Journal of Organometallic Chemistry, 49 (1973) 389–407
© Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

ELECTROCHEMISTRY OF TRIPHENYLGERMANIUM HALIDES*

R. J. BOCZKOWSKI** and R. S. BOTTEI***
Department of Chemistry, University of Notre Dame, Notre Dame, Indiana 46556 (*U.S.A.*)
(Received July 12th, 1972)

SUMMARY

The electrochemistry of the triphenylgermanium halides in 1,2-dimethoxyethane has been investigated by means of DC polarography, cyclic voltammetry and controlled-potential coulometry. The reduction of Ph_3GeF was a pseudo-reversible process involving the transfer of only one-half a Faraday per mole. The reduction of both Ph_3GeCl and Ph_3GeBr were irreversible single-electron processes resulting in the formation of a germyl radical. The Ph_3GeI reduction exhibited both a kinetically controlled and an irreversible diffusion-controlled process. Anodic processes were also observed for Ph_3GeCl, Ph_3GeBr, and Ph_3GeI. These were interpreted as being mercury dissolution processes resulting in the formation of a mercurous halide salt and the germonium ion, Ph_3Ge^+.

INTRODUCTION

In recent years electrochemical techniques have been applied to the study of organometallic compounds. These techniques are helpful in characterizing, identifying or isolating reactive intermediates that may play a part in the chemical reactions of organometallic species. Electrochemical techniques also aid in detailing and unravelling mechanistic pathways to provide further insight into the chemical reactivity of organometallic species.

Organic compounds of the Group IVA elements of silicon, germanium, tin and lead have been investigated electrochemically to varying extents. Organotin compounds[1–13] have been most studied, followed by organosilicon[1,14–27], organolead[1,28–31], and organogermanium[1,20,21,34–36] compounds. Interest in organogermanium chemistry as evidenced by publications from these laboratories[32,33] has prompted the authors to investigate further the electrochemical behavior of organogermanium compounds.

The first electrochemical study involving organogermanium compounds was reported by Foster and Hooper in 1935[34]. They electrolyzed triphenylgermyl sodium

---

[*] Presented at the 162nd National Meeting of the American Chemical Society, Washington, D.C., September 17, 1971.

[**] Present address: Armtex, Inc., Pilot Mountain, N.C. 27041 (U.S.A.)

[***] Author to whom correspondence should be addressed.

in liquid ammonia and produced both triphenylgermane and hexaphenyldigermane at a mercury or a platinum anode suggesting the following:

$$\begin{tikzcd}[row sep=small] & & Ph_3GeH \\ Ph_3Ge^- \arrow[r, "-e"] & {[Ph_3Ge\cdot]} \arrow[ur, "H^+"] \arrow[dr] & \\ & & \tfrac{1}{2}Ph_3GeGePh_3 \end{tikzcd}$$

Further study of the electrochemical behavior of organogermanium compounds was not reported until thirty years later when Curtis and Allred[20] employed polarography and cyclic voltammetry in conjunction with ESR studies of 4-(trimethylgermyl)biphenyl and 4,4′-bis(trimethylgermyl)biphenyl in *N*,*N*′-dimethylformamide. Reduction of these compounds was determined to be reversible from cyclic voltammetric data and an anion radical was formed of sufficient stability to permit observation of an ESR spectrum. The polarographic $E_{\frac{1}{2}}$ was used to calculate the energy of the lowest unoccupied molecular orbital which corresponded well with results obtained from ESR data.

An analogous study was undertaken by Allred and Bush[21] of 1,4-bis(trimethylgermyl)benzene, 4,4′-bis(trimethylgermyl)biphenyl, 1,4-bis(trimethylgermyl)-naphthalene, 4,4‴-bis(trimethylgermyl)terphenyl in dimethylformamide. All of these compounds except the first gave a reversible one-electron reduction, as was confirmed by small amplitude a.c. polarography. In addition all of the above polyphenyl compounds except the last gave an irreversible two-electron reduction wave corresponding to the formation of the dianion radical. Again the calculated energy of the lowest unoccupied molecular orbital was essentially the same when calculated from either ESR data or $E_{\frac{1}{2}}$ values.

The most comprehensive study of organogermanium compounds was reported by Dessy and coworkers[1,35]. The compounds studied were Ph_3GeCl, Ph_2GeCl_2, $Ph_3GeGePh_3$, $Ph_3SnSeGePh_3$, and $Ph_4C_4GePh_2$ in 0.1 *M* tetrabutylammonium perchlorate/1,2-dimethoxyethane and the following indicates the proposed electrochemical reaction sequence for each.

$$Ph_3GeCl \xrightarrow[-2.8\ V]{e} [Ph_3Ge\cdot] \xrightarrow{solvent} Ph_3GeH$$

$$Ph_2GeCl_2 \xrightarrow[-2.6\ V]{2e} Ph_2GeH_2$$

$$Ph_3GeGePh_3 \xrightarrow[-3.5\ V]{2e} 2Ph_3Ge^-$$

$$\begin{tikzcd}[row sep=small] & Ph_3SnSe^- + [Ph_3Ge\cdot] \arrow[r, "solvent"] & Ph_3GeH \\ Ph_3SnSeGePh_3 \arrow[ur, "e", "-2.4\ V"'] \arrow[dr, "2e", "-2.9\ V"'] & & \\ & Ph_3SnSe^- + Ph_3Ge^- & \end{tikzcd}$$

$$Ph_4C_4GePh_2 \xrightarrow[-3.2\ V]{2e} (Ph_4C_4GePh_2)^{2-} \qquad \text{(unstable)}$$

All of the above half-wave potentials refer to a Ag/10^{-3} *M* $AgClO_4$ reference electrode.

Russian workers[36] investigating the electroactivity of organic compounds of Group IVA elements in various solvents have included polarographic data on Et_3GeBr. The Et_3GeBr reduction in 0.1 *M* LiCl/dimethylsulfoxide appeared to be diffusion-controlled while in 0.1 *M* LiCl/*N*,*N*′-dimethylformamide it appeared to have some kinetic complication. The half-wave potential reported for Et_3GeBr in 0.1 *M* LiCl/*N*,*N*′-dimethylformamide was −1.80 V *vs.* SCE.

One of the more elusive organogermanium species thought to be involved as an intermediate in certain chemical reactions is the germonium ion species, R_3Ge^+. A number of attempts have been made to detect the existence of a germonium ion[37–41], but only two reports[37,41] have provided some positive evidence for its existence. All attempts to detect Ph_3Ge^+ have been unsuccessful[38–40]. Rochow and Allred[37], however, have suggested that the hydrolysis of dimethyldichlorogermane in water may proceed via $(CH_3)_2Ge^{2+}$. The most recent evidence for a germonium ion was provided by the aluminum chloride catalyzed reaction of ferrocene with bis(*N*,*N*′-dimethylamino)dichlorogermane and with tetrakis(*N*,*N*′-dimethylamino)germane[41]. Based on the products formed in these reactions a non-classical intermediate was proposed in which a germonium ion is π-bonded to a cyclopentadienyl ring of ferrocene. The present work on the electrochemical behavior of triphenylgermanium halides also provides some evidence for the existence of a germonium ion intermediate, as shall be discussed.

EXPERIMENTAL

Chemicals

Most of the organogermanium compounds were synthesized according to standard procedures[42–45]. Purification was achieved by multiple recrystallization and vacuum sublimation procedures. Reported preparations of trimethylgermanium perchlorate[46], triphenylsilicon perchlorate[47], trimethyltin perchlorate[48], and triphenyltin perchlorate[49] were adapted to synthesize triphenylgermanium perchlorate. Triphenylgermanium bromide and anhydrous silver perchlorate reacted metathetically in 1,2-dimethoxyethane. Silver bromide was filtered off and the solvent evaporated leaving a white residue. After recrystallization from 1,2-dimethoxyethane the material apparently still containing traces of impurities thermally decomposed in the range 171–176°. An IR spectrum (see Fig. 10 and discussion) of this material confirmed it to be triphenylgermanium perchlorate.

1,2-Dimethoxyethane (DME) (Ansul Company) was purified by distillation from $LiAlH_4$ in a nitrogen atmosphere. Tetrabutylammonium perchlorate (G. F. Smith Company) was used directly after vacuum drying overnight at 140°. While there are a number of references[50 and 51] detailing procedures for preparing electrochemically pure tetrabutylammonium perchlorate (TBAP), they have not been directed toward recovering TBAP from spent solutions which may contain a variety of impurities. The following procedure was found to be quite satisfactory for this purpose in the present study. Polarographic solutions containing no metal ions were concentrated to about 20% of their original volume. Solutions containing metal ions were not concentrated. Water added to this solution precipitated the TBAP which was filtered and washed several times with water. The TBAP was placed in a Soxhlet extraction apparatus and extracted with diethyl ether overnight. The TBAP was then redissolved in a minimum volume of 1,2-dimethoxyethane (DME) and added to a beaker containing activated alumina (20 g per 200 ml solution). After stirring and allowing to stand for an hour, the alumina was filtered off and the TBAP was again precipitated with water, filtered and washed. After drying the TBAP showed no detectable electroactive impurities.

Electrochemical measurements

Data were obtained using conventional three-electrode operational amplifier circuitry[52-55]. Polarography and cyclic voltammetry were performed using a Heath model EUW-201 polarograph[56] and i–E curves were displayed on either a Hewlett–Packard 7004 X,Y recorder or a Hewlett–Packard 120 B oscilloscope. A Hewlett–Packard 3300A function generator supplied the triangular wave voltage function necessary for cyclic voltammetry. Controlled-potential electrolyses were performed using a high voltage potentiostat previously described[57]. Coulometry performed simultaneously with controlled-potential electrolysis was accomplished by recording the IR drop across a standard resistance in series with the electrochemical cell and manually integrating the resultant $i-t$ curve. A polarographic cell similar to one described by Dessy *et al.*[1] was employed and General Electric lamp nitrogen ($>99.999\%$) was used without further purification for degassing cell solutions. An $AgNO_3$ (saturated), TBAP (0.1 M)/Ag reference electrode[58,59] and a platinum counter electrode were used with either a dropping mercury electrode ($m=1.90$ mg/sec, $t=3.92$ sec at 25° in 0.1 M TBAP at a mercury column height of 59.2 cm with an open circuit), a hanging mercury drop electrode (Metrohm E-410, Brinkmann Instruments), or a mercury pool electrode. All experiments were performed at ambient temperatures ($25\pm1°$) in a Metalab H-521 stainless steel glove box maintained with a nitrogen atmosphere.

A large uncompensated resistance was present in all the electrochemical measurements due to the high specific resistivity (2740 ohms·cm^{-1}) of the solvent–

TABLE 1

POLAROGRAPHIC DATA OF THE TRIPHENYLGERMANIUM HALIDES

Compound	$E_{\frac{1}{2}}$	$E_{\frac{3}{4}}-E_{\frac{1}{4}}$[a]	I[b]	*Process*[c]
Ph_3GeF	-3.15 ± 0.01 V	0.06 ± 0.01 V	1.28 ± 0.08	Cathodic, d.c.
Ph_3GeCl	-2.85	0.09	2.76 ± 0.06	Cathodic, d.c.
Ph_3GeBr	-0.14	0.09	2.48 ± 0.09	Anodic, d.c.
	-2.63	0.09	2.53 ± 0.06	Cathodic, d.c.
Ph_3GeI	-0.36	0.09	2.3 ± 0.2	Anodic, d.c.
	-1.9	0.08	2.8 ± 0.1	Cathodic, k.c.
	-2.45			Cathodic, d.c.

[a] In each case the value of $E_{\frac{3}{4}}-E_{\frac{1}{4}}$ was the same as the value of the slope of an E *vs.* log $i/(i_d-i)$. [b] The diffusion current constant (I) is defined as $I=i/(Cm^{\frac{2}{3}}\cdot t^{\frac{1}{6}})$ where i is the instantaneous current at the end of the drop life (μA), C is the bulk concentration (mmoles/l), m is the mercury flow rate (mg/sec), and t is the drop life (sec). [c] d.c.—diffusion-controlled, the instantaneous diffusion current was found to be proportional to the square root of the mercury column height; k.c.—kinetically-controlled, the instantaneous diffusion current was independent of the mercury column height.

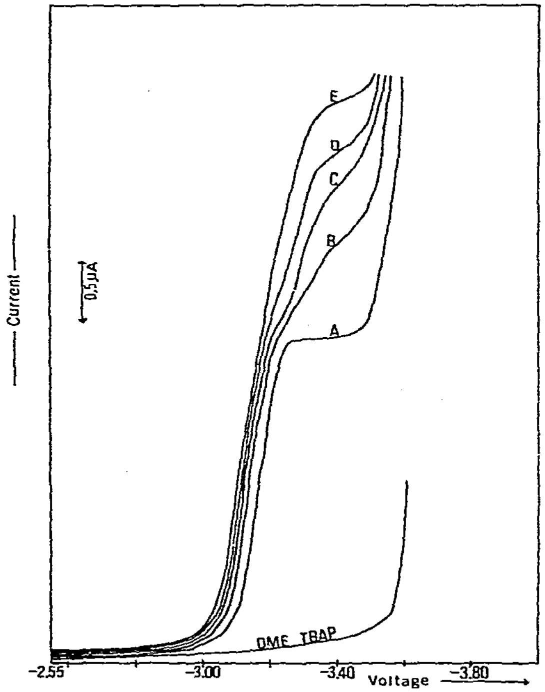
electrolyte system, 0.1 *M* TBAP in DME. Compensation for ohmic potential losses was made mathematically. For polarography a method involving the measurement of the $E_{\frac{3}{4}}-E_{\frac{1}{4}}$ parameter of a reversible system was used to calculate the uncompensated cell resistance ($\approx 10^4$ ohms) as described by Thomas and Schaap[60]. Once this resistance is known, corrections can be applied to the nominal voltage recorded and such corrections were found to be reproducible to ±10 mV over the entire polarographic concentration range employed. For cyclic voltammetry of irreversible electrochemical processes the method of Roffia and Lavacchielli[61] was applied.

Mass electrolysis products were isolated from solution by first removing DME on a rotary evaporator, extracting the residue with diethyl ether (in which TBAP is insoluble) and evaporating the diethyl ether. The products pressed into KBr discs were identified by their infrared spectrum (4000–250 cm^{-1}) obtained with a Perkin–Elmer 457 infrared spectrophotometer. Mixed melting points were also obtained to confirm product identity.

RESULTS

Polarography

Table 1 summarizes the polarographic data for the triphenylgermanium



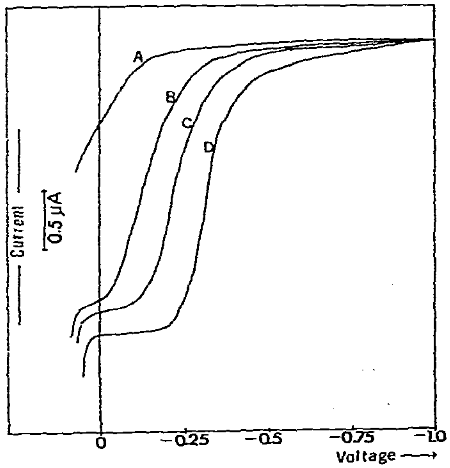


Fig. 1. The effect of the addition of tert-butanol to a 1.21 × 10^{-3} *M* Ph_3GeF solution. Polarogram (A), no tert-butanol added; polarograms (B) to (E), increasing amounts of tert-butanol added.

Fig. 2. Polarograms of a 3.68 × 10^{-4} *M* Ph_3GeCl solution with no water added (A) and with increasing amounts of water added (B) to (D).

halides in 0.1 *M* tetrabutylammonium perchlorate/1,2-dimethoxyethane (TBAP/DME). The reduction of Ph_3GeF was significantly different from that of the other halides. A $E_{\frac{3}{4}}-E_{\frac{1}{4}}$ value[62] [Tomes reversibility criterion[63]] of 0.06 V for Ph_3GeF suggests electrochemical reversibility or quasi-reversibility. All other electrochemical processes listed appear to be irreversible. Additionally, the diffusion current constant for Ph_3GeF is half the value of the others where a constant of about 2.5 reflects a single electron transfer process[64,65].

Ph_3GeF demonstrates further differences if water or alcohol (methanol, ethanol, or tert-butanol) is added to the polarographic solution. Figure 1 shows the effect of adding tert-butanol to a Ph_3GeF solution and similar results are obtained with water, methanol or ethanol. A new polarographic wave appears on the plateau portion of the original wave (A) and grows larger [(B) to (D)] while shifting to more positive potentials until a single wave is formed, (E). Wave (E) does not appear to shift significantly with further additions of water or alcohol. The $E_{\frac{1}{2}}$ value for this new wave is -3.15 V, $E_{\frac{3}{4}}-E_{\frac{1}{4}}$ is 0.10 V, and the wave is diffusion-controlled and exactly double the height of (A) yielding a diffusion current constant of 2.56. While a quantitative study of the addition of water or alcohol was not attempted, it was observed that about 3 mmoles of water was required to produce wave (E) when added to a solution containing 0.02 mmoles of Ph_3GeF. Larger amounts of alcohol were required to produce the same effect, while the amounts required followed the pattern $(CH_3)_3COH > C_2H_5OH > CH_3OH$.

Ph_3GeCl was amenable to polarographic study in the concentration range of $0.1\text{–}4 \times 10^{-3}$ *M*. Beyond 4×10^{-3} *M* the reduction wave exhibited a maximum of the first kind[66]. Addition of water, methanol, ethanol or tert-butanol to a Ph_3GeCl solution produced polarograms similar to those shown in Fig. 2. Curve (A) represents the case in which no water was added. No polarographic wave is apparent and the current increase reflects the normal anodic background discharge. Addition of water

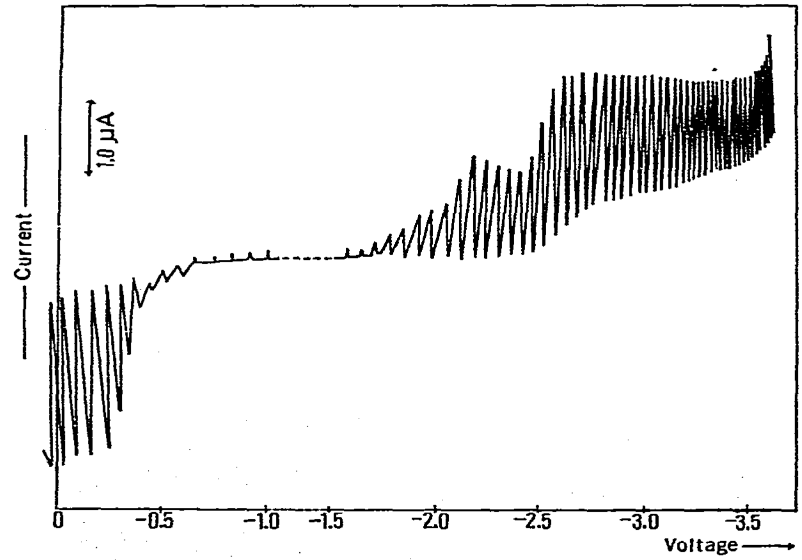


Fig. 3. Polarogram of a 5.36×10^{-4} *M* Ph_3GeI solution. Mercury column height at 50.9 cm.

produces a wave which shifts to more cathodic potentials (B) to (D) as more water is added. A quantitative study of the effects of adding water or alcohol was not attempted. The cathodic wave at -2.85 V shows no change when water was added. The anodic wave produced is diffusion-controlled and has a $E_{\frac{3}{4}}-E_{\frac{1}{4}}$ value of 0.09 V and a diffusion current constant of 2.89.

Ph_3GeBr at concentrations greater than the working range of 0.1–3×10^{-3} M exhibited a cathodic wave with a maximum of the first kind[66]. An anodic wave for this compound appeared without addition of water or alcohol.

Figure 3 shows a typical polarogram obtained of Ph_3GeI in the concentration range 0.1–3×10^{-3} M. Above 3×10^{-3} M a maximum of the first kind is exhibited in the last cathodic wave. The first cathodic wave appears to be kinetically controlled as shown in Table 2 and possesses an unusual wave shape.

TABLE 2

MERCURY COLUMN HEIGHTS AND INSTANTANEOUS DIFFUSION CURRENTS FOR A 0.305 mM SOLUTION OF Ph_3GeI

h (*cm*)	*Anodic wave* $i_d: h^{-\frac{1}{2}}$ ($\mu A\cdot cm^{-\frac{1}{2}}$)	*Cathodic wave* 1 $i_d(\mu A)$	*Cathodic wave* 2 $i_d: h^{-\frac{1}{2}}$ ($\mu A\cdot cm^{-\frac{1}{2}}$)
58.2	0.138	0.70	0.108
66.3	0.135	0.65	0.118
73.8	0.133	0.65	0.119
81.4	0.133	0.69	0.115

Beginning at about -1.5 V the current increases in a gradual slope until about -2.0 V at which point the current rises more rapidly and peaks at about -2.1 V. Both cathodic waves are dependent on the Ph_3GeI concentration and a diffusion current constant calculated to include both cathodic waves gave a value of 2.8. The diffusion current constant for the second cathodic wave alone was 1.5.

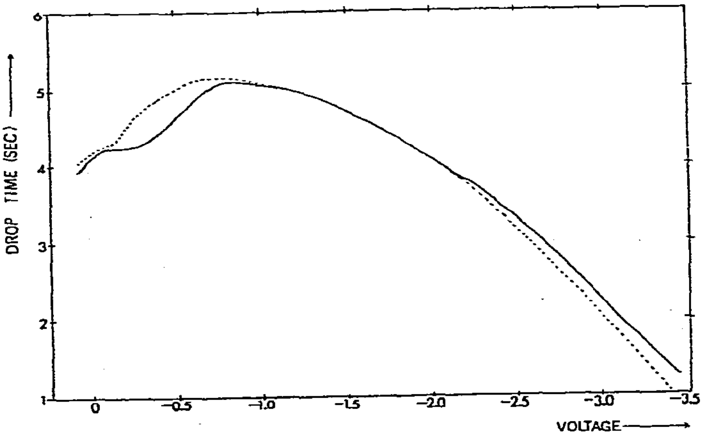


Fig. 4. Electrocapillary curves, DME/TBAP (– – –) and a 1.73×10^{-3} M Ph_3GeI solution (——), mercury column height 47.5 cm.

Addition of water to a Ph_3GeI solution caused the anodic and second cathodic wave to decrease in height while the first cathodic wave increased. A new anodic wave appeared at 0.95 V which increased as more water was added. An identical wave could be produced in DME/TBAP with hydriodic acid which suggests that this wave is due to the oxidation of mercury in the presence of iodide ion.

Figure 4 shows the electrocapillary curves for a DME/TBAP solution alone and for a solution containing Ph_3GeI. A slight depression is observed in the region of potentials associated with the anodic process. A similar depression is observed in the electrocapillary curves for a solution of Ph_3GeBr and for a solution of Ph_3GeCl with small amounts of water added.

Cyclic voltammetry

Ph_3GeF exhibited a single organogermanium related voltammetric peak at -3.4 V. This cathodic peak is not coupled to a corresponding anodic peak even at the fastest scanning rates employed (50–100 V/sec). Because of the presence of uncompensated resistance the relationship of the cathodic peak current to the sweep rate could not be determined. However, because of the polarographic behavior, it is not likely that this process is a simple irreversible one. When water was added to the Ph_3GeF solution the voltammetric peak increased in height but it remained the only organogermanium related peak present throughout the range of scans employed.

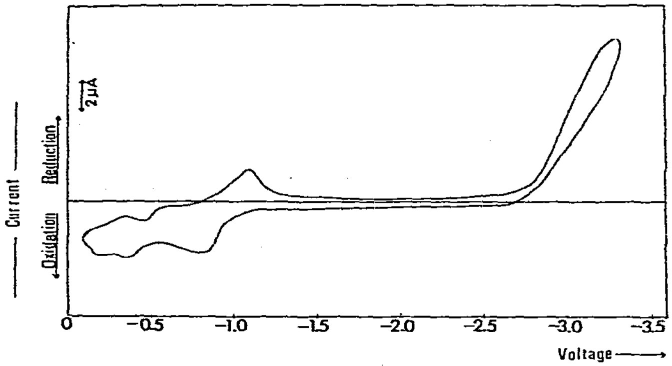


Fig. 5. Cyclic voltammogram of a 1.96×10^{-3} *M* Ph_3GeCl solution. Multicycle steady-state pattern, sweep rate unspecified.

Figure 5 shows a typical cyclic voltammogram for Ph_3GeCl. The cathodic peak at -3.3 V represents the only organogermanium related process while the peaks below -1.2 V are attributed to mercury–chloride ion processes. Since the cathodic peak appeared to be irreversible from the polarographic work, the method of Roffia and Lavacchielle[67] was employed to determine the transfer coefficient (αn) and the potential-dependent rate constant for the electron transfer (kE). The value obtained for αn was 0.60 and for kE was 2×10^{-32} cm·sec^{-1} (referenced to 0 V in this system). As a check on these values the polarographic method of Koutecky[68] as modified by Oldham and Parry[69] was adopted. The values of αn and kE calculated from polarographic data were 0.59 and 3×10^{-32} cm·sec^{-1}, respectively. This good correspondence between independent methods suggests that the peak is indeed irreversible.

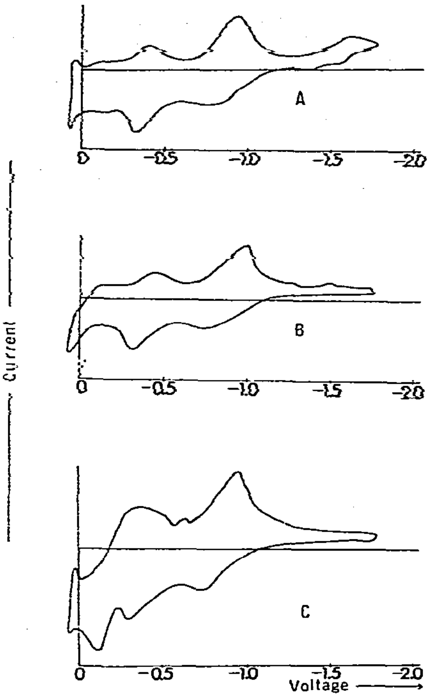


Fig. 6. Cyclic voltammograms of mercurous chloride (A), mercurous chloride with Ph_3GeCl (B) and mercurous chloride, Ph_3GeCl and added water (C). Sweep rate 396 $mV \cdot sec^{-1}$, HMDE area 1.38 mm^2, multicycle steady-state pattern.

Figure 6 demonstrates that the peaks below −1.2 V are mercury–chloride ion related and also shows the effect of water added to a Ph_3GeCl solution. Voltammetric Curve (A) obtained for a solution of mercurous chloride alone does not change when Ph_3GeCl is added [curve (B)]. The four peaks will increase in height if the scan includes the cathodic peak at −3.3 V. Since this cathodic process involves the splitting of a Ge–Cl bond (see below), the increase in peak heights is attributed to the release of chloride ion in solution. Curve (C) is obtained using the same solution used for Curve (B) but with the addition of a small amount of water. In this instance a new anodic peak and a new cathodic peak appear. The new cathodic peak will not appear unless the voltage scan sweeps through the new anodic peak first. This indicates that these two processes are related in some way. These peaks do not represent a reversible couple, however, since the polarographic data clearly shows the anodic process to be irreversible. Additionally their peak potentials approximately corrected for uncompensated resistance showed large shifts with increasing scan rates, which also indicates that the two peaks do not represent a reversible couple[70].

The cyclic voltammetric behavior of Ph_3GeBr is very similar to Ph_3GeCl. An apparently irreversible cathodic peak appears at −2.9 V which corresponds to the observed polarographic cathodic process. The values of αn (0.59) and kE (2×10^{-29} $cm \cdot sec^{-1}$) were essentially the same whether calculated from cyclic voltammetric or polarographic data. An anodic peak appears at −0.1 V whose kinetic parameters were also the same whether calculated from cyclic voltammetric or polarographic data, $(1-\alpha)n$ (0.58) and kE (3×10^{-2}). After sweeping through the anodic peak, a new cathodic peak appears at about −0.3 V. Again these peaks, while related to each other, are not related as a reversible couple.

Cyclic voltammograms of Ph_3GeI are shown in Fig. 7. The first sweep shows peaks at −0.2, −2.2 and −2.7 V corresponding to the three polarographic waves. A cathodic peak at −0.5 V is related to the anodic peak at −0.2 V and is observed only

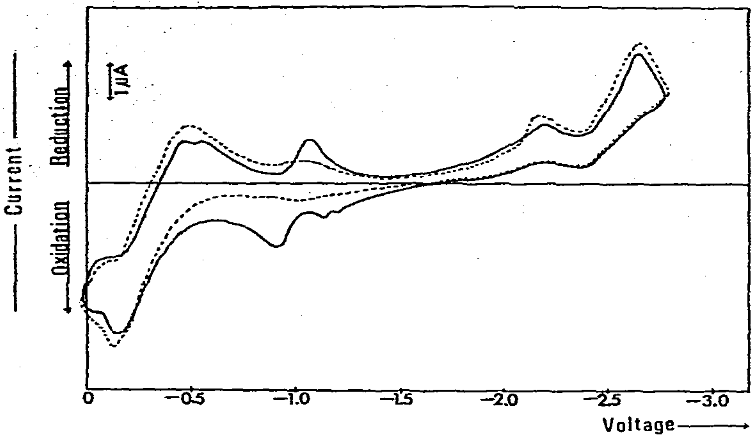


Fig. 7. Cyclic voltammograms of a 8.94×10^{-4} *M* Ph_3GeI solution. First sweep (- - -) and second sweep (——), sweep rate 169 $mV\cdot sec^{-1}$, HMDE area 1.38 mm^2.

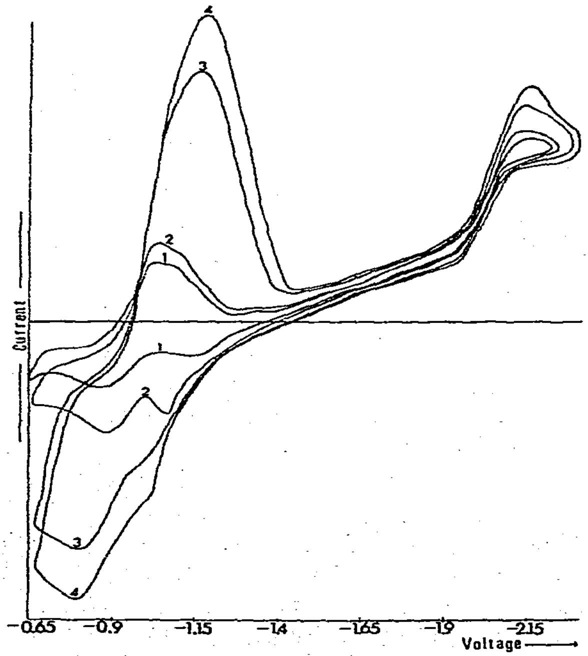


Fig. 8. Cyclic voltammograms for a Ph_3GeI solution. Sweep 1 at 235 $mV\cdot sec^{-1}$, sweep 2 at 336 $mV\cdot sec^{-1}$, sweep 3 at 1.00 $V\cdot sec^{-1}$, and sweep 4 at 1.68 $V\cdot sec^{-1}$, multicycle steady-state pattern.

after sweeping through the anion peak first. The anodic and cathodic peaks at -0.9 and -1.1 V, respectively, are mercury–iodide ion related peaks. The double anodic peaks at -1.2 V are related to the kinetically controlled reduction occurring at -2.2 V as can be more clearly observed in Fig. 8. Figure 8 further demonstrates the kinetic influence on the peak at -2.2 V. The peak height changes only slowly with increasing sweep rate and is not proportional to the square root of the sweep rate as are normal diffusion-controlled processes[70]. Calculation of $(1-\alpha)n$ and kE for the anodic process occurring at -0.2 V yielded values of 0.59 and 9×10^{-4} $\text{cm}\cdot\text{sec}^{-1}$, respectively.

Cyclic voltammetry of the various organogermanium halides was also performed at a platinum button electrode. The halides which had exhibited a polarographic and cyclic voltammetric anodic process yielded no anodic process at a platinum electrode.

Controlled-potential coulometry

The results of controlled-potential reduction of the various organogermanium halides is given in Table 3. In order to achieve reasonable precision with the coulometer employed it was necessary to electrolyze 25–50 ml of solution containing 10^{-4} to 10^{-3} mole of sample. Identification of isolated products was accomplished by infrared spectroscopy. Ultraviolet spectroscopy as employed by Dessy *et al.*[1] for product identification did not provide positive enough characterization of the various compounds involved. Indeed, many compounds had identical UV spectra.

TABLE 3

CONTROLLED-POTENTIAL COULOMETRIC RESULTS FOR CATHODIC PROCESSES OF THE TRIPHENYLGERMANIUM HALIDES

Compound	*Faradays per mole*	*Products isolated*
Ph_3GeF	0.65 ± 0.06	$(Ph_3Ge)_2O$, $(Ph_3Ge)_2$
Ph_3GeF with water	$1.4\ \pm0.4$	$(Ph_3Ge)_2O$
Ph_3GeCl	1.07 ± 0.06	Ph_3GeOH, $(Ph_3Ge)_2O$ Ph_3GeH, $(Ph_3Ge)_2$
Ph_3GeBr	0.95 ± 0.08	Ph_3GeOH, $(Ph_3Ge)_2O$ Ph_3GeH, $(Ph_3Ge)_2$
Ph_3GeI	$1.3\ \pm0.3$	$(Ph_3Ge)_2O$

Coulometry for Ph_3GeF appeared to be susceptible to rather large errors. This problem was due to a large background current contribution arising during electrolysis at -3.4 V using a large mercury pool working electrode. The reduction of Ph_3GeF without added water appears to be about a half-a-Faraday per mole as is also suggested by the polarographic behavior. The actual value of 0.65 strongly suggests a two-thirds-of-a-Faraday per mole reduction. However, in view of the polarographic results, error in coulometric determination and the possibility of trace amounts of water affecting the reduction process, the result of a half-a-Faraday per mole is considered the more likely result.

The coulometry of Ph_3GeF reduced with added water is notably imprecise and ranges between 1–1.8 Faradays per mole. While the problem of contributory background current exists in this instance as well, there is also the problem of adding sufficient water to be able to generate the process indicated in Fig. 1 as wave (E). For the more concentrated solutions used in controlled-potential analysis the added water may be as much as 3% of the total solvent volume. Certainly the nature of the solvent is altered and perhaps also the Ph_3GeF reduction process.

The major product isolated for Ph_3GeF reduction both with and without added water was hexaphenyldigermoxane. Some hexaphenyldigermane was also isolated for Ph_3GeF reduction without added water. In this instance an electrolyzed solution of Ph_3GeF in a stoppered flask was allowed to stand for a number of hours in the dry box during which time hexaphenyldigermane precipitated from solution. This latter fact suggests that certain chemical reactions are continuing after the electrolysis.

The reductions of both Ph_3GeCl and Ph_3GeBr appear to be well-defined single electron processes. The same products were isolated for both these compounds. The major product was hexaphenyldigermoxane and occasionally traces of the precursor of this compound, triphenylgermanium hydroxide, was observed. Small amounts of triphenylgermanium hydride were observed in the electrolysis of more concentrated organogermanium solutions. The use of highly concentrated solutions (0.01–0.05 *M*) and higher current densities produced hexaphenyldigermane as the major product.

The reduction of Ph_3GeI yielded 1.3 Faradays per mole. Since this reduction

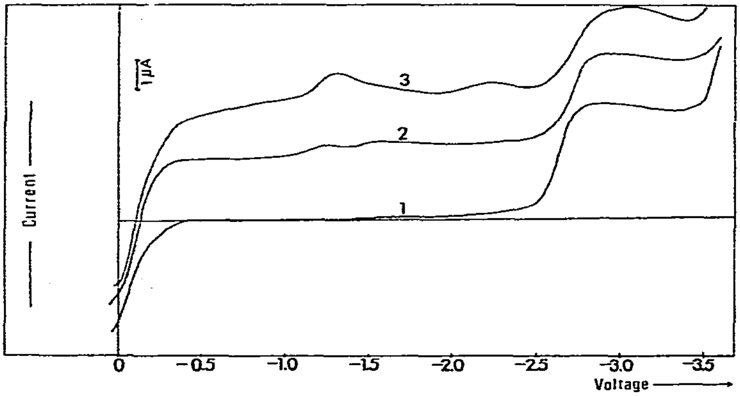


Fig. 9. Polarograms of a 1.33×10^{-3} *M* Ph_3GeBr solution before (1) and during (2 and 3) anodic electrolysis.

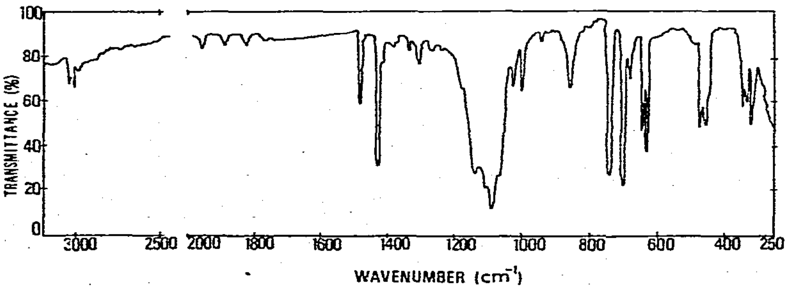


Fig. 10. Infrared spectrum of triphenylgermanium perchlorate.

includes both the cathodic waves observed in Fig. 3, it is possible that the kinetic process complicates the reduction so that it is not an overall single electron process. Exhaustive electrolysis on the plateau portion (−2.3 V) of the kinetic wave caused both cathodic waves to disappear. This indicates that the kinetic wave and the last cathodic wave are related through a common species. The only product ever isolated from the reduction was hexaphenyldigermoxane.

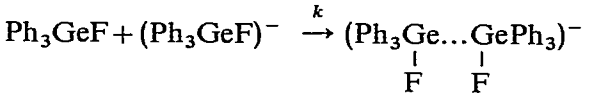
Anodic controlled potential coulometry was applied to Ph_3GeCl (with added water), Ph_3GeBr, and Ph_3GeI. The coulometric results were less than one but greater than a half-a-Faraday per mole in each case. Complete electrolysis was seldom achieved because the anodic process would shift to more anodic potentials and into a region with increasing background current contribution as the electrolysis proceeded. This is demonstrated in Fig. 9 for Ph_3GeBr. A developing cathodic process at −0.2 V can also be noted. This cathodic process is the same as observed in a cyclic voltammogram after sweeping first through the anodic process. Product analysis in each case yielded a mercurous halide salt and a compound giving an IR spectrum identical to that shown in Fig. 10. If controlled-potential anodic electrolysis was followed by cathodic electrolysis at −0.5 V, hexaphenyldigermoxane was the isolated product.

DISCUSSION

Cathodic process

Ph_3GeF. While the data on Ph_3GeF are insufficient to allow a definitive mechanism to be proposed, certain reaction steps can be postulated to account for some of the electrochemical behavior. The following steps appear to explain much of the polarographic and cyclic voltammetric data.

$$Ph_3GeF \overset{e}{\rightleftarrows} (Ph_3GeF)^-$$



$$Ph_3GeF + (Ph_3GeF)^- \xrightarrow{k} (Ph_3\underset{F}{\underset{|}{Ge}}\ldots\underset{F}{\underset{|}{Ge}}Ph_3)^-$$

The reduction of a Ph_3GeF molecule followed by reaction with another Ph_3GeF molecule to form some intermediate species would yield an overall half-a-Faraday per mole reduction. Since the polarographic behavior of Ph_3GeF suggests electrochemical reversibility while the cyclic voltammetric behavior does not, a pseudoreversible reduction is invoked to satisfy both conditions. The chemical reaction following reduction would have to be relatively fast because the cyclic voltammetric data indicate that no anodic peak is coupled to the cathodic peak even at the fastest scan rates employed. Restated in kinetic terms this implies that the second-order chemical reaction following reduction completed within the time scale of the experiment would have to have a rate constant greater than $10^5\ l \cdot mole^{-1} \cdot sec^{-1}$.

The exact nature of the intermediate is not known. A germanium–germanium single electron bonded species is postulated above based on the reactants involved. It is obvious that such an intermediate would undergo further reactions. Thus, for instance, the hexaphenyldigermane precipitated from an electrolyzed solution on standing would have to have originated from the intermediate species. Also, hexaphenyldigermoxane isolated immediately after electrolysis would have to originate from the intermediate species. In this case water absorbed while handling the solution for product isolation or peroxides formed in the ether solution could interact with the intermediate to eventually form hexaphenyldigermoxane. During cyclic voltammetric scans, peaks due to the presence of fluoride ion are also in evidence and, therefore, the intermediate must rapidly decompose to release fluoride ion.

The appearance of a new polarographic wave with the addition of water or alcohol suggests involvement of the intermediate. If, for example, water interacted with Ph_3GeF, the original wave would be changed in some manner. Since neither the half-wave potential nor wave height of the original wave are affected by the addition of water, this interaction presumably does not occur. On the other hand, if water interacted with the reduced species, $(Ph_3GeF)^-$, the chemical reaction following reduction would be hindered. It would then be expected that the original wave would increase in height as more Ph_3GeF became available for reduction. This, however, does not occur. A more satisfactory explanation would be for water or alcohol to react with the intermediate or some species derived from the intermediate. This reaction could take the form of some protonation reaction since the amount of water or alcohol required seems to decrease approximately in proportion to the increasing acidity of the additive. In addition, the involvement of an acid–base equilibrium reaction would account for the shifting of the growing wave to more anodic potentials, as more of a weak acid was added.

Precedents for this type of reaction can be found in the literature. Billon[71] observed that the second polarographic wave in the oxidation of phenothiazine perchlorate in acetonitrile would shift to more cathodic potentials as water was added. This wave represented the oxidation of a product produced in the first oxidation. The behavior with added water was interpreted as interaction of water with this first formed product. Zuman[72] describes the theoretical case of a second cathodic wave shifting to more anodic potentials with decreasing pH. This case involves an initial reduction to form an electro-inactive product whose subsequent protonation then allows further reduction to occur.

Ph_3GeCl and Ph_3GeBr. The electrochemical behavior of both Ph_3GeCl and Ph_3GeBr appears to be very much the same and, thus, the following mechanism is proposed for both.

$$Ph_3GeX \xrightarrow{e} Ph_3Ge\cdot + X^- \quad (X = Cl, Br)$$

$$Ph_3Ge\cdot \xrightarrow{DME} Ph_3GeH$$

$$2\ Ph_3Ge\cdot \longrightarrow (Ph_3Ge)_2$$

$$Ph_3GeH + \text{peroxide} \longrightarrow Ph_3GeOH$$

$$2\ Ph_3GeOH \longrightarrow (Ph_3Ge)_2O + H_2O$$

The first step is an irreversible single-electron transfer resulting in the formation of a triphenylgermyl radical. The oxidation of this radical was not observed at the fastest cyclic scan rates indicating either that the radical had undergone rapid chemical reaction or that the oxidation of a germyl radical to a germonium ion does not occur in the potential range of the solvent/electrolyte system. The former interpretation is probably correct since Dessy and co-workers failed to detect a germyl radical during the reduction of Ph_3GeCl monitored using ESR spectroscopy[1].

Reaction steps subsequent to the reduction represent a variety of reactions postulated on a basis of the products observed. Dessy *et al.* have indicated that hydrogen abstraction from solvent is the principal reaction pathway of the germyl radical[1]. The present work, however, indicates that by increasing the organogermanium halide concentration and, thereby, the current density during electrolysis, hexaphenyldigermane can be made the principal product. Hydrogen abstraction and coupling are typical radical reactions[73] and the occurrence of both is further evidence for the presence of a germyl radical intermediate.

At lower organogermanium halide concentrations hexaphenyldigermoxane was observed to be the principal product. Triphenylgermanium hydroxide presumably is first formed since hexaphenyldigermoxane is formed by the intermolecular reaction of triphenylgermanium hydroxide species[74,75]. It is not apparent that triphenylgermanium hydroxide could be formed in some direct radical reaction. Some secondary chemical reaction, therefore, must occur involving a product of the radical reaction. The most likely prospect is a secondary reaction of triphenylgermanium hydride which has known reducing properties[32,76–78]. It is possible that the hydride could react with a peroxide formed by autoxidation of the ether, DME, to eventually produce triphenylgermanium hydroxide. Peroxides form readily in DME/TBAP when exposed to air and can be observed polarographically. Since the isolation of reduction products involved some handling outside the glove box, it is probable that peroxides formed in solution during this time.

Ph_3GeI. A total mechanism for Ph_3GeI cannot be postulated because of an incomplete knowledge of the phenomenon relating to the kinetic process. The unusual polarographic wave shape of the kinetic process cannot be explained from the data obtained. The double anodic peaks observed in the cyclic voltammogram only after sweeping through the kinetic peak is also difficult to explain. Further work utilizing a wide variety of solvents would be necessary to unravel this process.

There is, however, certain evidence which permits a tentative description of the electrochemical behavior to be made and the following mechanism is proposed.

Normal reduction: $Ph_3GeI \xrightarrow{e} Ph_3Ge\cdot + I$

Kinetic process: $Ph_3GeI + H_2O \rightleftharpoons (Ph_3GeIH)^+ + OH^-$

$(Ph_3GeIH)^+ + OH^- \xrightarrow{e} Ph_3Ge\cdot + I^- + H_2O$

Excess water: $Ph_3GeI + OH^- \longrightarrow Ph_3GeOH + I^-$

$I^- \xrightarrow[Hg]{-e} \frac{1}{2}Hg_2I_2$

The last cathodic process is presumed to be analogous to the reduction of Ph_3GeCl or Ph_3GeBr. The Ph_3GeI wave is irreversible and its transfer coefficient is the same as for Ph_3GeCl and Ph_3GeBr. Because of this fact and because the assumption of identical operating mechanisms for the reduction of simple organic halides has been cited to have some validity[79], the reduction step above is proposed for the last cathodic process.

The kinetic process appears to depend on both the Ph_3GeI and the water concentration. For this reason a preceding protonation reaction is suggested. When excess water is added, the equilibrium is shifted towards products. Increased amounts of hydroxyl ion are produced which can react with Ph_3GeI to liberate iodide ion. It appears that water itself cannot be involved in hydrolyzing Ph_3GeI since hydriodic acid would be produced. Hydriodic acid can be detected polarographically with a reduction wave at -1.2 V, but no such wave was observed. A protonated germanium species is suggested as the species that is reduced. The reaction is written to indicate that the proton is neutralized in the reduction. It might be, however, that the proton is also reduced. This would explain why the coulometric results were consistently greater than one Faraday per mole of Ph_3GeI reduced.

Anodic processes

The anodic processes observed for Ph_3GeCl, Ph_3GeBr, and Ph_3GeI at a mercury electrode appear to involve identical mechanistic steps. The following is suggested for the overall mechanism.

$$Ph_3GeX \xrightarrow[Hg]{-e} Ph_3Ge^+ + \tfrac{1}{2}Hg_2X_2$$

$$Ph_3Ge^+ + ClO_4^- \longrightarrow Ph_3GeOClO_3$$

$$Ph_3Ge^+ \xrightarrow{e} Ph_3Ge\cdot$$

The initial anodic step is a mercury dissolution process. The fact that an anodic process is not observed at a platinum electrode further emphasizes this conclusion. Presumably the mercury surface would interact with the halide end of the molecule. In order to accomplish this, the germanium moiety would have to closely approach the electrode. The depressions observed in electrocapillary curves may reflect double layer effects due to a closer approach of the germanium species to the electrode. In the case of Ph_3GeCl, a proton or a water or alcohol molecule may be necessary to affect the polarity of the Ge–Cl bond allowing more favored interaction between Cl and Hg.

The product isolated after anodic controlled-potential electrolysis gave a spectrum identical to the one shown in Fig. 10. This spectrum was obtained for synthesized triphenylgermanium perchlorate. A cursory analysis of this spectrum indicates that the compound is a covalently bound perchlorate species. Ionic perchlorate salts have infrared active frequencies at 1050–1170 and 630 cm^{-1} representing ν_3 (asymmetric stretch) and ν_4 (asymmetric bend), respectively[80,81]. For TBAP, the former is a single broad band centered at about 1090 cm^{-1} and the latter is a sharp peak at 625 cm^{-1}. In Fig. 10, fine structure is observed in the region from 1050–1200 and the peak at 630 cm^{-1} is split. In addition to this evidence, a peak is observed at 860 cm^{-1} which is characteristic of the Ge–O stretching frequency[32,82]. A comparison of this spectrum with one for hexaphenyldigermoxane showed significant differences, particularly in the region 250–500 cm^{-1}, to eliminate the possibility of a partially hydrolyzed sample giving rise to a Ge–O stretching frequency.

The question arises whether triphenylgermanium perchlorate exists in solution as a covalent species or an ion pair. To decide this question a polarogram of synthetically prepared triphenylgermanium perchlorate was obtained and is shown in Fig. 11. The polarogram shows the main wave occurring at -1.0 V, an unusual maximum at

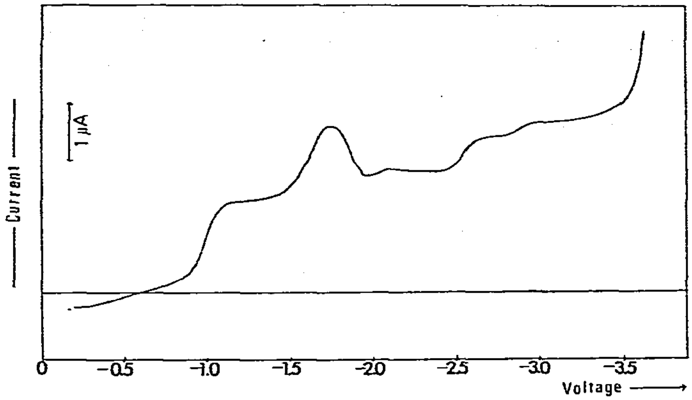


Fig. 11. Polarogram of synthesized triphenylgermanium perchlorate.

− 1.8 V and minor waves beyond − 2.0 V. The latter are probably due to impurities in the synthesized sample. The presence of the maximum is not understood. The important feature, however, is that triphenylgermanium perchlorate reduces at − 1.0 V. The reduction wave observed with solutions after anodic electrolysis (Fig. 9) occurs at approximately − 0.2 V. The conclusion made as a result of this information is that a germonium ion is formed in solution on anodic electrolysis and exists in solution as an ion pair with perchlorate as the gegenion. The product isolation procedure causes the ion pair to form the covalent species observed. If this is indeed the case, then the production of triphenylgermonium ion in solution may afford unique opportunities for simplified organogermanium synthesis.

ACKNOWLEDGEMENTS

The authors would like to thank Mr. Don Schifferl for lending his expertise to the instrumentation aspects of this study. R.J.B. also expresses appreciation for a predoctoral fellowship from the Texaco Company.

REFERENCES

1 R. E. Dessy, W. Kitching, and T. Chivers, *J. Amer. Chem. Soc.*, 88 (1966) 453.
2 H. Mehner and H. Jehring, *Z. Chem.*, 3 (1963) 472.
3 H. Jehring and H. Mehner, *Z. Chem.*, 3 (1963) 34; *ibid.*, 4 (1964) 273.
4 H. Jehring and H. Mehner, *Fresenius' Z. Anal. Chem.*, 224 (1967) 136.
5 H. Mehner, H. Jehring and H. Kriegsmann, *J. Organometal. Chem.*, 15 (1968) 97, 107.
6 H. Jehring, H. Mehner, and H. Kriegsmann, *J. Organometal. Chem.*, 17 (1969) 53.
7 V. N. Flerov and Y. M. Tyurin, *Zh. Obshch. Khim.*, 38 (1968) 1669; *Chem. Abstr.*, 69 (1968) 102484c.
8 M. D. Morris, *J. Electroanal. Chem.*, 16 (1968) 569.
9 M. Devaud, *J. Chim. Phys. Physicochim. Biol.*, 63 (1966) 1335; *ibid.*, 64 (1967) 791.
10 M. Devaud, P. Souchay, and M. Person, *J. Chim. Phys. Physicochim. Biol.*, 64 (1967) 646.
11 M. Devaud and E. Laviron, *Rev. Chim. Miner.*, 5 (1968) 427.
12 A. Vanachayangkul and M. D. Morris, *Anal. Lett.*, 1 (1968) 885.
13 M. D. Booth and B. F. Fleet, *Anal. Chem.*, 42 (1970) 825.
14 E. A. Abrahamson and C. A. Reynolds, *Anal. Chem.*, 24 (1952) 1827.
15 S. G. Mairanovskii, V. A. Ponomarenko, N. V. Barashkova, and A. D. Snegova, *Dokl. Akad. Nauk SSSR*, 134 (1960) 387; *Proc. Acad. USSR, Phys. Chem. Sect.*, 134 (1960) 867.

16 S. G. Mairanovskii, V. A. Ponomarenko, N. V. Barashkova, and M. A. Kadina, *Izv. Akad. Nauk SSSR, Ser. Khim.*, (1964) 1951; *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, (1964) 1858.
17 V. Gutmann, P. Heilmayer, and G. Schöber, *Monatsh. Chem.*, 92 (1961) 240.
18 T. Damokos, *Chem. Zvesti*, 16 (1962) 325; *Chem. Abstr.*, 58 (1963) 7610e.
19 T. Damokos, *Magy. Khem. Foly.*, 68 (1962) 175.
20 M. D. Curtis and A. L. Allred, *J. Amer. Chem. Soc.*, 87 (1965) 2554.
21 A. L. Allred and L. W. Bush, *J. Amer. Chem. Soc.*, 90 (1968) 3352.
22 V. M. Kazakova, I. G. Makarov, M. E. Kurek, and E. A. Chernyshev, *Zh. Strukt. Khim.*, 9 (1968) 525; *Chem. Abstr.*, 69 (1968) 10573*j*.
23 H. Bock and H. Alt, *Angew. Chem., Int. Ed. Engl.*, 6 (1967) 940.
24 J. Cermak and P. Dostal, *Collect. Czech. Chem. Commun.*, 28 (1963) 1384.
25 A. P. Terent'ev, E. A. Bodarevskaya, and T. V. Kirillova, *Zh. Anal. Khim.*, 23 (1968) 625; *J. Anal. Chem. USSR*, 23 (1968) 534.
26 R. A. Benkeser and C. A. Tincher, *J. Organometal. Chem.*, 13 (1968) 139.
27 N. P. Kharitonov, B. P. Nechaev, and G. T. Fedorova, *Zh. Obshch. Khim.*, 39 (1969) 824; *J. Gen. Chem. USSR*, 39 (1969) 787.
28 L. Riccoboni, *Gazz. Chim. Ital.*, 72 (1942) 47.
29 G. Costa, *Ann. Chim.*, 40 (1950) 541.
30 I. A. Korshunov and N. I. Malyugina, *Zh. Obshch. Khim.*, 31 (1961) 1062; *J. Gen. Chem. USSR*, 31 (1961) 982.
31 M. D. Morris, *J. Electroanal. Chem.*, 20 (1969) 263.
32 D. Quane and R. S. Bottei, *Chem. Rev.*, 63 (1963) 403.
33 R. S. Bottei and L. J. Kuzma, *J. Inorg. Nucl. Chem.*, 30 (1968) 415, 2345.
34 L. S. Foster and G. S. Hooper, *J. Amer. Chem. Soc.*, 57 (1935) 76.
35 R. E. Dessy and R. L. Pohl, *J. Amer. Chem. Soc.*, 90 (1968) 1995.
36 U. M. Tyurin, V. N. Flerov, and U. K. Goncharuk, *Zh. Obshch. Khim.*, 41 (1971) 494.
37 E. G. Rochow and A. L. Allred, *J. Amer. Chem. Soc.*, 77 (1955) 4489.
38 A. B. Thomas and E. G. Rochow, *J. Amer. Chem. Soc.*, 79 (1957) 1843.
39 O. H. Johnson and E. A. Schmall, *J. Amer. Chem. Soc.*, 80 (1958) 2931.
40 M. E. Peach and T. C. Waddington, *J. Chem. Soc.*, (1961) 1238.
41 G. P. Sollot and W. R. Peterson, Jr., *J. Amer. Chem. Soc.*, 89 (1967) 6783.
42 C. A. Kraus and L. S. Foster, *J. Amer. Chem. Soc.*, 49 (1927) 457.
43 G. T. Morgen and H. D. K. Drew, *J. Chem. Soc.*, 127 (1925) 1760.
44 O. H. Johnson and D. M. Harris, *J. Amer. Chem. Soc.*, 72 (1950) 5566.
45 R. West, *J. Amer. Chem. Soc.*, 75 (1953) 6080.
46 I. Ruidisch and M. Schmidt, *Z. Naturforsch. B*, 18 (1963) 508.
47 U. Wannagut, F. Brandmair, W. Liehr, and H. Neiderprüm, *Z. Anorg. Allg. Chem.*, 302 (1950) 185.
48 H. C. Clark and R. J. O'Brien, *Inorg. Chem.*, 2 (1963) 740.
49 H. C. Clark and R. G. Goel, *Inorg. Chem.*, 4 (1965) 1428.
50 C. K. Mann, in A. J. Bard (Ed.), *Electroanalytical Chemistry*, Vol. 3, Marcel Dekker, Inc., New York, N.Y., 1969, p. 132.
51 H. O. House, E. Feng, and N. P. Peet, *J. Org. Chem.*, 36 (1971) 2371.
52 M. T. Kelley, H. C. Jones, and D. J. Fisher, *Anal. Chem.*, 37 (1959) 488.
53 G. L. Booman and W. B. Hollbrooke, *Anal. Chem.*, 35 (1963) 1793.
54 C. F. Morrison, *Generalized Instrumentation for Research and Teaching*, Washington State University Press, Pullman, Washington, 1964.
55 L. P. Morgenthaler, *Basic Operational Amplifier Circuits for Analytical Chemical Instrumentation*, McKee-Pederson Instruments, Danville, Calif., 1967.
56 C. G. Enke and R. A. Baxter, *J. Chem. Ed.*, 41 (1964) 202.
57 R. S. Bottei and R. J. Boczkowski, *J. Chem. Ed.*, 47 (1970) 312.
58 C. K. Mann, *J. Chem. Ed.*, 47 (1970) 99.
59 A. K. Hoffmann, W. G. Hodgson, D. L. Maricle, and W. H. Jura, *J. Amer. Chem. Soc.*, 86 (1964) 631.
60 W. E. Thomas and W. B. Schaap, *Anal. Chem.*, 41 (1969) 136.
61 S. Roffia and M. Lavacchielli, *J. Electroanal. Chem.*, 22 (1969) 117.
62 L. Meites, *Polarographic Techniques*, 2nd ed., Interscience Publishers, New York, 1965. p. 224.
63 J. Tomes, *Collect. Czech. Chem. Commun.*, 9 (1937) 12.
64 E. B. Rupp, D. E. Smith, and D. F. Shriver, *J. Amer. Chem. Soc.*, 89 (1967) 5562.

65 D. E. Smith, E. B. Rupp, and D. F. Shriver, *J. Amer. Chem. Soc.*, 89 (1967) 5568.
66 L. Meites, *J. Amer. Chem. Soc.*, 89 (1967) 303.
67 S. Roffia and M. Lavacchielli, *J. Electroanal. Chem.*, 22 (1969) 117.
68 J. Koutecky, *Collect. Czech. Chem. Commun.*, 18 (1953) 597.
69 K. B. Oldham and E. P. Parry, *Anal. Chem.*, 40 (1968) 65.
70 R. S. Nicholson and I. Shain, *Anal. Chem.*, 36 (1964) 706.
71 J. P. Billon, *Bull. Soc. Chim. Fr.*, (1960) 1912.
72 P. Zuman, *The Elucidation of Organic Electrode Processes*, Academic Press, New York, 1969, p. 44.
73 W. A. Pryor, *Free Radicals*, McGraw Hill, New York, 1966.
74 O. H. Johnson, *Chem. Rev.*, 48 (1951) 259.
75 F. Rijkens, *Organogermanium Compounds*, Germanium Research Committee, Utrecht, 1960, p. 17.
76 J. Stage, *Ann. Chim. (Paris)*, 6 (1961) 519.
77 R. Rijkens and G. J. M. Van der Kerk, *Organogermanium Chemistry*, Germanium Research Committee, Utrecht, 1964, p. 10.
78 F. Glockling, *The Chemistry of Germanium*, Academic Press, London, 1969, Chap. 4.
79 P. Zuman, *Substituent Effects in Organic Polarography*, Plenum Press, N.Y., 1967, p. 8.
80 H. Cohn, *J. Chem. Soc.*, (1952) 4282.
81 S. D. Ross, *Spectrochim. Acta*, 18 (1962) 225.
82 F. Glockling, *Spectrochim. Acta*, 18 (1962) 16.