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Preliminary communication

Electrochemical studies on organometallic compounds

XXXIV *. Redox properties of tetraphenyldistibane

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Abstract

The uptake of two electrons by $(Ph_2Sb)_2$, **1**, yields Ph_2Sb^-, **2**. Two-electron oxidation of **1** gives the cationic species Ph_2Sb^+, **3**. At room temperature **3** is reduced in two steps to **2** via the intermediate Ph_2Sb, **4**.

There have been only a few electrochemical studies on organoantimony compounds [1–4]. Following our investigations of the electrochemistry of organotransition metal species containing metal–metal bonds [5], we report here the electrochemical behaviour of tetraphenyldistibane **1**, a compound containing an Sb–Sb bond.

The polarogram of **1** in tetrahydrofuran (with 0.2 *M* tetrabutylammonium hexafluorophosphate as supporting salt) exhibits a reduction wave *D* ($E_{1/2} = -1.84$ V) and an oxidation wave *E'* ($E_{1/2} = 0.17$ V vs SCE(aq)) (see Fig. 2a). In cyclic voltammetry on a platinum electrode after reduction at the potential of peak *D*, a peak A'_1 is observed (Fig. 1a) that corresponds to the oxidation of Ph_2Sb^-. This anion has been generated by electrochemical [2] and chemical [6] methods. Reversal of the anodic sweep after peak *E'* gives rise to a reduction peak E_1 (Fig. 1b).

Electrolysis of **1** at −30 °C at the potential of peak *E'* consumes two faradays and the polarogram of the electrolyzed solution exhibits two reduction waves, E_1 and *D* (Fig. 2b). When the temperature in raised wave *D* disappears, and a new reduction wave, A_1, appears (Fig. 2c). The same polarogram is obtained after electrolysis of **1** at room temperature.

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* For part XXXIII see ref. 9.

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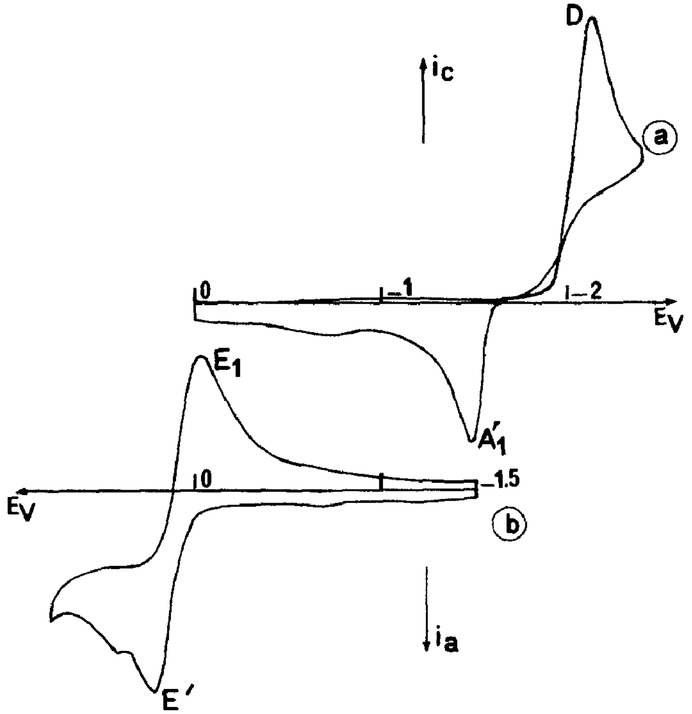


Fig. 1. Cyclic voltammograms of $(Ph_2Sb)_2$ in tetrahydrofuran on platinum electrode. Sweep rate 0.2 V s^{-1}. (a) Cathodic sweep, starting potential 0 V; (b) anodic sweep, starting potential −1.5 V.

In cyclic voltammetry after reduction at peak A_1 the peak A_1' is not observed. If chloride ions (LiCl in THF) are introduced into to the electrolyzed solution the reduction waves of Ph_2SbCl [7] appear. These results can be rationalized in terms of Scheme 1.

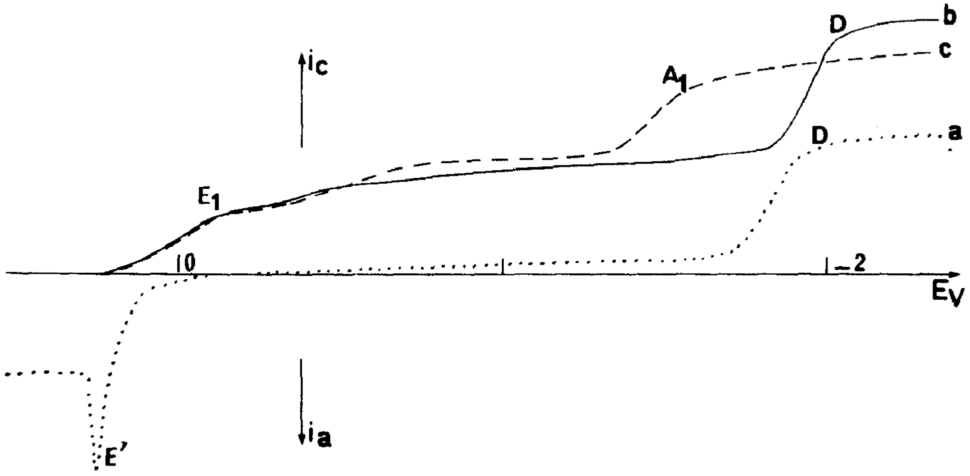
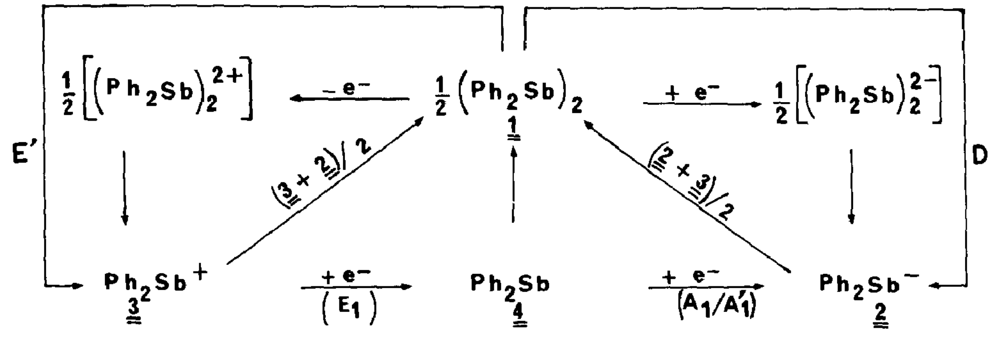


Fig. 2. Polarogram (average current) of $(Ph_2Sb)_2$ in tetrahydrofuran. (a) Before electrolysis; (b) after two-electron oxidation at +0.2 V at −30 °C; (c) at room temperature.



Scheme 1

The oxidation of **1** yields quantitatively a cationic species that we believe to be Ph_2Sb^+, **3**. The following results are in accordance with the formation of this cation:

1. Species **3** is obtained by two-electron oxidation of **1**, which implies that there is a change from Sb(II) in **1** to Sb(III) in **3**.
2. The reduction potential of the cation **3** is, as would be expected, lower than the reduction potential of neutral Sb(III) species.
3. The reduction of **3** at −30 ° C yields **1**, which is reduced at the potential of wave *D* (see Fig. 2b, Scheme 1, path **3** ⇒ **4** ⇒ **1** ⇒ **2**).
4. Addition of Cl^- to the solution of **3** gives Ph_2SbCl.
5. If the electrolysis is performed with Bu_4NClO_4 as supporting salt, $Ph_2Sb^+ClO_4^-$ is obtained [2,8].

At room temperature the second reduction step of **3** (wave A_1) appears close to the potential of oxidation of **2** (wave A_1'). Therefore the wave A_1 contributes to the reduction of the intermediate Ph_2Sb, **4**, formed close to the electrode, to yield Ph_2Sb^-, **2**. The oxidation peak of **2** is not observed in cyclic voltammetry of **3** because electrogenerated **2** reacts with **3** give **1**.

We are currently investigating the chemical oxidation of **1**.

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