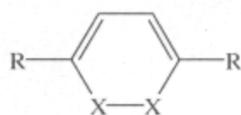


Oxidation of 1,2-Dichalcogenins: An Electrochemical, Computational and Photoelectron Spectroscopic Study

Richard S. Glass,^a Edward Lorance,^a T. Benjamin Schroeder,^a George S. Wilson,^b Quangsheng Qian,^b Eric Block,^c Marc Birringer,^c Russell DeOrazio,^c Chunhong He,^c Zhixing Shan,^c Xing Zhang,^c and Jürgen Fabian^d

^aDepartments of Chemistry, The University of Arizona, Tucson, AZ 85721, ^bThe University of Kansas, Lawrence, KS 66045, ^cState University of New York at Albany, Albany, NY 12222, ^dTechnische Universität Dresden, D-01062, Dresden, Germany

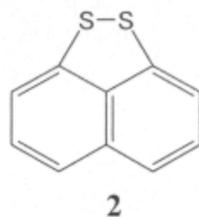
1,2-Dithiins, **1**, X=S, occur naturally in plants of the sunflower (*Asteraceae*) family and show a wide range of biological activity. These compounds^{1,2} and their



1a, X=S, R=H ; **f**, X=S, R=Ph
b, X=S, R=Me ; **g**, X=S, R=CF₃
c, X=S, R=i-Pr ; **h**, X=S, R=CF₃CF₂
d, X=S, R=t-Bu ; **i**, X=Se, R=H
e, X=S, R=CH₂OH ; **j**, X=Se, R=t-Bu

selenium analogues³ have become available synthetically. Consequently, their oxidation, which is of chemical and potential biological interest, was studied. To more fully understand their unusual redox behavior electrochemical, computational and photoelectron spectroscopic approaches were undertaken.^{4,5}

1,2-Dithiins **1a-f** were studied by cyclic voltammetry in acetonitrile using a platinum electrode. Typically a reversible one-electron oxidation followed by an irreversible oxidation at a more positive potential were found. The peak potentials versus a Ag/0.1M AgNO₃ in acetonitrile reference electrode measured at a scan rate of 100 mV/s are listed in the Table. 1,2-Dithiins **1g** and **1h** and 1,2-diselenins **1i** and **1j** provided analogous results, if a glassy carbon electrode was used instead of a platinum electrode. These results are listed in the Table also. The gas phase ionization potentials of lowest energy for these compounds were determined by photoelectron spectroscopy. These results are compiled in the Table. Comparison of these results with the electrochemical results reveal that the gas phase ionization potentials of lowest energy do not correlate with the peak potentials at lowest potential. Furthermore, the lowest oxidation potential of compound **2**⁶ is comparable with that of **1a**

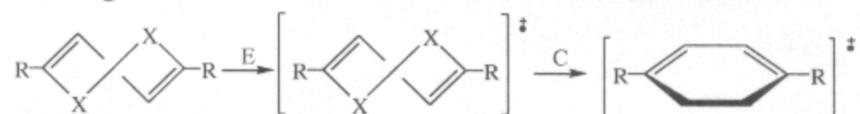


but its lowest ionization potential⁷ is about 1 eV lower than that of **1a**. A more detailed cyclic voltammetric study of **1b** and **1f** over a range of scan rates and concentrations provided data that could be fitted assuming an EC mechanism.

Theoretical calculations on **1a**, **1b** and **1i** and the corresponding radical cations were carried out at the MP2/6-31+G* level for **1a** and **1b** and MP2/6-311+G** for **1i**. The geometries of each of the species were optimized to give the lowest energy. In each case, the 1,2-dichalcogenin adopted a puckered conformation but the radical cations were flattened or planar. Comparison of the calculated lowest energy geometry for **1a** with the

geometry obtained by gas phase microwave spectroscopic analysis⁸ showed excellent agreement. Furthermore, the calculated ionization potentials agreed with the experimental values.

These complementary studies provide mechanistic insight into the electrochemical oxidation of 1,2-dichalcogenins. It is proposed that one-electron oxidation of the puckered 1,2-dichalcogenin provides the metastable puckered radical cation (E step) which then undergoes a conformational change to the flattened or planar form (C step) as shown below. Since the rate of heterogeneous electron transfer for these oxidations is in



the normal range, geometry change concerted with electron transfer, which is expected to result in a small heterogeneous rate constant, is not believed to occur.

Table. Oxidation of 1,2-Dichalcogenins

Compd	E_p^1, V^a	E_p^2, V^a	I.P. ^b
1a	0.70	c	8.16
1b	0.65	1.21	7.78
1c	0.68	1.22	7.67
1d	0.68	1.10	7.65
1e	0.58	1.23	8.01
1f	0.75	1.04	-
1g	1.25	1.40	9.10
1h	1.48	1.67	9.06
1i	0.53	1.3	7.93
1j	0.57	1.1	7.52

^aPeak potentials determined by cyclic voltammetry at a scan rate of 100 mV/s versus Ag/0.1 M AgNO₃ in acetonitrile reference electrode

^bLowest ionization potential determined by gas phase photoelectron spectroscopy

^cNo other oxidation peak is observed up to +1.6 V

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