a very short life. The insolubility of the dimer formed may reduce its lifetime.

The second polarographic wave, observed only in the reduction of Ph_3GeX, corresponds to transfer of two electrons, producing the anion. Without proton donor, the anion reacts with the initial Ph_3GeX (or Ph_3SiX) giving digermane (or disilane). The overall reduction process again requires one Faraday per mole of initial halide since a chemical reaction involving two molecules of halides fol-

lows the transfer of two electrons corresponding to the anion formation:

$$Ph_3GeX \xrightarrow{+2e} Ph_3Ge^- + X^-$$

$$Ph_3Ge^- + Ph_3GeX \longrightarrow Ph_3Ge\text{---}GePh_3 + X^-$$

$$2\,Ph_3GeX \xrightarrow{+2e} Ph_3Ge\text{---}GePh_3 + 2\,X^-$$

This hypothesis is confirmed by the use of weak acids which can trap the anion. Trapping with phenol (or acetic acid) gives a good yield of germane, and the number of Farafays per mole increase to 1.8 in the case of halogermanes. But under the same conditions the value of $n_e \sim 1, 2$ is obtained with the halosilanes. This is explained by the formation of Ph_3SiOPh, which was isolated in experiment 2 (Table 2); in that case after abstraction of the proton by the anion, the nucleophile PhO^- attacks a second molecule of Ph_3SiX. The following coupled reactions then occur, giving a ratio of two electrons used per two molecules of halides consumed:

$$Ph_3Si^- + PhOH \rightarrow Ph_3SiH + PhO^-$$

$$PhO^- + Ph_3SiX \rightarrow Ph_3SiOPh$$
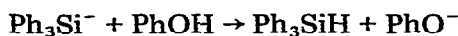
No similar product (Ph_3GeOPh) is isolated with halogenogermanes and the number of Faradays used per mole is about 1.8.

Moreover the shift to more anodic value of the second wave, observed in the polarographic reduction curves of Ph_3GeX, is a proof of the existence of formation of an anion assisted by protonation. It should be noted that the position of this second wave depends on the acidity of the proton donor, and that the wave height does not change with increase of the proton donor concentration. Zuman [14] describes the theoretical case of a second cathodic wave shifting to more anodic potential with decreasing pH.

On the other hand, the addition of Me_3SiCl, known to be a good nucleophilic trap, produces substantial amount of $Ph_3Ge\text{---}SiMe_3$ along with the $Ph_3Ge\text{---}GePh_3$ in the electrolysis of Ph_3GeBr at -1.6 V. A competition between both electrophiles takes place for reaction with the anion. But when the macroelectrolysis of the same mixture is performed at -1.3 V the only product is $Ph_3Ge\text{---}GePh_3$. This is a good evidence for the coexistence of both processes: the one electron step corresponding to the radical duplication at low cathodic potential and a two electron transfer at higher cathodic potential giving an anionic species which reacts with the electrophiles present (Me_3SiCl and Ph_3GeX).

To test the possibility of the existence of radical intermediates, we examined the effect of adding hydrogen atom donors such as Ph_3CH or 1,10-dihydroanthracene (DHA). The smallness of the increase of the hydride yields rules out hydrogen abstraction from DME postulated by Dessy et al [1]. This suggests that the neutral free radical $Ph_3M^{\cdot}$ does not exist alone in the solution; it is certainly associated with X very close to the electrode, but its dimerization occurs more rapidly than its reaction with a radical trapping species present in the solution.

Anion formation by reduction of $Ph_3Ge\text{---}GePh_3$ formed in the solution by radical dimerization has been previously proposed [17], and $Ph_3Ge\text{---}GePh_3$

presents a single reduction wave at high cathodic potential ($\sim$—2.3 V), very close to the second wave potential observed in the reduction of Ph_3GeX. But this proposal must be rejected for three reasons:

a) The second wave has the same height as the first in the reduction of Ph_3GeX and both waves increase with the halide concentration. If this second wave is that of the dimer formed during the electrolysis, its height would be very small, since the concentration of this dimer is very low.

b) The wave height of a saturated solution of Ph_3Ge—$GePh_3$ is only about 2 μA, while the second reduction wave height of Ph_3GeBr can be greater than 6 μA.

c) In the reduction of Ph_3Ge—$GePh_3$ the wave at (—2.3 V) does not shift when weak acid is added.

Thus the similarity of the positions of the half wave potential of this second wave of Ph_3GeX reduction and the single wave of Ph_3Ge—$GePh_3$ is fortuitous, and such an intermediate can be rejected.

Conclusion

All our experimental results indicate that in the aprotic solvent used triorganohalo-silanes and -germanes (R_3MX) undergo two consecutive electrode reductions involving radical anion and anion, repectively. Both processes give dimers, the first by radical dimerization following the one electron reduction step, and the second by nucleophilic attack of the anion on the initial halide following the two electron transfer. That anion can be trapped with a proton donor (Cf. Scheme 1).

The occurence of two different electrochemical processes in a narrow potential range has been also proposed by Mazzochin et al. [15] for the reduction of triphenyltin chloride in acetonitrile. They observed similar behaviour, although the first polarographic wave appeared at very low cathodic potential. These compounds seem to accept electrons more easily than halogeno-silanes and -germanes, which are poor one-electron acceptors [16].

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