Polarographic Reduction of Diphenyldiselenide

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Polarography, Coulometry, Diphenyldiselenide

The electroreduction of diphenyldiselenide has been investigated by polarography, cyclic voltammetry and coulometry. A mechanism for the reduction based on the initial two-electron transfer followed by cleavage of the Se-Se bond is proposed.

The polarographic behaviour of organic disulphides has been the object of much interest because of both their biological importance and their industrial applications.

On the other hand, homo- and hetero-dimetallic phenyl compounds of the elements of the fourth, fifth and sixth groups of the periodic table, of formula (Ph)₃M-M(Ph)₃ (x = 3, 2 or 1) have not been investigated systematically. We believe such a study would be of interest and would contribute to an understanding of the chemical reactivity of the metal-metal bond in such complexes.

As part of a research programme concerned with the electrochemical behaviour of complexes of the above type, we report some results concerning the polarographic behaviour of diphenyldiselenide, PhSe-SePh and suggest a mechanism for the overall electrode process.

Experimental

Diphenyldiselenide was prepared and purified as described in the literature.

Since diphenyldiselenide is only slightly soluble in water, the polarographic determinations were made in solutions 60% vol. in ethanol. Solutions were buffered over the pH range 1-10. Britton-Robinson buffers (0.08 M acetic acid, 0.08 M boric acid, 0.08 M potassium phosphate and 0.4 M NaOH) were used for weakly acidic, neutral and alkaline media. Buffers of the Sorensen and Clark type (0.1 M HCl and 0.1 M sodium citrate) were used for strongly acid media.

pH measurements were carried out using an Amel mod. 330 pH-meter. Conventional polarographic measurements were obtained on an Amel mod. 462 polarograph and oscillograms on an Amel mod. 448 instrument. The capillary used had the characteristics: t = 6 sec, m = 1.3 mg/sec at open circuit in distilled water and with a mercury column height of 60.0 cm.

All solutions were first deaerated via prolonged bubbling of argon, and then thermostatted at 25 ± 0.5 °C.

Results

a) Polarographic measurements

Under the conditions of conventional dc polarography diphenyldiselenide exhibits two reduction waves (I and II), of which only the first is well developed (Fig. 1 and Table I). The total heights mod. 462 polarograph and oscillograms on an Amel mod. 448 instrument. The capillary used had the characteristics: t = 6 sec, m = 1.3 mg/sec at open circuit in distilled water and with a mercury column height of 60.0 cm.

All solutions were first deaerated via prolonged bubbling of argon, and then thermostatted at 25 ± 0.5 °C.

Fig. 1. Conventional polarograms for reduction of diphenyldiselenide at pH 2.8 and 9.0.

0 2 3 4 5 6
p H

0.3 0.5 0.7

0.3 0.5 0.7
e v

0.3 0.5 0.7

p H 2.8

p H 9

of the two waves are independent of the pH and proportional to the concentration of the depolariser, over the whole concentration range investigated (10⁻⁴-10⁻³ M). On detailed examination, the first wave appears composed of two steps which are very close together (I' and I''). This splitting becomes especially evident in weakly acidic or alkaline media, since the half-wave potential of step I'' moves sensibly towards more negative values with
Table I. Half-wave potential values of diphenyldiselenide 0.6 • 10⁻³ M at different pH.

<table>
<thead>
<tr>
<th>pH</th>
<th>-(E(1/2)I)</th>
<th>-(E(1/2)II)</th>
<th>-(E(1/2)III)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.8</td>
<td>0.375</td>
<td>—</td>
<td>0.620</td>
</tr>
<tr>
<td>9.0</td>
<td>—</td>
<td>0.455</td>
<td>0.640</td>
</tr>
</tbody>
</table>

referred to S.C.E.

increase in pH (Fig. 2). Fig. 2 also shows that the dependence of \(E_{(1/2)}\) on pH consists of two linear parts, of which that having a greater slope gives \(-\Delta E_{(1/2)}/\Delta pH \approx 70 \text{ mV}\). The ratio between the heights of \(I'\) and \(I''\) depends on the concentration, going from 0.25 to 0.45 when \(c = 0.47\) and 1.5 mM, respectively. It was, however, not possible to more fully characterise waves \(I'\) and \(I''\) because of the low accuracy encountered in measuring their limiting currents.

![Fig. 2. The pH-dependence of the half-wave potentials for the reduction of diphenyldiselenide.](image)

The second wave (II) has a much lower height than I (II/I \(\approx 1/5\)) and is characterised by \(-\Delta E_{(1/2)}/\Delta pH \approx 65 \text{ mV}\). Its limiting current is proportional to the mercury column height: the electrode process involved is thus controlled by the depolariser adsorption.

The total number of electrons involved in the reduction processes of PhSe-SePh, determined by comparison with diphenyldisulfide, is 2.

b) Coulometric measurements

Coulometric reductions were carried out at a mercury pool electrode on solutions of depolariser at different concentration and varying pH, with controlled-potentials corresponding to the limiting currents of the first and second steps, respectively.

The experimental data obtained show that the number of electrons involved in the overall electrode processes referred to the two steps, is equal to one, and is independent of the pH and initial concentration.

The reduction product is the acid, PhSeH, the concentration of which, in all the experiments, is half that of the initial diphenyldiselenide. Another product is formed simultaneously during electrolysis, which Dessy et al.⁹, in a note on the electrochemical scission of metal-metal bonds, identify as being the compound PhSeHg.

c) Linear Potential sweep voltammetry

The oscillographic measurements gave results in substantial agreement with those obtained by conventional polarography. In both acidic and alkaline media the oscillograms consisted of three peaks. However, while in alkaline medium all three peaks are well developed and separated, in acidic medium the second and third peaks are very poorly developed and not clearly distinguishable (Fig. 3 and Table II). Inverting the sense of the potential scan,

![Fig. 3. Cyclic voltammetry of diphenyldiselenide at pH 2.5 and 5.5, scan rate = 0.4 Volt/s.](image)

Table II. Peak potential values of diphenyldiselenide 0.6 • 10⁻³ M at different pH.

<table>
<thead>
<tr>
<th>pH</th>
<th>-(E_p)I</th>
<th>-(E_p)II</th>
<th>-(E_p)III</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.05</td>
<td>0.410⁹</td>
<td>0.520⁹</td>
<td>0.580⁹</td>
</tr>
<tr>
<td>5.50</td>
<td>0.494⁹</td>
<td>0.684⁹</td>
<td>0.818⁹</td>
</tr>
</tbody>
</table>

⁹: cathodic peak; a: anodic peak; scan rate: 0.4 Volt/s.
indicate that the overall process is bielectronic and that waves I' and II are adsorption waves, whilst I'' has diffusion character.

In addition, it is known that PhSe–SePh has a marked tendency to react with mercury to form PhSe–Hg–SePh and that this reaction is relatively fast, if carried out with vigorous stirring of the reaction medium.

Given the above points, we suggest that, under the conditions in which coulometric reductions were carried out (30 min. each), the last-mentioned reaction may go almost to completion. The reduction then occurs almost exclusively via the mercury complex and the resulting process is monoelectronic and gives rise to scission of the Hg-Se bond:

\[
(\text{PhSe})_2\text{Hg} + \text{H}^+ + \text{e} \rightarrow \text{PhSeH} + \text{PhSeHg} \quad (1)
\]

Under polarographic conditions, i.e. in the absence of stirring and with relatively short reaction times, however, the above reaction with mercury should involve only a small fraction of the depolariser. It appears thus reasonable to suppose that waves I'' and II correspond to reduction of the diphenyldiselenide and to reduction of the mercury complex formed, respectively:

\[
\begin{align*}
\text{PhSe–SePh} + 2\text{H}^+ + 2\text{e} & \rightarrow 2\text{PhSeH} \quad \text{(wave I')} \\
(\text{PhSe})_2\text{Hg} + \text{H}^+ + \text{e} & \rightarrow \text{PhSeH} + \text{PhSeHg} \quad \text{(wave II)}
\end{align*}
\]

Support for this suggestion comes from the fact that wave I'' corresponds to a diffusion-controlled process, whilst wave II corresponds to the reduction of a depolariser strongly adsorbed on the electrode, as would be expected for a substance formed by reaction with the electrode itself. The origin of wave I' is less clear. In our opinion, it may correspond to the same process found to correspond with wave I'', but this time with formation of \((\text{PhSeH})_{\text{ads}}\):

\[
\text{PhSe–SePh} + 2\text{H}^+ + 2\text{e} \rightarrow 2(\text{PhSeH})_{\text{ads}}. \quad \text{(wave I')}
\]

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