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Electrochemical studies on organometallic compounds

XXXVI *. New aspects of the electroreduction of $(Ph_2Sb)_2O$, $(Ph_2Sb)_2$, $Ph_2Sb(^nBu)$, and Ph_3Sb

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Abstract

Electroreduction of $(Ph_2Sb)_2O$ (1) in THF gives Ph_2Sb^-, which can also be obtained by uptake of two electrons on $(Ph_2Sb)_2$ (2). Ph_2Sb^- reacts with the supporting salt ($^nBu_4NPF_6$) to yield tributylamine and $Ph_2Sb(^nBu)$ (3). The electroreduction of 3 and Ph_3Sb (4) gives also the anion Ph_2Sb^-. There is a considerable influence of the electrode surface on the redox properties of 1–4. Mechanistic aspects are discussed.

Introduction

Redox reactions are important in the synthesis of organoantimony compounds [1] but there have been only a few electrochemical studies in this field [2]. We describe here a full investigation of the electroreduction of $(Ph_2Sb)_2O$ (1), $(Ph_2Sb)_2$ (2), $Ph_2Sb(^nBu)$ (3) and Ph_3Sb (4). Preliminary results concerning the redox properties of 2 have been reported [3].

Results

The polarogram of 1 in tetrahydrofuran (THF) exhibits a reduction wave O * ($E_{1/2} = -1.95$ V). The same wave is observed in RDE voltammetry. In cyclic

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* Part XXXV see ref. 15.

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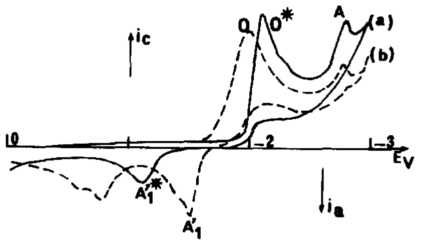


Fig. 1. (a) Cyclic voltammogram of $(Ph_2Sb)_2O$ in THF in normal platinum electrode. (b) an activated electrode. Starting potential 0 V, sweep rate 0.2 V s^{-1}.

voltammetry a second reduction peak, A, is observed at higher potential than O *; in the anodic sweep an oxidation peak, A'_1 *, appears (Fig. 1a). When the platinum electrode is activated (see Experimental section), the form of the voltammogram is changed considerably. A new system with the peaks O and A'_1 is obtained (Fig. 1b).

After electrolysis of 1 at −2 V and consumption of 2 F, a red solution is formed which exhibits the oxidation wave A'_1 * and the reduction wave A (an ill-defined oxidation wave is also observed at lower cathodic potentials, Fig. 2b). If the solution is left at room temperature it becomes colorless and the oxidation wave A'_1 * disappears, and only the reduction wave A is observed. From this solution $Ph_2Sb(^nBu)$ (3) and Bu_3N may be isolated (Ph_3Sb (4) is also present in trace amounts).

The cyclic voltammogram of 4 in THF is shown in Fig. 3. After reduction at peak A the peak A'_1 * appears in anodic sweep and a new reduction peak D * is observed in the second sweep (Fig. 3a). If the platinum electrode is activated the peaks A'_1, A'_3, A'_4, D are obtained (Fig. 3b).

After electrolysis of 4 on a platinum or mercury electrode in THF with the consumption of 2 F, a red solution is formed. The current is hardly lowered and an oxidation wave A'_1 appears in polarography. If this solution is left at room temperature under argon the colour fades away rapidly, and wave A'_1 is no longer found. Extraction of the electrolysed solution gives Bu_3N, $Ph_2Sb(^nBu)$ (3) and Ph_3Sb.

In contrast, when the electrolysis is performed in *N*,*N*-dimethylformamide (DMF), after the consumption of two electrons the current is close to zero, and a red solution is formed which is relatively stable, and waves A'_1 and A'_3 are observed by polarography. After one hour the colour disappears and instead of wave A'_1 an reduction wave M at −1.7 V is observed.

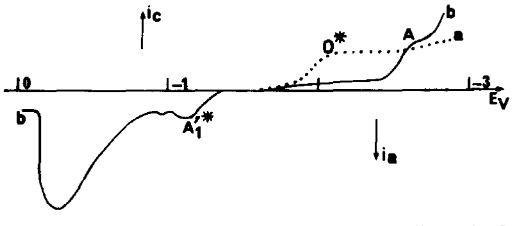


Fig. 2. Polarogram (average current) of $(Ph_2Sb)_2O$ in THF. (a) before electrolysis. (b) immediately after two electron reduction at −2 V.

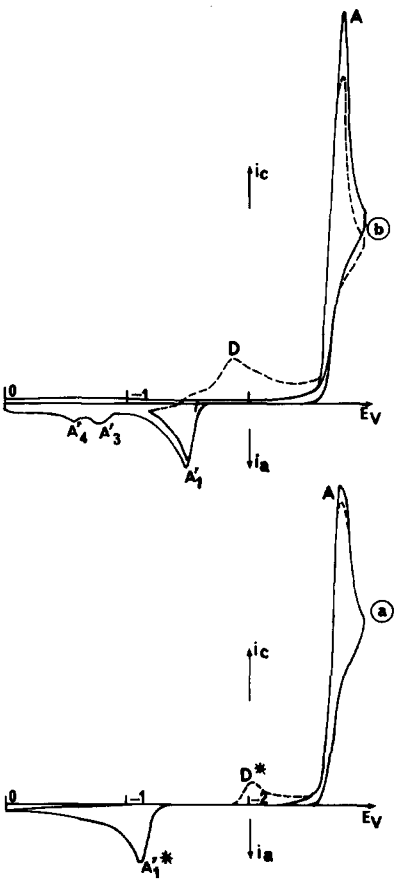


Fig. 3. (a) Cyclic voltammogram of Ph_3Sb in THF on platinum electrode. (b) on activated platinum electrode. Starting potential 0 V, sweep rate 0.1 V s^{-1}.

In THF, **3** presents, by polarography, a reduction wave at −2.85 V; the cyclic voltammogram is similar to that of **4**.

After two electron reduction of $(Ph_2Sb)_2$ (**2**) wave A'_1 is also obtained [3].

Discussion

The two electron reduction of **4** yields the anion Ph_2Sb^- that also can be prepared by reduction of **4** with alkali metals [1].

In THF this anion is oxidized at the potential of the peak A'_1 * and in cathodic sweep a peak D * is observed on the normal platinum electrode (Fig. 4a). If the platinum electrode is activated the peak system changes considerably and the peaks A'_1 and D appear. Peak D (or D *) corresponds to the reduction of $(Ph_2Sb)_2$ [3] (Fig. 4b).

Activation of the electrode may increase the number of active sites on the surface of the platinum metal [4]. In the case of the normal electrode the partial blocking of the electrode surface towards electron transfer reaction results in a non-linear

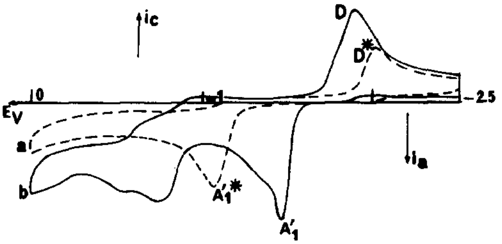


Fig. 4. (a) Cyclic voltammogram of Ph_2Sb^- in THF on platinum electrode. (b) on activated electrode. Starting potential -2.5 V. Sweep rate 0.2 V s^{-1}.

diffusion of Ph_2Sb^- and the difference of potentials between the two peak increases.

The transformation of **4** to Ph_2Sb^- can proceed via two alternative reaction paths (Scheme 1).

The path (a) corresponds to ECE process. The intermediate Ph_2Sb can also give $(Ph_2Sb)_2$, which is reduced at the potential of peak D. Path (b) represents an EC process leading to the anion Ph_2Sb^- with the loss of $Ph\cdot$, which is reduced to Ph^-.

For the reductive elimination step the latter process has been described in the case of Ph_3P [5].

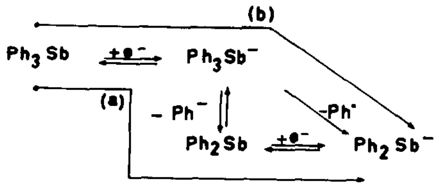
A similar mechanism can be postulated in the case of the electroreduction of **3** giving Ph_2Sb^- and Bu^-.

The low stability of Ph_2Sb^- in THF cannot be attributed to a reaction of this anion with the solvent [1]. Instead a degradation of Ph_2Sb^- by electrolyte salt [6] can be suggested according to.

$$Ph_2Sb^- + Bu_4N^+ \rightarrow Ph_2SbBu + Bu_3N \qquad (1)$$

We have confirmed that in THF the addition of Bu_4N^+ to the solution of chemically prepared Ph_2Sb^- yields Bu_3N, which has been characterized by mass spectroscopy (*m/e*: 185, 80%, Bu_3N^+; 128, 70%, Bu_2N^+; 72, 60%, $BuNH^+$). Ph_2SbBu (**3**) can be also detected (m/e: 332/334, 10%, Ph_2SbBu^+; 275/277, 100%, Ph_2Sb^+, 197/199). Ph_2SbBu which is formed in reaction 1 is reduced at the potential of peak A. Ph_3Sb (**4**) is also present in trace amounts.

When **4** is electrolyzed in DMF, Ph_2Sb^- is more stable towards the electrolyte salt. The observed difference of the reactivity of Ph_2Sb^- in the various solvents used may be due to solvatation effects. The wave M corresponds probably to the reduction of Ph_2SbH formed by reaction of Ph_2Sb^- with residual H_2O in DMF. Ph_2SbH is relatively unstable and decomposes into Ph_3Sb and SbH_3 [7].



Scheme 1.

The anion Ph_2Sb^- is also accessible by a two electron reduction of **1**, which should also produce Ph_2SbO^-. The arsenic analogue of this species has been obtained by reduction of $(Ph_2As)_2O$ [2a], In contrast Ph_2SbO^- is not detected even when voltammetry is used.

The formation of Ph_3Sb, in trace amounts, may be attributed to the reaction of Ph_2Sb^- with phenyl radicals, which can be formed by decomposition of Ph_2SbO^-. This $S_{RN}1$ mechanism has been described in the case of the reaction of Ph_2Sb^- with aryl halides [8]. In THF this mechanism is unlikely [9]. Another argument against the $S_{RN}1$ mechanism is provided by the amount of electricity consumed for the reduction of **1**. Since the $S_{RN}1$ process is catalytic the consumption should be much less than two electrons per mole.

The oxidation of the anions Ph_2Sb^- gives $(Ph_2Sb)_2$ which is reduced at the potentials of peak D [3]. This corresponds to the preparation of **2** by oxidation of Ph_2SbLi with $BrCH_2CH_2Br$ in THF [10].

Experimental

All manipulations were performed under argon. Tetrahydrofuran was purified by distillation from sodium benzophenone ketyl under argon.

The reference electrode was a saturated calomel electrode separated from the solution by a sintered glass disk. The auxiliary electrode was a platinum wire electrode. The supporting electrolyte was tetrabutylammonium hexafluorophosphate (0.2 *M*) in all cases; the salt (Fluka) was dried and deoxygenated before use.

A Tacussel UAP4 unit connected to a Tektronix oscilloscope (linear potential sweep experimental), an Amel 552 potentiostat and a Tacussel IG5 integrator were used. The platinum electrode was activated by immersing it in a $HClO_4$ 1 *M* solution and maintaining its potential below 6 V voltage versus a platinum wire for a few minutes.

Ph_3Sb was purchased from Merck-Schuchardt and used as received. $(Ph_2Sb)_2$ [11], Ph_2SbCl[12], $(Ph_2Sb)_2O$ [13] and $Ph_2Sb(^nBu)$ [14] were prepared by published methods.

Reactivity of Ph_2Sb^- on $^nBu_4NPF_6$

Ph_2Sb^- was prepared by treatment of Ph_3Sb with an excess of lithium in THF. The mixture was stirred at room temperature and after 30 min one equivalent of ^tBuCl was added to the solution, to reacts with PhLi. After addition of $^nBu_4NPF_6$ to the red solution of Ph_2Sb^-, the mixture was stirred for 30 min. The solution changed from red to colorless. The solvent was removed under vacuum and Ph_2SbBu and Bu_3N were extracted with hexane and characterized by mass spectroscopy.

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