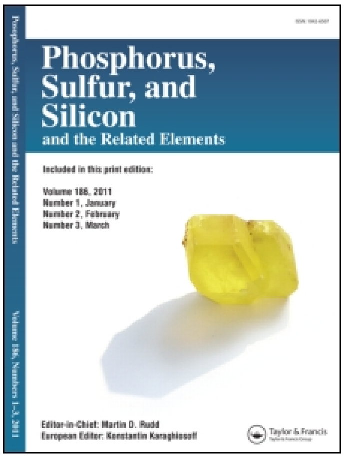

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CHEMICAL STRUCTURE AND ELECTROCHEMICAL REACTIVITY OF ORGANIC ARYLSELENIDES

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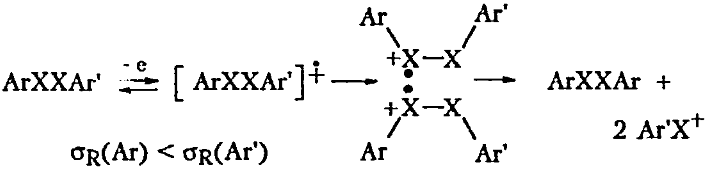
Factors of chemical structure of arylselenides are considered in relation with their reactivity in the electrooxidation processes following stepwise or dissociative electron transfer (ET) mechanism. The reactivity of electrogenerated cation radicals (CRs) is determined by electronic and stereoelectronic effects affecting the charge distribution. Compensation of the charge on Se and lowering of the energy of the CRs favour the radical properties as compared to the ionic properties of these species.

Keywords: electrochemical reactivity; electrooxidation; selenides

RESULTS AND DISCUSSION

The HOMO of arylselenides (such as AlkSeAr, Ar_2Se, ArSeSeAr') mainly involves the orbitals of ArSe moiety. Due to this fact, the redox properties of these compounds are very close ($E_{1/2}$ are about 1.1 V *vs.* Ag/0.1 M Ag^+ electrode), but variations of bond strength as well as some electronic and stereoelectronic effects can remarkably modify their electrochemical reactivity. So within the family of diaryldichalcogenides one finds three different types of oxidation mechanisms. For diselenides, the stepwise process follows an E+C2+C1+E mechanism involving the potential-determining dimerisation according to the Scheme 1.



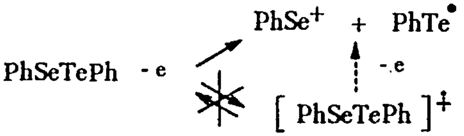
SCHEME 1

Though the Se-Se and S-Te bond strength are comparable (both *ca.* 80 kcal/mol), the CRs of diselenides dimerise ($\Delta E_{1/2}/\Delta \lg(\omega) = 20$ mV; ω is the speed of rotation of a disk electrode) while those of PhSTePh cleave ($\Delta E_{1/2}/\Delta \lg(\omega) = 30$ mV) owing to larger polarisability of S-Te bond as compared to Se-Se. The process corresponds now to an E+C1+E mechanism, as shown on the Scheme 2.

$$\text{PhS-TePh} \overset{-e}{\rightleftharpoons} [\text{PhS-TePh}]^{+\bullet} \xrightarrow[-\,\text{PhS}^{+}]{} \text{PhTe}^{\bullet} \xrightarrow{-e} \text{PhTe}^{+}$$

SCHEME 2

The increasing of the HOMO's level, the decrease in the strength of the chalcogen-chalcogen bond and a considerable lengthening of this bond in the order SSe > STe ≅ SeSe > SeTe are unfavourable for the stepwise mechanism. In PhSeTePh, bond energy is smallest ($D_{SeTe} = 69$ kcal/mol) and the bond is the most stretched (2.38-2.43 Å). It lowers the attractive portion of Morse curve[1] so that the dissociative ET becomes more favourable than the pathway involving a CR (Scheme 3).



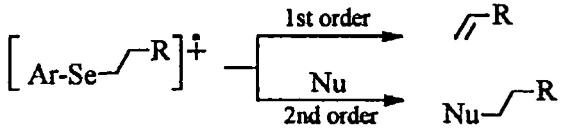
SCHEME 3

The choice between deprotonation and disproportionation of CRs of AlkSeAr is sensible to the proton-donor properties of the media. Deprotonation, the main reaction of selenides having a proton at the α-carbon, can be suppressed by addition of CF_3COOH giving rise to the disproportionation of the CRs (E+C1+E mechanism yields to an E+C2).

Another factors able to change the reactivity of CRs are field-effect and hyperconjugation. The role of the first one was shown for AlkSeAr bearing a substituent with the C=O group whose oxygen can approach the Se atom to an appropriate distance enabling a sufficient interaction in the CR. For the CRs of *p*-$MeSeC_6H_4COOH$, the *ab-initio* SCF/3-21G* calculations have shown the Se···O distance to be 2.56Å and for a purely coulombic interaction the stabilisation energy (in CH_3CN, $\varepsilon = 36$) has been esteemed as being *ca.* 30 kcal/mol. The reaction centre thus stabilised is not hard enough to cleave the Se-C_{sp3} bond nor to react with an Nu; the process involves the formation (by orbital-controlled disproportionation) of a dication which is more reactive than the CR and can undergo charge-controlled electrophilic interactions.

The n-σ conjugation in β-silyl substituted arylselenides strongly affects their electrochemical reactivity. Due to β-effect, the $E_{1/2}$ potentials of β-Me_3Si substituted selenoanisoles (R = H, MeO, Me, Cl, Br) are less positive, than those of non-silylated compounds. The potential-determining reaction of CRs is of second order ($\Delta E_{1/2}/\Delta \lg(\omega) = 20\pm3$ mV) so the behaviour of β-silylselenides (E+C2+C1+E scheme) differs from that of non-silylated AlkSeAr[2]. The β-effect is the smallest for selenides compared to the compounds of other elements of the VIA group ($-\Delta E_{1/2} = 800$ mV, 150 mV and 50 mV for O, S and Se, respectively[3,4]), but it is critical for the reactivity due to higher susceptibility of the Se atom to direct electronic effects than to the effects transmissible through the aromatic ring.

For AlkSeAr, there is an important synthetic consequence of the above mechanistic study. As usual, the eliminated alkyl group is then transformed into an unsaturated compound. The alkyl group of selenides whose CRs disproportionate, give a saturated product of addition of an nucleophile (*e.g.* Nu = CH_3CN), as shown on the Scheme 4. The study of others application is under progress now.



SCHEME 4

EXPERIMENTAL

Voltammetric study have been performed with a PU-1 universal polarograph. Analytical grade Et_4NBF_4 have been used. Synthesis of selenides, purification and preparation of solutions have been described earlier[2,4].

Acknowledgement

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