



## EFFECT OF CONCENTRATION ON OXIDATION POTENTIALS OF ALKYLARYLSELENIDES

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**Abstract**—For the processes of electrochemical oxidation of alkylarylselenides, implying the reversible electron transfer followed by potential-determining 1st order or 2nd order reaction (taking into account the concentration dependence of  $E_{1/2}$  due to consecutive kinetics), an extrapolation of oxidation potentials to infinite diluted solution ( $C \rightarrow 0$ ) allows the elimination of a non-specific adsorption contribution into the effective  $E_{1/2}$  value.

**Key words:** electrochemical oxidation, reactivity, alkylarylselenides, adsorption.

### INTRODUCTION

Organic selenides became a family of compounds widely used for various electrochemical functionalizations of organic molecules, as can be seen from a large number of papers published during the last ten years[1–13]. As usual, even if the starting compounds are diselenides, the key intermediates of such processes are alkylarylselenides[3–6, 8]. It was shown that anodic processes of arylselenides generally occur with the assistance of a radical cation on the reaction co-ordinate, *ie* the electron transfer is electrochemically reversible[14, 15]. On the other hand, it is known that organoelement compounds, especially those of S and Se, reveal a large affinity to the metallic surface of an electrode[16, 17]. Indeed, despite of the reversible character of electron transfer upon the oxidation of organic selenides, the feature and slopes of oxidation waves remarkably differ[18–23] from those revealed by reversible processes[24, 25], what makes the interpretation of their electrochemical behaviour more difficult.

We have made an attempt to estimate the rôle of adsorptional interactions in electrochemical reactions of alkylarylselenides through the consideration of their anodic oxidation on solid electrodes.

### EXPERIMENTAL

#### Instrumentation

Voltammetric measurements were carried out using the PI-I and PU-I polarographs with a recorder type LKD-4. Rotation sweep was controlled with the FP-37 numeric counter. A rotating disk electrode in the three electrode system was used with the platinum wire auxiliary electrode. The platinum oxidised

electrode was prepared by oxidising the platinum electrode in the melt eutectic mixture of  $\text{KNO}_3$ - $\text{NaNO}_3$  according[26] (procedure *a*) or by anodic polarisation of the platinum electrode in 40% solution of  $\text{HClO}_4$ [27] (procedure *b*). For obtaining the most dense layer of platinum oxides the time and oxidising potential were varied in order to get the least possible oxidation wave slope of  $\text{C}_6\text{H}_5\text{SeC}_3\text{H}_7$ . All the potential values cited are given vs. the  $\text{Ag}/0.1\text{M AgNO}_3$  (acetonitrile) reference electrode (+0.337 V vs. *sce*).

Measurements were performed in acetonitrile containing 0.1 M  $\text{Et}_4\text{NClO}_4$  as supporting electrolyte.

#### Reagents and solutions

The Pure for Analysis grade acetonitrile was treated as follows. To the pink (saturated) solution of  $\text{KMnO}_4$  in  $\text{CH}_3\text{CN}$  the phosphorus pentoxide was added provoking a light-brownish precipitation. After this  $\text{CH}_3\text{CN}$  was twice distilled over  $\text{P}_2\text{O}_5$  taken in excess. Tetraethylammonium perchlorate was obtained by reaction of  $\text{Et}_4\text{NBr}$  with  $\text{KClO}_4$  and dried over  $\text{P}_2\text{O}_5$  in vacuum. Studied compounds were synthesised: 1–8 according to[28–30]; 9 according to[27]; 10 according to[31]; 11 according to[32]; 12, 13 according to[33, 34]. All the substances were distilled or recrystallised before using.

### RESULTS AND DISCUSSION

The characteristics of electrooxidation of a number of alkylarylselenides in acetonitrile are collected in Table 1. As can be seen, the studied selenides differ by the mechanism of oxidation—not only the number of waves, but also the *n* value and wave slopes are different. It was found that the slopes of oxidation waves obtained at freshly polished platinum electrodes are larger than those obtained at the glassy carbon or a platinum oxidised

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