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Short communication

Anodic reactivity of alkylphenylselenides

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1. Introduction

The alkylarylselenides are a class of compounds which are interesting in many respects such as reagents in organic synthesis [1,2] and biologically active compounds [3]. The study of their electrochemical reactivity allows one to simulate their transformations in metabolic processes [4] and to reveal details of the reactivity of organo-element compounds relative to the properties of the media [5–8] as well as to the chemical structure of the compound [9–13]. To date, studies have been concentrated on selenides and diselenides which bear the aromatic group at the Se atom [14–19], and the anodic reactivity of alkylseleno derivatives is not very well documented [20]. Therefore a study of the role of an alkyl group directly linked to the Se atom in the anodic behaviour of alkylarylselenides is of interest.

2. Experimental

A potentiostat PI-50-1 combined with a LKD-4 recorder and a C8-13 oscilloscope was used. The electrodes for the rotating-disc electrode (RDE) experiments were prepared as described previously [21]. A Pt cylinder anode with an area of 36 cm^3 was used for large-scale electrolyses. The reference electrode was Ag|0.1 M $AgNO_3$ in CH_3CN. Analytical grade CH_3CN was distilled twice over P_2O_5 + $KMnO_4$ prior to use. Et_4NBF_4 was dried and stored over P_2O_5. Alkylphenylselenides were synthesized as described in Ref. [22] and distilled before use.

3. Results and discussion

Upon oxidation, alkylarylselenides (APS) **1–9** (see Table 1) show a single wave on the anodic branch of the voltammogram (Fig. 1), similar to other arylselenides bearing more complex functional substituents [4,10,11]. The limiting current I_{lim} of this wave varies linearly with the concentration of the selenide and with the square root of both the rotation speed ω in the RDE method (Fig. 2) and the potential sweep rate ν in CV; these observations indicate the diffusion nature of the limiting current. The activation energy, estimated from the plot of I_{lim} vs. $1/T$, was found to be 6.34 kJ mol^{-1}, which is also in good agreement with diffusion control of the process. By comparison of the value of I_{lim} with the one-electron limiting current of oxidation of phenothiazine under similar conditions ($c = 10^{-3}$ mol l^{-1}; $\omega = 25$ s^{-1}; $T = 20°C$) it was found that two electrons were involved in the process. The characteristic value of the slope of the plot of $E_{1/2}$ vs. log ω, which is 30 mV (Fig. 2), together with the lack of dependence of $E_{1/2}$ on log c in the range of concentrations 10^{-4}–10^{-2} mol l^{-1}, indicate a reversible electron transfer followed by the first-order potential-determining reaction of the primary intermediates.

The cyclic voltammograms of selenides **1–9** do not show any reversal peaks, which would correspond to oxidation peaks, up to a sweep rate of 200 V s^{-1}, although the use of commutative voltammetry on RDE revealed a signal corresponding to the reduction of primary short-lived intermediates at a switch frequency $f = 100$ Hz (Fig. 1). Using nitrosodurol as a spin trap, a spread signal of Ph-containing radicals was detected by ESR. However, in view of the longer time-scale involved when using this method, this signal should be attributed to secondary radical species resulting from further oxidation of Ph_2Se_2 in the cavity of the ESR cell (Ph_2Se_2 is the main Se-contain-

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