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Electrochemical studies on organometallic compounds

XXXVIII *. Electrosynthesis of ethyl-, propyl- and butyl-antimony

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Abstract

Two-electron reduction of $RSbBr_2$ (**1**: R = C_2H_5; **2**: R = n-C_3H_7; **3**: R = n-C_4H_9) in tetrahydrofuran in presence of Bu_4NPF_6 followed by extraction with toluene has given the cyclic and polymeric organoantimony(I) compounds $(RSb)_n$ ($n = 4, 5$) and $(RSb)_x$ ($x \gg 5$), which have been identified by ^1H NMR and mass spectroscopy. Mechanistic aspects are discussed.

Introduction

In the course of our investigations of the electrochemical behaviour of organoantimony compounds [1,2] we became interested in the electrosynthesis of alkylantimony(I) compounds, which have recently been prepared by dehalogenation of alkylantimony dibromides $RSbBr_2$ (R = C_2H_5, n-C_3H_7, n-C_4H_9) with magnesium in THF. This reaction gives yellow solutions containing mainly five-membered antimony rings $(RSb)_5$ and four-membered antimony rings $(RSb)_4$. Evaporation of the solutions gives reversibly black solid polymers $(RSb)_x$ ($x \gg 5$) [3].

It was of interest to see if the product spectrum of alkylantimony rings or polymers would be different in electrochemical synthesis, and we report here an investigation of the electroreduction of $C_2H_5SbBr_2$ (**1**), n-$C_3H_7SbBr_2$ (**2**) and n-$C_4H_9SbBr_2$ (**3**) in tetrahydrofuran (THF) in the presence of 0.2 *M* Bu_4NPF_6 as supporting electrolyte.

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* For Part XXXVII see ref. 8.

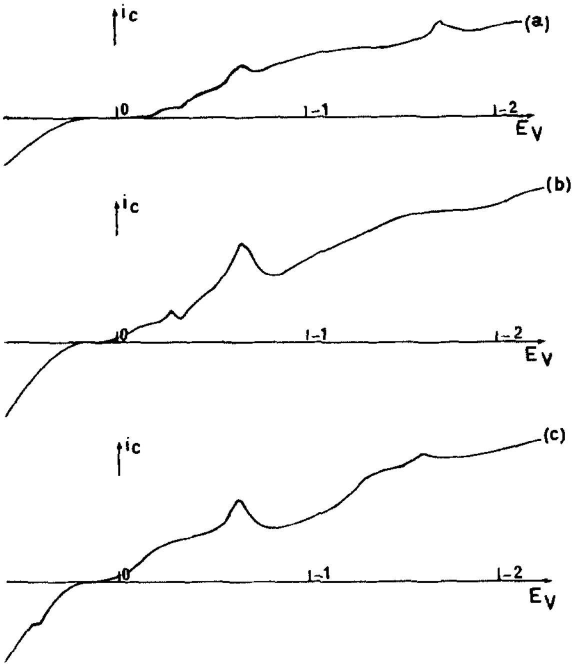

Fig. 1. Polarograms of **1** (a) **2** (b) **3** (c) in THF (average current).

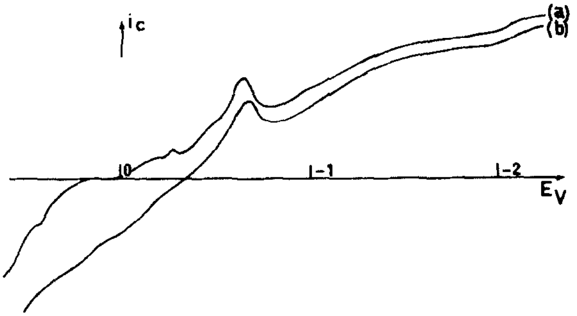

Fig. 2. Polarogram of **2** in THF (average current). (a) **2** alone (b) in the presence of Bu_4NBr.

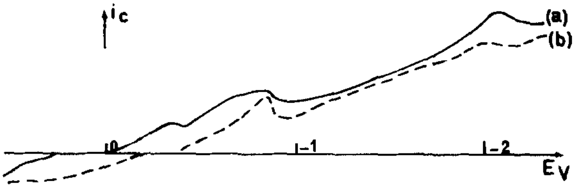

Fig. 3. Polarogram of **2** in THF (average current). (a) before electrolysis (b) after electrolysis at −0.4 V.

Results

The polarograms of **1**–**3** (Fig. 1) exhibit ill-defined waves which undergo no change in shape as the temperature or concentration is varied.

The addition of Bu_4NBr, however, causes a change of the polarogram, the cathodic current appearing at more negative potentials. This is shown in Fig. 2 for the case of compound **2**.

When electrolysis of **2** is carried out at a potential of −0.4 V in the absence of Bu_4NBr the current decreases to zero after consumption of 0.2e (Fig. 3).

When the electrolysis of **1**–**3** is performed at a mercury cathode at −1.7 V, after consumption of almost 2e green solutions are obtained which do show no EPR signals. The polarograms of the electrolyzed solutions of **1**–**3** exhibit oxidation waves A'_1 situated aproximately at the same potentials (Fig. 4). In the case of **1** and **2** there are also small reduction waves (**1** : B_1,B_2;**2** : B).

In the case of **3**, reoxidation of the potential of wave A'_1 regenerate the polarogram of the initial compound. The electrolyzed species are thermally relatively stable in an argon atmosphere [4*]. When the solution is heated to 60 °C the wave A'_1 is unchanged. After evaporation of the solvent and extraction of the residue with toluene the yellow products **1'**, **2'**, **3'**; which are derivatives of **1**, **2** and **3**, respectively are obtained. The polarogram of these products in THF is shown in Fig. 5. In the case of **1'** two well-defined reduction waves B_1 and B_2 are seen. The oxidation wave A'_1 also appears. The intensities of the reduction waves relative to those of the oxidation waves depend on the extraction conditions (temperature, time).

In the case of **2'** and **3'** only one reduction wave is observed.

In cyclic voltammetry in the case of **2'** an oxidation peak B'_1 is observed when the potential is reversed after reduction peak B (Fig. 6).

Electrolysis [5*] at the potential of peak B gives a red solution which in polarography shows the oxidation wave B'_1 (Fig. 7). Reoxidation at −0.5 V regenerates back the polarogram of the yellow product **2'**.

The yellow products **1'**, **2'**, **3'** become black and insoluble when stored under argon. This process is faster for **1'** and **2'** than for **3'**, and it was possible to obtain a ^1H NMR spectrum of **3'** showing the signals of $[n\text{-}C_4H_9Sb]_5$ [3].

The mass spectra of the black materials are identical with those of $(C_2H_5Sb)_x$, $(n\text{-}C_3H_7Sb)_x$ and $(n\text{-}C_4H_9Sb)_x$ prepared from **1**–**3** and magnesium in THF [3].

Discussion

The absence of the oxidation wave of Br^- in the polarogram of **1**, **2** and **3** indicates that these dibromides are not ionized under the reaction conditions. The effect of added bromide ions indicates a ionization of **1**, **2**, **3** under the influence of the electrochemical reaction (C.E process; path a, c, d, Scheme 1). When the amount of electrogenerated Br^- has increased (see Fig. 3) or Br^- is added from Bu_4NBr (see, Fig. 2), this ionization is no longer possible and operation of the E.C process (path a, b, d) may account for the observations.

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* A reference number with an asterisk indicates a note in the list of references.

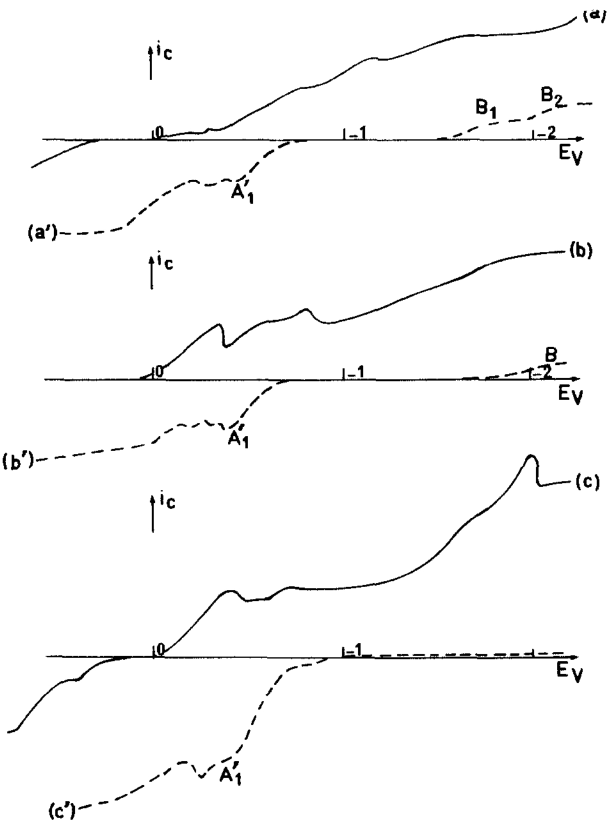
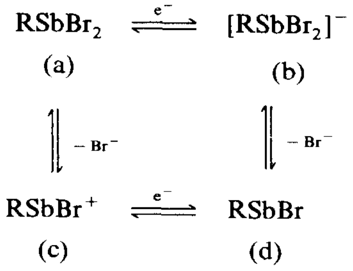


Fig. 4. Polarograms (average current) in THF of **1** (a) **2** (b) and **3** (c) before electrolysis. After two electron reduction of **1** (a′) **2** (b′) and **3** (c′).

The complicated shape ot the polarograms is consistent with the electrogeneration of unsaturated species that form electroactive adducts.

The two electron reduction of **1**–**3** gives species containing Sb^I which are oxidized at the potential of wave A'_1. Formation of compounds of the type $RSbBr^-$ is unlikely because such an anionic species should be oxidizable at a higher cathodic potential than A'_1 and it should not be possible to extract these species with a



Scheme 1

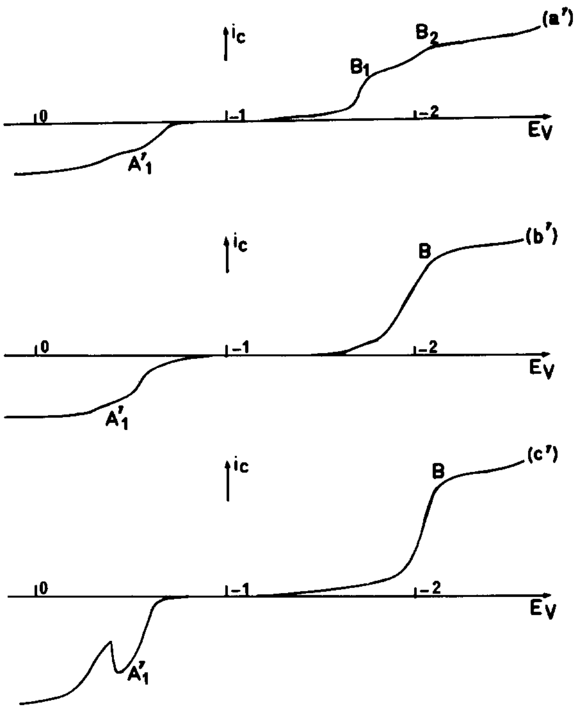


Fig. 5. Polarograms (average current) in THF of **1′** (a′) **2′** (b′) and **3′** (c′).

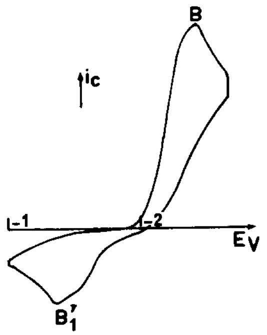


Fig. 6. Cyclic voltammogram of **2′** in THF on platinum electrode. Starting potential: −1 V. Sweep rate 0.5 V s^{-1}.

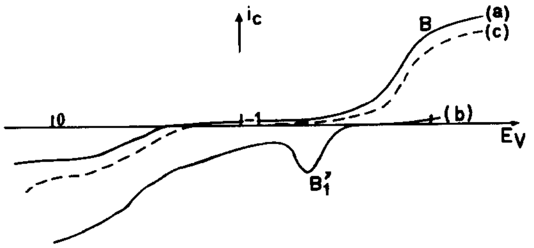
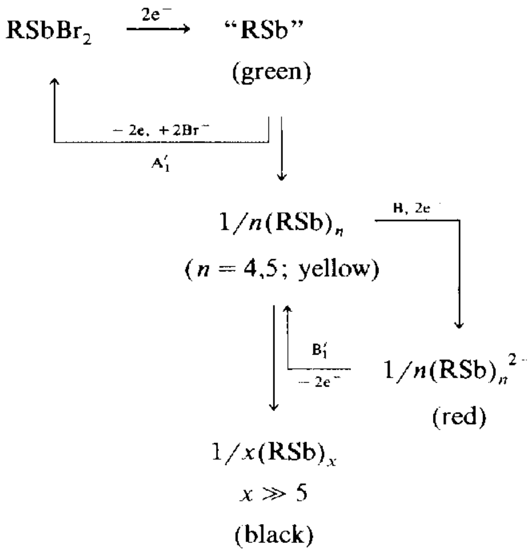


Fig. 7. Polarogram of **2′** in THF (average current) (a) before electrolysis (b) after reduction at −2 V (c) after reoxidation at −0.5 V.



Scheme 2

non-polar solvent like toluene. A neutral species is more probable and we formulate this intermediate as "RSb" because we do not have information about the structure. Oligomers of the type $BrSb(R)(SbR)_nSb(R)Br$ solvated with THF are possible. The presence of THF has been demonstrated by ^1H NMR spectroscopy after extraction in the case of compound **1′**.

Oxidation of the "RSb" species in the presence of Br^- regenerates the dibromides **1**–**3**.

Evaporation of the THF and extraction with toluene give a yellow solution containing **1′**, **2′**, **3′** as cyclic species rings of the type $(RSb)_4$ and $(RSb)_5$, which have described in ref. 3 and identified in this work by ^1H NMR and mass spectroscopy. These cyclic species are reduced at the potential of wave B [6*] to give a red solution possibly containing open chain dianions $(RSb)_n^{2-}$ [5*]. Oxidation of the anionic species at the potential of wave B_1' regenerates the cyclic species **1′**, **2′** and **3′**.

The black solids obtained when the cyclic species are stored in the absence of the solvent are the polymeric species $(RSb)_x$ ($x \gg 5$), which have also been obtained by chemical methods [3]. The results are summarized in Scheme 2.

Conclusion

Despite the unsatisfactory shapes of the polarograms of **1**–**3** we were able to study the electrochemistry of these compounds and to prepare the cycle species $(RSb)_n$ ($n = 4,5$) and polymers of the type $(RSb)_x$ ($x \gg 5$) electrochemically. The properties of these products are very similar to those obtained by chemical methods.

This is to our knowledge the first electrosynthesis of organoantimony compounds. We have also been able to determine the redox properties of the intermediates of the reduction.

Experimental

The apparatus and technique have been described previously [2]. The reference electrode was an aqueous saturated calomel electrode separated from the solution by a sintered glass disk.

Compounds **1**, **2** and **3** were prepared by published procedures [7]. A Bruker WH 360 spectrometer was used for the ^{1}H NMR spectrum. The mass spectra were recorded on a Finnigan MAT 8222 spectrometer.

References

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4 The green solutions are immediately decolorized in the air.
5 The amount of electricity consumed could not be determined owing to solubility problems and the presence of several products in solution. A solution of the crystalline solid (^{t}BuSb)$_4$ is reduced at the same potential consuming 2e mol^{-1}. H.J. Breunig and Y. Mugnier, unpublished.
6 In the case of **1'** the two reduction waves correspond to the four and five membered ring species. In contrast, solutions of **2'** and **3'** contain larger the amounts of the pentamers.
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