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1,5-Diselenacyclooctane. Reversible Electrochemical Oxidation with Remarkably Low Oxidation Potential in Dialkyl Selenides

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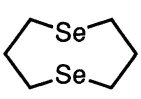
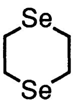
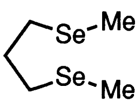
The electrochemical oxidation of dialkyl selenides was studied by cyclic voltammetry. The cyclic voltammogram of a new cyclic bis-selenide, 1,5-diselenacyclooctane shows one reversible oxidation wave with remarkably low oxidation potential.

Recently, considerable interest has been focused on the study of the electrochemical redox properties of medium-sized cyclic compounds containing di- and poly-heteroatoms.[1,2] As such an example, Wilson *et al.* reported that the sulfide is oxidized readily when neighboring groups containing lone pairs can interact with the sulfur atom.[2] However, the electrochemical behavior of medium-sized cyclic bis-selenides has never been reported. Normally, the cyclic voltammogram for dialkyl selenides shows the irreversible oxidation wave. More recently, we have synthesized a new cyclic bis-selenide, 1,5-diselenacyclooctane (**1**).[3] In this communication we report the first electrochemically reversible oxidation with remarkably lower oxidation potential of **1** as compared with that of dialkyl selenides and the facile oxidation of aliphatic selenides by intramolecular Se-Se interaction.

The electrochemical oxidation of selenides was studied by cyclic voltammetry. The cyclic voltammetries for all selenides were measured in CH_3CN containing 0.1 M $NaClO_4$ as supporting electrolyte using glassy carbon working electrode and platinum counter electrode and Ag/0.01 M $AgNO_3$ in CH_3CN reference electrode (scan rate: 300 mV/s). The peak potentials (*Ep*) of first oxidation peak for a few acyclic selenides showed the following values: bis(n-hexyl)selenide (**4**), +0.98 V; 2,6-diselenaheptane (**3**), +0.55 V; and diphenyl selenide (**5**), +0.97 V versus Ag/0.01 M $AgNO_3$ in CH_3CN reference electrode (Table 1). All of the oxidations are irreversible and the peak potentials are reproducible.[4] In general, since the cation radicals and dications of heteroatoms having alkyl groups would be expected to deprotonate or react with nucleophiles very rapidly, the lifetime of these species is short, resulting in the irreversible oxidation wave. Interestingly, comparison of the

Table 1. Electrochemical Oxidation of Selenides[a]

				$(n\text{-}C_6H_{13})_2Se$	$(C_6H_5)_2Se$
	1	**2**	**3**	**4**	**5**
Ep	+0.25	+0.86	+0.55	+0.98	+0.97

a) Ep/V vs. Ag/0.01 M $AgNO_3$; scan rate, 300 mV/s.

acyclic bis-selenide **3** with mono-selenides **4** and **5** shows a peak potential about 430 mV more cathodic for the former, so that **3** should be oxidized more readily. Thus, this large negative potential shifts of the bis-selenide **3** is undoubtedly ascribed to the neighboring-group Se-Se interaction.

On the other hand, in 1,4-diselenacyclohexane (**2**) as cyclic bis-selenide, transannular interaction of the two selenium atoms in the 1,4-position should be minimal. The cyclic voltammogram of **2** showed the irreversible wave at potential of +0.86 V (Ag/0.01 M $AgNO_3$).[4]

In contrast, when the cyclic voltammogram of cyclic bis-selenide **1** was measured in the voltage range of -0.5 to +1.5 V vs. Ag/0.01 M $AgNO_3$ in CH_3CN, only *one reversible oxidation peak* appeared at extremely low oxidation potential, +0.25 V.[5] Figure 1 shows the cyclic voltammogram of **1**. This facile oxidation of **1** and the unusual stability of the cationic species of **1** are attributed to the destabilization of **1** by transannular lone-pair-lone-pair repulsion and the stabilization of the oxidized products by neighboring-group participation, that is, bond formation between the two selenium atoms. The similar one reversible redox wave was observed in the electrochemical oxidation of 1,5-dithiacyclooctane (1,5-DTCO) as a sulfur analogue of **1**, which was shown to result in two closely spaced ($\Delta E \approx 20$ mV) reversible one-electron-transfer steps.[2] Thus, the oxidation of the cation radical of 1,5-DTCO to the dication proceeds more easily than that of the parent sulfide. Accordingly, the cyclic voltammogram of **1** suggests an overall two-electron oxidation, namely the formation of dication takes place spontaneously without detecting the cation radical as an intermediate.[6]

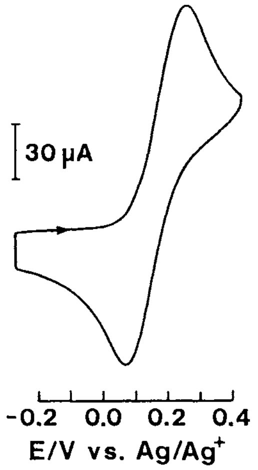


Fig. 1. Cyclic voltammogram of 2 mM, **1** in CH_3CN, 0.1 M $NaClO_4$: potentials *vs.* Ag/0.01 M $AgNO_3$ reference; scan rate, 300 mV/s.

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4) The oxidations of **2**, **3**, **4**, and **5** were irreversible at scan rates, from 50 mV/s to 1 V/s.

5) The reversibility in electrochemical oxidation of **1** was independent of the scan rates, from 50 mV/s to 1 V/s.

6) Two-electron oxidation of **1** with two equivalents of $NOPF_6$, a one-electron oxidizing agent, gave a novel diselena dicationic salt, R_2Se^+-$^+SeR_2$, 1,5-diselenoniabicyclo[3.3.0]octane bis(hexafluorophosphate) as a stable crystal.[3]

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