

1,2-Oxathiolane – A Photoelectron Spectroscopic Study

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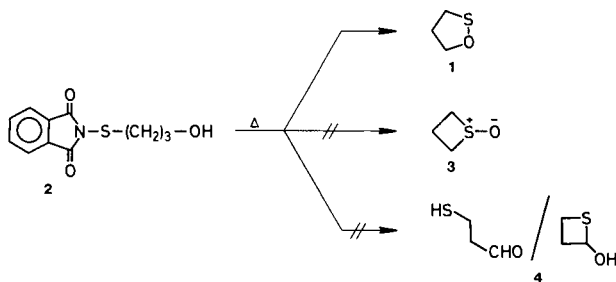
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1,2-Oxathiolan – Eine photoelektronenspektroskopische Studie

Der cyclische Sulfensäureester 1,2-Oxathiolan (**1**) wurde durch milde Thermolyse von 3-(Phthalimidothio)-1-propanol (**2**) gewonnen und durch Photoelektronen-Spektroskopie identifiziert. – Die Möglichkeiten zur photoelektronenspektroskopischen Bestimmung der Konformation von Sulfensäureestern werden diskutiert.

In connection with our current studies on disulfides¹⁾ (R–S–S–R') and sulfenates²⁾ (R–S–O–R'), we here report a photoelectron (PE) spectroscopic study of the cyclic sulfenate 1,2-oxathiolane (**1**), which can be generated by smooth thermal decomposition of 3-(phthalimidothio)-1-propanol (**2**)^{3,4)}. Assuming the C–C–C moiety being intact cracking of **2** may *a priori* lead to 1,2-oxathiolane (**1**), thietane 1-oxide (**3**) and/or 3-mercaptopropanal/thietan-2-ol (**4**)⁵⁾. Chemical evidence supports the presence of 1,2-oxathiolane (**1**) in solution, but thietane 1-oxide (**3**) cannot be ruled out³⁾. In the gas phase the only observed product is 1,2-oxathiolane (**1**)⁴⁾.



PE spectroscopy has proven to be a powerful method for real-time gas phase characterization of species generated by pyrolysis⁶⁾. The PE spectrum of the thermal decomposition product of **2**, depicted in Figure 1 together with the PE spectra of thietane 1-oxide (**3**) and 3-mercaptopropanal/thietan-2-ol (**4**), clearly reveals 1,2-oxathiolane (**1**) as being the product. The alternative products (*i. e.* **3** and **4**) both exhibit two low energy ionizations with relatively small separation (cf. Table 1), in agreement with the PE spectra of related compounds⁷⁾.

The PE spectrum of 1,2-oxathiolane (**1**) (cf. Figure 1) exhibits a single low energy ionization at 8.51 eV followed by a second ionization at 10.89 eV. The two ionizations can be assigned to arise

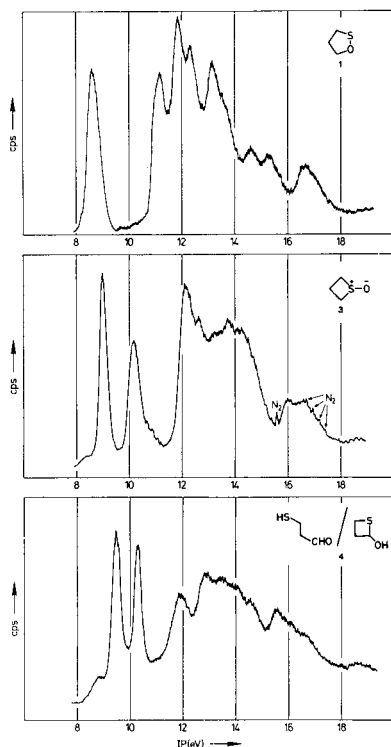


Figure 1. Photoelectron spectra of 1,2-oxathiolane (**1**), (top), thietane 1-oxide (**3**) (middle) and 3-mercaptoopropanal/thietan-2-ol (**4**) (bottom) recorded on a Perkin-Elmer PS-18 spectrometer at room temperature with a resolution of 35 meV, using Ar and Xe as internal calibrants

Table 1. Experimentally determined ionization energies (*IE*) for 1,2-oxathiolane (**1**), thietane 1-oxide (**3**) and 3-mercaptoopropanal/thietan-2-ol (**4**) together with assignments based on model compounds (all values in eV)

Band	1		3		4	
	<i>IE</i>		<i>IE</i>		<i>IE</i>	
1	8.51	$n_S(\pi)$	8.96	n_S	9.45	n_S
2	10.89	$n_O(\pi)$	10.14 ^{a)}	π_{SO}	10.28	n_O
3	11.8		12.00		11.8	

^{a)} The slope of the high energy side of this band suggests the presence of a minor impurity (cf. Figure 1).

predominantly from the $n_S(\pi)$ and $n_O(\pi)$ lone pair orbitals⁸⁾, respectively, as illustrated in the qualitative orbital interaction diagram in Figure 2.

The observed energy gap in non-symmetrical systems such as sulfenates ($\Delta IE_{obs} = 2.38$ eV for **1**) has to be corrected with the difference in basis orbital energies^{9,10)}.

$$\Delta IE_{corrected} = \Delta IE_{observed} - \Delta IE_{basis} \quad (\text{eqn. 1})$$

The basis orbital energies can be deduced from the ionization energies of the $n_S(\pi)$ and $n_O(\pi)$ lone pairs in tetrahydrothiophene and tetrahydrofuran, respectively⁸⁾, by applying already known values for the inductive stabilization caused by replacement of a methylene group by an oxygen (≈ 0.7 eV)^{8b,11,12)} and sulfur (≈ 0.4 eV)¹²⁾, respectively.

The corrected energy difference for 1,2-oxathiolane (**1**) $\Delta IE_{\text{corrected}} = (10.89 - 8.51) - [(9.57 + 0.40) - (8.40 + 0.70)] = 1.51$ eV (cf. Figure 2 and eqn. 1) can be compared with the energy differences for the symmetrical species 1,2-dithiolane (1.72 eV)¹³⁾ and 1,2-dioxolane (1.27 eV)¹¹⁾ which suggests the dihedral angle about the hetero-hetero bond in **1** to be between the values found in 1,2-dithiolane ($\approx 30^\circ$)^{10,13)} and 1,2-dioxolane ($\approx 50^\circ$)¹⁴⁾.

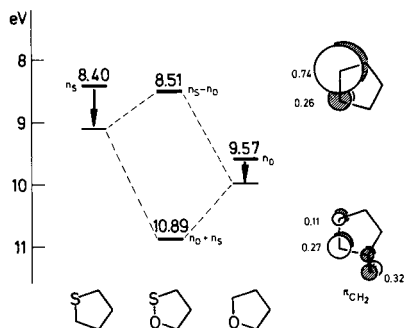


Figure 2. Correlation diagram for the highest occupied orbitals of 1,2-oxathiolane (**1**), tetrahydrofuran and tetrahydrothiophene. The black arrows represent the inductive effects introduced by the second hetero atom. The numbers shown at the levels are vertical ionization energies (eV). The shapes of the two highest occupied molecular orbitals calculated by MNDO for the planar form of 1,2-oxathiolane (**1**) are given by circles; the numbers shown beside are the square of the atomic orbital coefficients

Preliminary MNDO calculations^{15,16)} of 1,2-oxathiolane (**1**) seem to favour a planar structure; however, the stabilization of the planar structure relative to conformations with a dihedral angle about the S–O bond up to 30°C is calculated to be less than 1 kcal/mol. The calculated preference for a planar structure may be an artefact due to the well-known tendency of the MNDO method to overestimate the stability of planar structures¹⁶⁾. Nevertheless, the MNDO calculations find the two highest occupied orbitals predominantly to be the $n_S(\pi)$ and $n_O(\pi)$ orbitals, respectively (cf. Figure 2), with a separation on 2.41 eV for the planar form and a decreasing separation for increasing dihedral angle.

An exact PE spectroscopic determination of the dihedral angle about the S–O bond in sulfenates may only be possible if a series of sulfenates with different conformations are available, and if reasonable basis orbital energies can be derived in each case.

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