

Flash Vacuum Thermolysis of 4*H*-3,1-Benzoxathiin-4-thione: UV-Photoelectron Spectroscopy Characterization and Quantum Chemistry Studies

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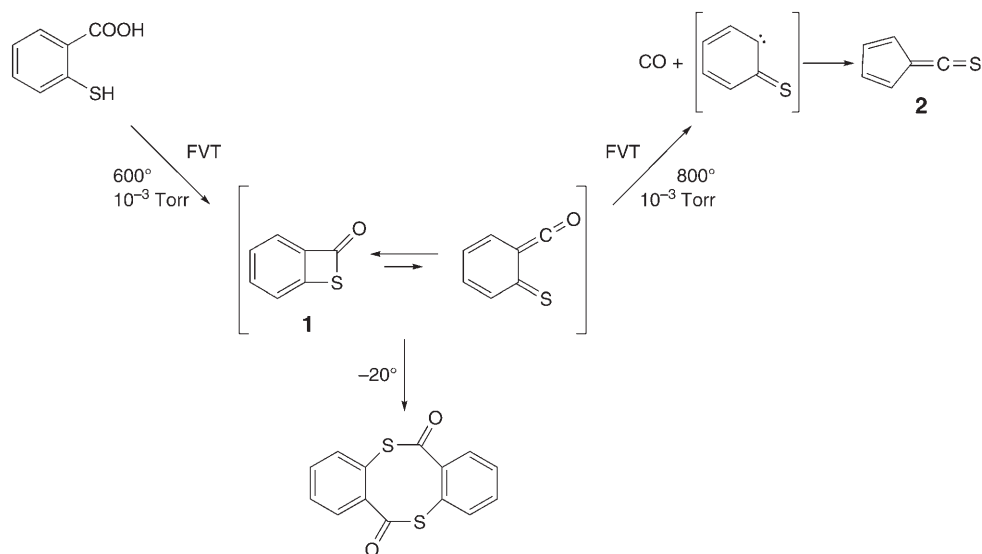
The mechanism of the reaction of 4*H*-3,1-benzoxathiin-4-thione (**3**) under flash vacuum thermolysis conditions has been studied by UV-photoelectron spectra. It was shown that in the first step of the reaction at 400° **3** underwent the *Schönberg–Newman–Kwart* rearrangement to give 4*H*-1,3-benzodithiin-4-one (**6**). Increasing of the temperature to 650° resulted in the elimination of thioformaldehyde and the formation of benzothiet-2-one (**1**). Subsequent elevation of the temperature prompted presumably the ring opening of **1** to (6-thioxocyclohexa-2,4-dien-1-ylidene)methanone (**7**) (at 680°), which at 700° eliminated CO and underwent a *Wolff*-type ring contraction to give (cyclopenta-2,4-dien-1-ylidene)methanethione (**2**). UV-Photoelectron spectra were recorded at different steps of the reaction and analyzed considering the theoretical evaluation of ionization potentials.

Introduction. – Benzothiet-2-one (= 7-thiabicyclo[4.2.0]octa-1,3,5-trien-8-one; **1**) has been shown to be a transient intermediate in many photochemical and thermal organic reactions. This product can be obtained by flash vacuum thermolysis (FVT) of 2-sulfanylbenzoic acid or benzo[*b*]thiophene-2,3-dione at 600–610° [1], as well as photolytically, starting either from 4*H*-1,2,3-benzothiadiazin-4-one [2] or from 2-phenyl-4*H*-3,1-benzoxathiin-4-one [3]. **1** is stable only below –20° in the solid state; above this temperature, rapid polymerization, as well as partial di- and trimerization takes place. Above 800°, the loss of CO from **1** and a *Wolff*-type ring contraction to give (cyclopenta-2,4-dien-1-ylidene)methanethione (**2**) were mentioned [4] (*Scheme 1*).

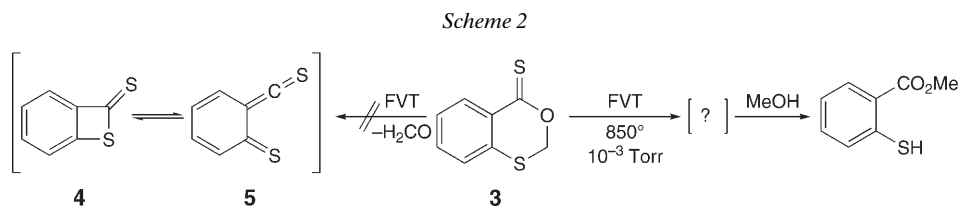
It is noteworthy that the analogous 2*H*-naphtho[2,3-*b*]thiet-2-one was successfully isolated and identified at room temperature [4]. Both thiet-2-ones were characterized by IR, ¹H- and ¹³C-NMR spectra [4], and, additionally, UV-photoelectron spectra of **1** were registered [1]. Although the more stable ring in **1** could exist in equilibrium with its ring-opened valence tautomer, the latter has not been detected until now. In contrast, the open keto-ketene form of the dioxygen analogue has been characterized by photoelectron spectra [1].

Recently, we have shown that **1** could also be obtained by flash vacuum thermolysis of 4*H*-3,1-benzoxathiin-4-thione (**3**) [5]. The present paper is mainly aimed at the study of relevant details of the mechanism of this transformation.

Scheme 1



Results and Discussion. – The preparative FVT experiment of **3** with MeOH trapping yielded 2-sulfanylbenzoic acid methyl ester as the sole product [5]. The elimination of formaldehyde and the formation of the sulfanylbenzoic acid ester *via* the reaction of MeOH with transient benzothiet-2-thione (= 7-thiabicyclo[4.2.0]octa-1,3,5-triene-8-thione; **4**) or its ring-opened isomer 6-thiocarbonyl-2,4-cyclohexadiene-1-thione **5** has not been detected (*Scheme 2*).



FVT of **3** in conjunction with variable-temperature UV-photoelectron spectral detection has been applied to directly follow the progress of this reaction, and thus to elucidate the mechanism of this transformation. In the first step of our experimental study, the spectrum of 4H-3,1-benzoxathiin-4-thione (**3**) has been recorded at 300° (*Fig. 1*). First, the broad band with three well distinguished bands at 8.2, 8.6 and 8.9 eV is observed in the lower energy part of the spectrum. Then, a sharp and intense ionization at 9.7 eV is followed by a broad and less intense one at 10.45 eV.

The interpretation of the photoelectron (PE) spectra is not straightforward, therefore the theoretical estimation of ionization potentials (IP) has been carried

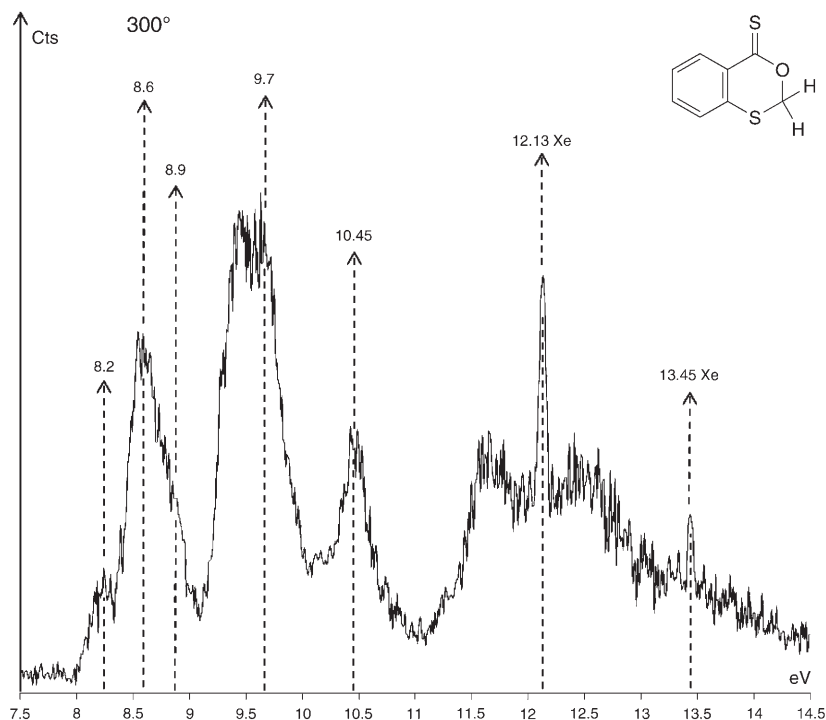


Fig. 1. Photoelectron spectrum of **3** at 300°

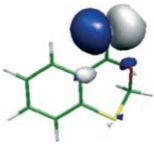
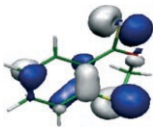
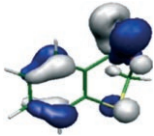
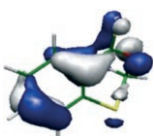
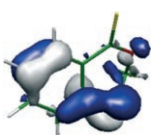
out after full optimization of geometrical parameters of **3**¹⁾ and is displayed in Table 1.

Considering these experimental and theoretical data for **3**, the first IP at 8.2 eV corresponds to the ejection of one electron from the S σ -lone pair of the C=S group, the second IP at 8.6 eV reflects mainly the antibonding interaction of the S π -lone pair and the π_3 orbital of the aromatic ring, 8.9 eV IP appears as a shoulder and has been attributed to the ionization of the C=S bond. Two PE bands at 9.7 and 10.45 eV correspond to the aromatic π electrons interacting with O and S lone pairs of the same symmetry. In this case, the good coherence between experimental and theoretical values should be underlined.

At 430°, the PES (photoelectron spectrum) has changed (Fig. 2), and the appearance of three new ionizations at 8.45, 8.8, and 10.2 eV is accompanied with modifications of the intensity of the bands at 9.4 and 9.6 eV. The comparison of these experimental data with the calculated ones of the thioketene **5**¹⁾ (for which the first two IPs are expected in the range of ca. 7.2–7.7 eV; Table 2), or with those of **4**¹⁾ (for which lower energy ionizations are expected at 8.2–8.4, 8.4–8.6, 9.2–9.3 eV; Table 3), (supposed reaction path in Scheme 2), excludes their formation, considering the most important fact, that the formaldehyde IP at 10.88 eV is not present in this spectrum.

¹⁾ The geometrical parameters are available as supporting material from the authors.

Table 1. Calculated and Experimental IPs of 4H-3,1-Benzoxathiin-4-thione (**3**) (all values in eV, * Δ SCF, **Exp. IP)

| Molecular orbital | $-\epsilon^{\text{KS}}$ | TD-DFT | 'Corrected' $x=2.00$ | OVGF | Exp. |
|--|-------------------------|--------|----------------------|-------|-------|
|  | 6.20 | 8.13* | 8.20** | 8.17 | 8.2 |
|  | 6.69 | 8.56 | 8.69 | 8.44 | 8.6 |
|  | 7.04 | 8.82 | 9.04 | 8.69 | 8.9 |
|  | 8.08 | 9.80 | 10.08 | 9.91 | 9.7 |
|  | 8.45 | 10.13 | 10.45 | 10.34 | 10.45 |

Therefore, the first step of FVT of **3** at 400° does neither lead to **5** or to **4**. Thus, the hypothesis that the first step of this reaction should correspond to the *Schönberg–Newman–Kwart* rearrangement [6] has been proposed (*Scheme 3*).

The analysis of the PES (*Fig. 2*) has been performed considering calculated (*Table 4*) and experimental data for the rearranged molecule **6** (=4H-1,3-benzodithiin-4-one), and the new band at 8.45 eV has been attributed to the ionization of the S π -lone pair. The second band at 8.8 eV corresponds to the ejection of an electron from the orbital corresponding to the antibonding interaction between the second S lone pair and the C=O group ($n_{\text{S}}^{\pi} - \pi_{\text{C=O}}$), while the third PE band at 9.4 eV is associated with the antibonding interaction between S and O σ -lone pairs. The fourth and fifth bands are due to the ionization of the π -system of the aromatic ring ($\pi_3, \pi_2 + n_{\text{S}}^{\pi}$). According to the total energy comparison, **6**¹) is more stable than **3** by 12.2 kcal/mol.

Further increase of the temperature allowed us to remark an important change in the spectrum at 650°: appearance of the very sharp and intense band at 9.4 eV (*Fig. 3*), corresponding to the ionization of the S σ -lone pair of H₂C=S [7]; this fact confirms the *retro-Diels–Alder* cleavage as presented in *Scheme 3*.

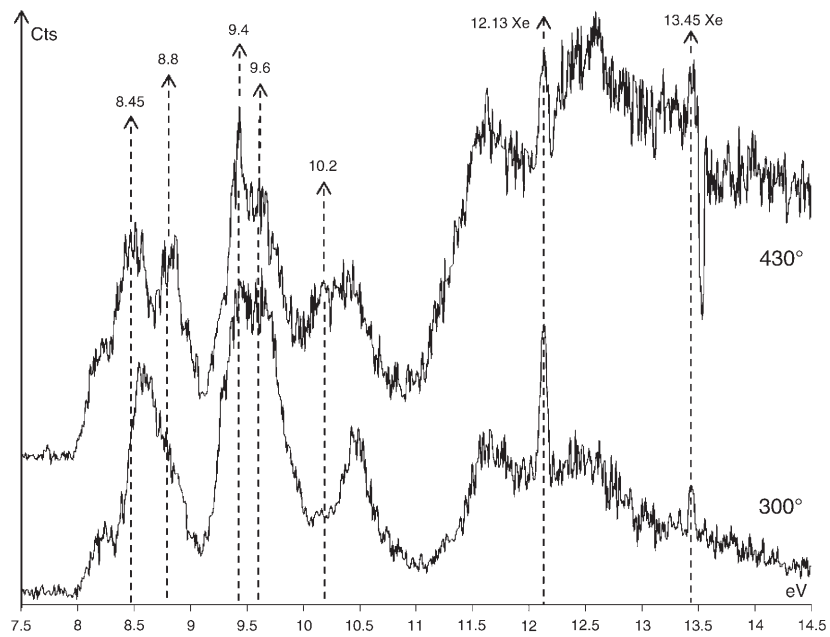


Fig. 2. Comparison of the photoelectron spectra of **3** at 300° and 430°

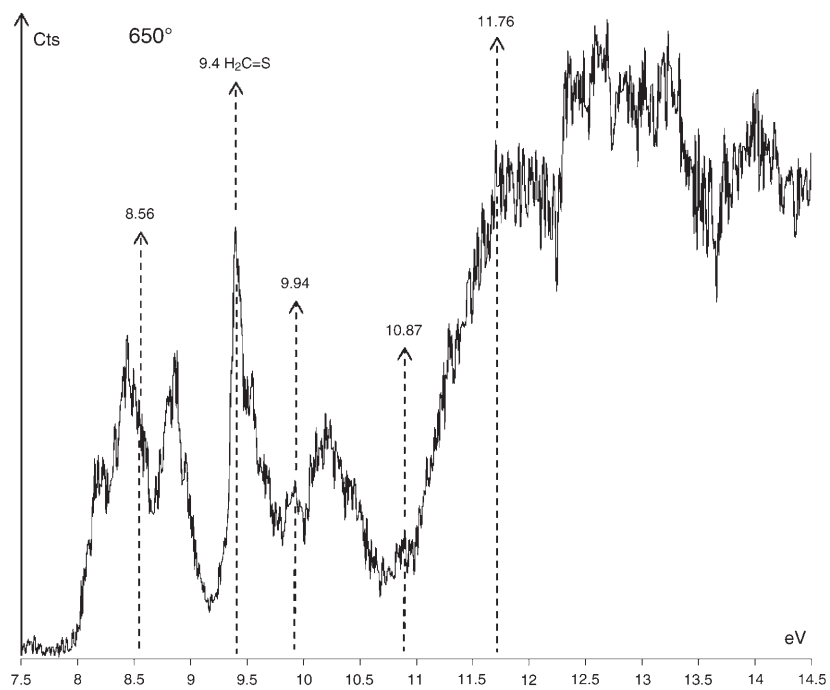
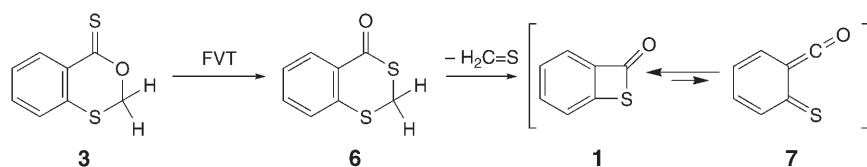


Fig. 3. Photoelectron spectrum of **3** at 650°

Table 2. Calculated IPs of Thioketene **5** (all values in eV, * Δ SCF)

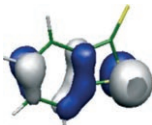
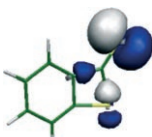
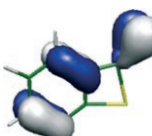
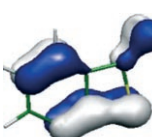
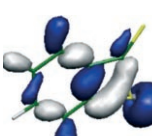
| Molecular orbital | $-\epsilon^{\text{KS}}$ | TD-DFT | 'Corrected' $x = 1.73$ | OVGf |
|-------------------|-------------------------|--------|------------------------|-------|
| A'' | 5.83 | 7.56* | 7.56* | 7.23 |
| A' | 5.86 | 7.68 | 7.59 | 7.63 |
| A'' | 7.86 | 9.62 | 9.59 | 9.36 |
| A'' | 8.44 | 10.62 | 10.17 | 10.00 |
| A' | 9.47 | 11.32 | 11.20 | 10.43 |

Scheme 3



For a reliable identification of these experimental data, the theoretical study has started by the energy comparison of two isomers¹), thus **1** is more stable than (6-thioxo-2,4-cyclohexadien-1-ylidene)methanone (**7**) by only 9.9 kcal/mol, and the barrier height of this transformation requires solely 10.1 kcal/mol (B3LYP/6-311G(d,p)). According to the earlier work of *Schweig* [1], four main ionizations at 8.56, 9.94, 10.87, and 11.76 eV are characteristic of **1**, and indeed they are clearly visible in our spectrum of **3** at 650° (*Fig. 3, Table 5*). The first IP corresponds to the ejection of an electron from the S-atom lone pair in antibonding interaction with π -electrons of the aromatic ring. The second band contains two ionizations; the first one of σ -symmetry reflects the

Table 3. Calculated IPs of **4** (all values in eV, * Δ SCF)

| Molecular orbital | $-\epsilon^{\text{KS}}$ | TD-DFT | 'Corrected' $x = 1.87$ | OVGf |
|---|-------------------------|--------|------------------------|-------|
| A''  | 6.54 | 8.41* | 8.41* | 8.16 |
| A'  | 6.69 | 8.48 | 8.56 | 8.57 |
| A''  | 7.48 | 9.27 | 9.35 | 9.21 |
| A''  | 8.31 | 10.23 | 10.18 | 10.06 |
| A'  | 9.33 | 11.24 | 11.20 | 11.25 |

antibonding interaction of the S and O σ -lone pairs, the second one is associated with the π_3 orbital. The third band corresponds to the antibonding interaction of the S π -lone pair, C=O group, and π_2 orbital. The last one is associated with σ -bond ionizations.

With a slight increase of the temperature (to 680°), the appearance of new bands at 8.15 eV and 10.2 eV has been noticed as well as the lowering of 9.94 eV band intensity (Fig. 4). Thus, the presence of the less stable ketene isomer **7** has been supposed.

In fact, on the basis of the time-dependent density functional theory (TD-DFT) and Outer Valence Green's Function (OVGF) theoretical predictions of the IPs for **7** (Table 6), its PES observation cannot be excluded. In this case, the first band observed at 8.15 eV should correspond to the ejection of an electron from the totally antibonding combination of π -orbitals ($\pi_{\text{C=C}}^- - n_{\text{S}}^{\pi} - n_{\text{O}}^{\pi}$) and the S-atom lone pair ionization n_{S}^{σ} . The band located at 10.2 eV should contain ionization of the π system: $\pi_3 - n_{\text{O}}^{\pi}$ and the one at 10.9 eV corresponds to $\pi_3 - \pi_{\text{C=S}}$. Finally, the 11.8 eV PE band should reflect the S σ -lone pair in interaction with σ -bonds of the molecule.

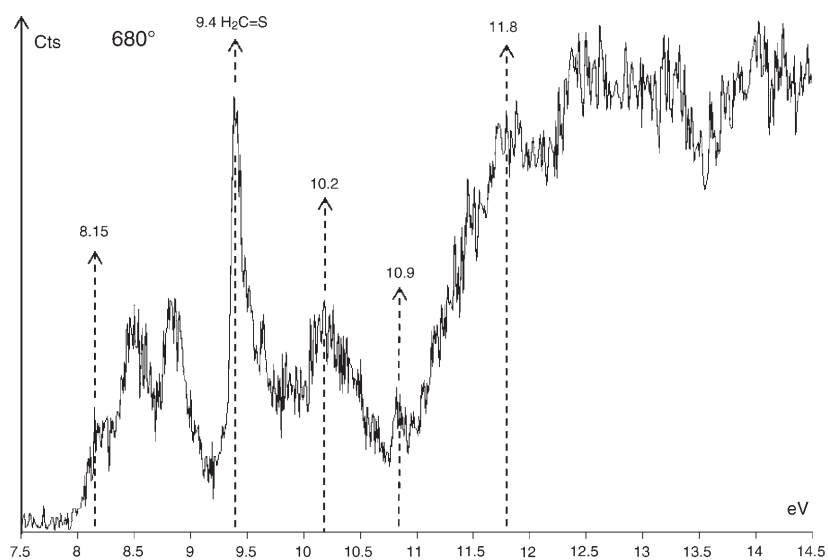


Fig. 4. Photoelectron spectrum of **3** at 680°

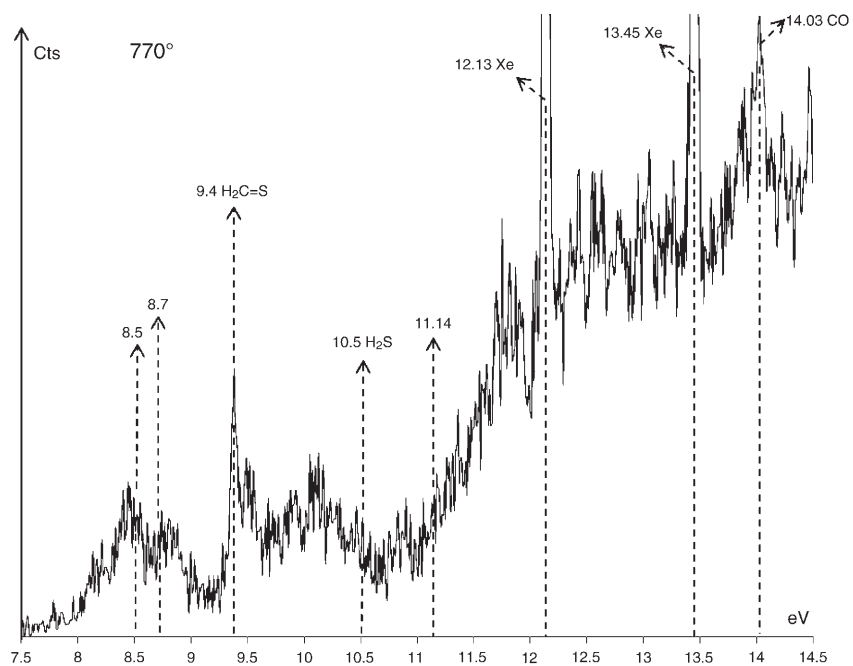
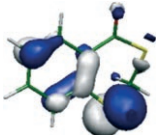
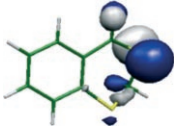
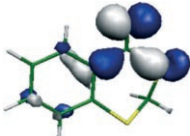
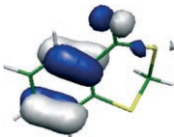
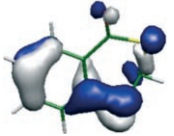
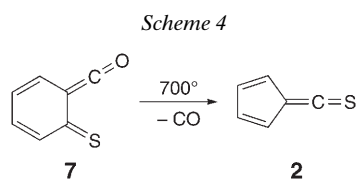


Fig. 5. Photoelectron spectrum of **3** at 770°

Table 4. *Calculated and Experimental IPs of 6* (all values in eV, * Δ SCF, **Exp. IP)

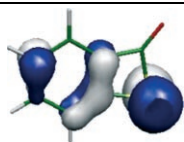
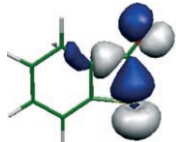
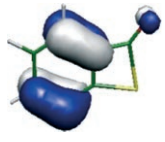
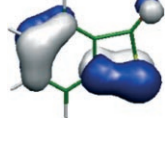
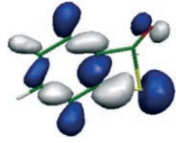
| Molecular orbital | $-\varepsilon^{\text{KS}}$ | TD-DFT | 'Corrected' $x = 1.89$ | OVSF | Exp. |
|--|----------------------------|--------|------------------------|-------|------|
|  | 6.56 | 8.44* | 8.45** | 8.30 | 8.45 |
|  | 7.13 | 8.77 | 9.02 | 9.02 | 8.8 |
|  | 7.44 | 9.03 | 9.33 | 9.30 | 9.4 |
|  | 7.67 | 9.35 | 9.56 | 9.88 | 9.6 |
|  | 8.33 | 10.31 | 10.22 | 10.03 | 10.2 |



In the next step of this thermal decomposition, **7** may lose C=O and generate **2** as suggested in *Scheme 4*.

In fact, the spectrum corresponding to the FVT of **3** at 770° (*Fig. 5*) contains the CO ionization at 14.03 eV. The first three IPs observed in this spectrum are in good agreement with the previously published data [1], and are equal to 8.5 eV, 8.7 eV and 11.14 eV. The band at 10.5 eV corresponds to the H₂S IP and indicates rather high instability of these intermediates and secondary reaction pathways. Moreover, the final state leading to the formation of CO and **2** is 26.3 kcal/mol energetically less stable than **7** and thus, corroborates the hypothesis of the latter formation at 680°.

Table 5. Calculated and Experimental IPs of **1** (all values in eV, * Δ SCF, **Exp. IP)

| Molecular orbital | $-\epsilon^{\text{KS}}$ | TD-DFT | 'Corrected' $x=2.16$ | OVGf | Exp. |
|---|-------------------------|--------|----------------------|-------|-------|
| A''  | 6.40 | 8.41* | 8.56** | 8.13 | 8.56 |
| A'  | 7.69 | 9.75 | 8.85 | 9.59 | 9.94 |
| A''  | 7.88 | 9.78 | 10.04 | 9.79 | 9.94 |
| A''  | 8.66 | 10.79 | 10.82 | 10.52 | 10.87 |
| A'  | 9.60 | 11.60 | 11.76 | 11.68 | 11.76 |

As a first step of the studied reaction, the *Schönberg–Newman–Kwart* rearrangement [6] has been postulated. To improve this hypothesis by an independent experiment, 2-benzofuran-1(3*H*)-thione (**8**) has been synthesized and submitted to the FVT-PES experiment (*Scheme 5*).

The spectrum of the starting compound has been recorded at 200° (*Fig. 6*), and its interpretation has been done, as previously, by comparison with theoretical estimation of ionization potentials (*Table 7*).

Calculated IPs have allowed the assignment of the first PE band at 8.5 eV to the ejection of an electron from the HOMO, which corresponds to the S lone pair in the σ -plane. The second band at 8.9 eV corresponds to the C=S group ionization, while the third one at 9.7 eV is attributed to the ejection of an electron from the π_3 orbital of the aromatic ring. The two next bands localized at 10.2 and 11.9 eV are significant of the ionization of the π_2 aromatic ring orbital in antibonding interaction with the S π -lone pair and σ -bond electron ejection, respectively. In this case, the third and fourth TD-DFT IPs are strongly incoherent with the rest of the calculated values.

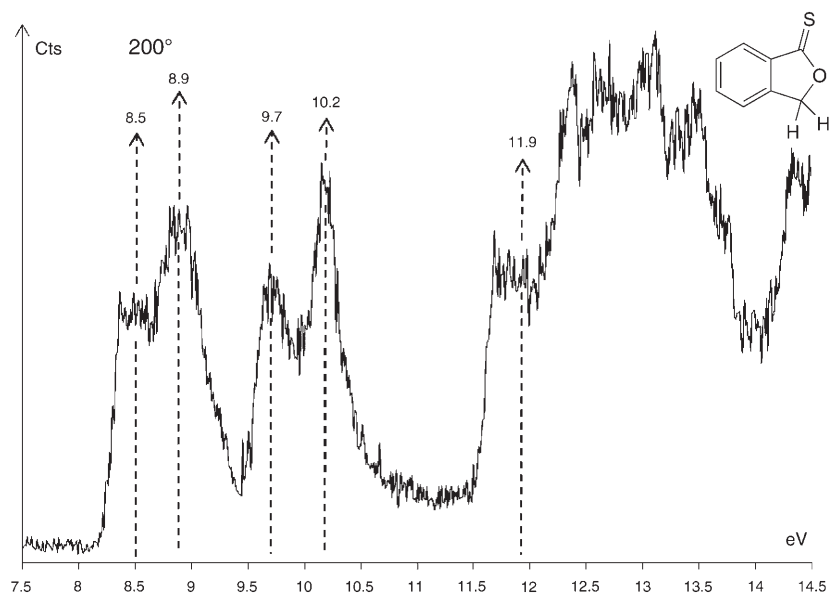
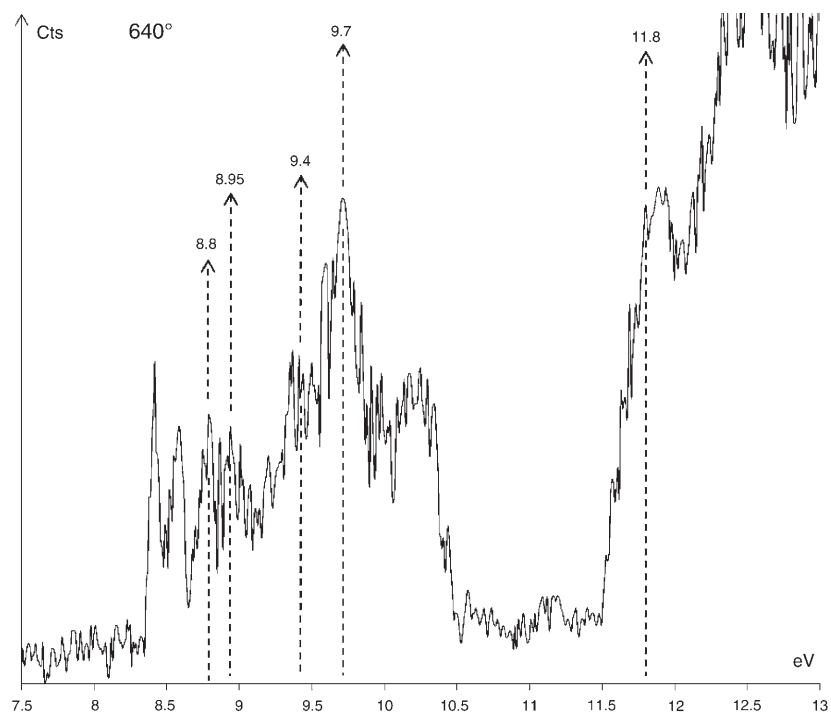
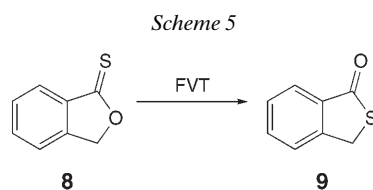
Fig. 6. Photoelectron spectrum of **8** at 200°Fig. 7. Photoelectron spectrum of **8** at 640°

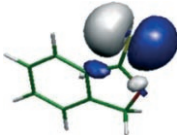
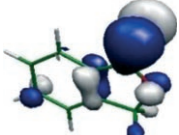
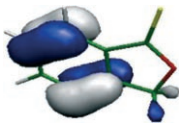
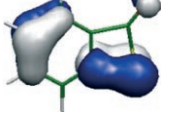
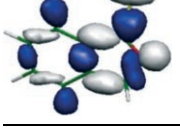
Table 6. *Calculated and Supposed Experimental IPs of 7* (all values in eV, * Δ SCF, **Exp. IP)

| Molecular orbital | $-\epsilon^{\text{KS}}$ | TD-DFT | 'Corrected' $x = 2.26$ | OVSF | Exp. |
|-------------------|-------------------------|--------|------------------------|-------|------|
| A'' | 5.89 | 7.77* | 8.15** | 7.41 | 8.15 |
| A' | 6.00 | 8.02 | 8.26 | 7.82 | 8.15 |
| A'' | 8.32 | 10.26 | 10.58 | 9.99 | 10.2 |
| A'' | 8.62 | 10.33 | 10.88 | 10.28 | 10.9 |
| A' | 9.77 | 11.81 | 12.03 | 11.75 | 11.8 |



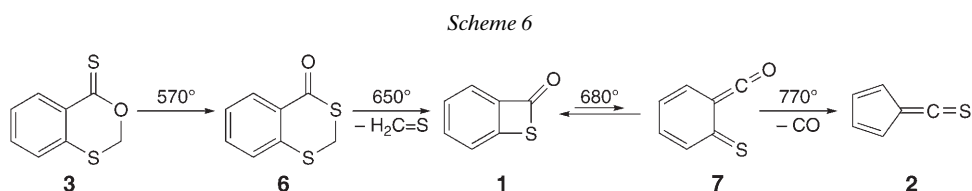
At 640°, the PES has changed (*Fig. 7*). Considering the B3LYP/6-311G(d,p) total energy values for **8**¹) and **9**¹), 2-benzothiophen-1(3*H*)-one (**9**) is more stable than 2-benzofuran-1(3*H*)-thione (**8**) by 14.3 kcal/mol. By comparison with the theoretical evaluation of the IPs of **9** (*Table 8*), the two first very close IPs at 8.8 and 8.95 eV have been attributed to the ejection of an electron from the orbital corresponding to the antibonding interaction of S and O lone pairs in π and σ plane, respectively. The third and fourth IPs are attributed to the ejection of an electron from the π aromatic ring

Table 7. Calculated and Experimental IPs of **8** (all values in eV, * Δ SCF, **Exp. IP)

| Molecular orbital | $-e^{\text{KS}}$ | TD-DFT | 'Corrected' $x = 2.34$ | OVSF | Exp. |
|--|------------------|--------|------------------------|-------|------|
|  | 6.16 | 8.34* | 8.5** | 8.19 | 8.5 |
|  | 6.76 | 8.56 | 9.10 | 8.50 | 8.9 |
|  | 7.66 | 8.86 | 10.00 | 9.58 | 9.7 |
|  | 8.03 | 9.56 | 10.37 | 9.92 | 10.2 |
|  | 9.71 | 11.27 | 12.05 | 11.94 | 11.9 |

bonds (π_2 and π_3), while the fifth PE band at 11.8 eV reflects mainly the S σ -lone pair ionization. Particularly good agreement of calculated values and experimental data has to be underlined, and thus confirms the formation of **9** by thermal rearrangement of **8**.

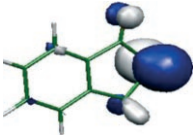
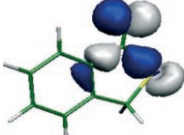
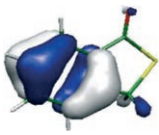
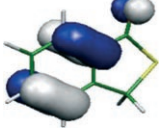
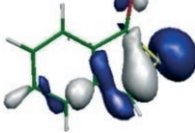
In summary, the detailed mechanism of the thermal decomposition of **3** has been proposed as shown in *Scheme 6*.



The following conclusions can be drawn:

- a) The first IP of the studied precursors **3** and **8** corresponds to the ejection of an electron from the σ -lone pair of the S atom of the C=S group.

Table 8. *Calculated and Experimental IPs of 9* (all values in eV, * Δ SCF, **Exp. IP)

| Molecular orbital | $-\varepsilon^{\text{KS}}$ | TD-DFT | 'Corrected' $x = 1.80$ | OVGf | Exp. |
|--|----------------------------|--------|------------------------|-------|------|
|  | 7.00 | 9.01* | 8.80** | 9.14 | 8.8 |
|  | 7.30 | 9.26 | 9.10 | 9.28 | 8.95 |
|  | 7.50 | 9.28 | 9.30 | 9.34 | 9.4 |
|  | 7.65 | 9.64 | 9.45 | 9.59 | 9.7 |
|  | 9.56 | 11.61 | 11.36 | 11.69 | 11.8 |

- b) The energetic position of the C=S bond is the same in the two precursors (**3** and **8**).
- c) The first step of the studied reactions occurs *via* a *Schönberg–Newman–Kwart* rearrangement.
- d) The S lone pair in the rearranged compounds **6** and **9** is subjected to the strong electron withdrawing effect of the C=O group and its IP is equal to 8.8 eV.
- e) UV-PES Experiments in conjunction with quantum calculations of IPs confirm the formation of **1** and **2** as thermal decomposition intermediates in FVT of **3**; formation of the less stable **7** is supposed.

The replacement of the O-atom in the C=O group of lactons by an S-atom results in an unexpected course of the FVT.

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Experimental Part

1. *Starting Material.* 4H-3,1-Benzoxathiin-4-thione (**3**) and 2-benzofuran-1(3H)-thione (**8**) were prepared following the literature procedures [5] and [8], resp.

2. *Thermolysis and Photoelectron Spectra.* The photoelectron spectra (PES) were recorded on a home-built, three-part spectrometer equipped with a spherical analyzer (*Omicron*), main body device (*Meca2000*), HeI radiation source (*Focus*), and monitored by a microcomputer supplemented with a digital–analog converter. The spectra were calibrated against the auto-ionization of Xe at 12.13 and 13.45 eV, and N₂ at 15.59 and 16.98 eV. They contain 2000 points and are accurate to 0.1 eV. Sample manipulations were carried out in a thermolysis oven attached directly to the inlet probe; the distance between the oven exit and the ionization head does not exceed 1 cm. Compounds **3** and **8** were slowly vaporized under low pressure (10^{−7} Torr in the ionization chamber) directly in the oven, and the gaseous thermolysate was continuously analyzed.

3. *Computational Details.* The calculations were performed using the Gaussian 98 [9] program packages. The 6-311G(d,p) basis set was used for all calculations since the inclusion of polarization functions is necessary for the accurate description of the neutral molecules containing third row atom and their cations. Geometry optimizations were carried out at the density functional theory (DFT) [10][11] level of theory with the B3LYP [12–14] functional and confirmed as true minima *via* frequency analysis¹). Ionization energies were calculated with Δ SCF-DFT which means that separate self-consistent field (SCF) calculations are performed to optimize the orbitals of the ground-state and the appropriate ionic state ($IE = E_{\text{cation}} - E_{\text{neut.mol.}}$). The time-dependent density functional theory (TD-DFT) [15][16] approach provides a first principles method for the calculation of excitation energies within a density functional context, taking into account the low lying ion calculated by Δ SCF method. The vertical ionization potentials were also calculated at the *ab initio* level according to the outer valence green's function (OVGF) [17][18] method. In this case, the effects of electron correlation and reorganization are included beyond the *Hartree–Fock* (HF) approximation and the self-energy part was expanded up to third order. To compare the ionization potentials resulting from these rigorous methods of calculation, we proceeded also to the currently used estimation of ionization potentials. Indeed, recent works [19–23] have shown that $\epsilon_{\text{f}}^{\text{KS}}$ could be linked up to experimental vertical ionization potentials (IP_{v}) by uniform shift $x = | -\epsilon_{\text{f}}(\text{HOMO}) - IP_{\text{v}}^{\text{exp}} |$. This approach gives a remarkable agreement with experimental values and is justified by the fact that the first calculated vertical ionization potential lies very close to experimental values. *Stowasser and Hoffman* [24] have shown that the localization of *Kohn–Sham* (KS) orbitals are very similar to those obtained after HF calculations.

DFT has been shown to predict various molecular properties successfully [12–14]. The advantages of the most employed method of calculations of the first ionization energies (Δ SCF-DFT calculations) have been thoroughly demonstrated [25–28]. On the other hand, the frequently used estimation of IPs by 'shifting' of calculated KF energies (a not very rigorous process, but nicely working) has also proved its efficacy. Nevertheless, we have to consider that each theoretical method of approaching ionization potentials is limited by the calculation procedure. In the Δ SCF method, we have to take into account that the single-configuration approximation is not valid when several ions of the same symmetry are near in energy. For the TD-DFT approach, the configuration interaction process is based on the quality of the evaluation of the low lying ion described by Δ SCF method. In the OVGF calculation, the quality of the theoretical results depends on the validity of the HF approximation.

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