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# Phenylsulfinyl Radical: Gas-phase Generation, Photoisomerization, and Oxidation

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**ABSTRACT:** Arylsulfinyl radicals are key intermediates in sulfoxide chemistry. As the parent molecule, phenylsulfinyl radical PhSO• has been generated for the first time in the gas phase through high-vacuum flash pyrolysis (HVFP) of PhS(O)R ( $R = CF_3$  and Cl) at about 1000 K. Upon UV light irradiation (365 nm), PhSO• isomerizes to a novel oxathiyl radical PhOS• in cryogenic matrices (2.8 K). Prolonged irradiation causes further isomerization of PhOS• to 2-hydroxyphenylthiyl radical, the formation of which has been also observed in the 193 nm laser photolysis of matrix-isolated 2-hydroxybenzenethiol. Concomitantly, ring-opening occurs during the UV photolysis of PhOS• and 2-hydroxybenzenethiol and forms an acyclic thioketoketene radical. Phenylsulfinyl radical reacts partially with molecular oxygen in the gas phase and yields phenyl radical Ph• and OSOO. Upon irradiation (365 nm), the isomeric oxathiyl radical also combines O<sub>2</sub> with immediate dissociation to phenoxy radical PhO• and SO<sub>2</sub>. The identification of the intermediates with IR and UV/Vis spectroscopy is supported by quantum chemical computations at the B3LYP/def2-TZVPP and UCCSD(T)/aug-cc-pV(D+d)Z levels of theory. The isomerization of PhSO• has been discussed based on the computed potential energy profile and the comparison with the intensively explored photochemistry of phenylperoxy radical PhO•.

#### INTRODUCTION

Sulfur-containing radicals like thiyl radicals R-S•,<sup>1-5</sup> sulfinyl radicals R-SO•,<sup>6-8</sup> sulfonyl radicals R-SO<sub>2</sub>•,<sup>9-12</sup> and sulfonyloxyl radicals R-SO<sub>3</sub>•<sup>13-15</sup> are highly relevant to atmospheric chemistry, biology, and organic synthesis. For instance, simple sulfinyl radicals HSO•<sup>16</sup> and CH<sub>3</sub>SO•<sup>17,18</sup> form as fleeting intermediates in the oxidation of volatile organic sulfur compounds (VOSCs) in the atmosphere. More complex cysteine sulfinyl radicals are involved in the oxidative damage of proteins induced by reactive oxygen species (ROSs).<sup>19,20</sup> Aryl-sulfinyl radicals ArSO• have been proposed as the key intermediates in a variety of chemical transformations, such as the thermal disproportionation of aryl arenethiolsulfinates,<sup>21-24</sup> the photolytic decomposition of arenesulfinate esters, aryl thiosulfinate,<sup>25-27</sup> and vic-disulfoxides,<sup>28</sup> the photochemical racemization of aryl sulfinamides,<sup>29,30</sup> the photosensitized oxidation aryl arenesulfoxides,<sup>31-33</sup> and the copper-catalyzed aerobic oxidation of thiols.<sup>34</sup>

As a member in the family of phenyl-substituted sulfurcentered radicals  $PhSO_x \cdot (x = 0-2, Scheme 1)$ , the parent arylsulfinyl radical  $PhSO \cdot$  has been frequently studied in solution. The first-time detection of  $PhSO \cdot$  in the photolysis and pyrolysis of S-aryl arenethiosulfonates and diaryl sulfoxides was accomplished using electron paramagnetic resonance (EPR) spectroscopy.<sup>27</sup> Later on, its presence in the photo-induced  $\alpha$ - cleavage of diphenyl sulfoxide was confirmed by nanosecond transient absorption spectroscopy with observed transitions ( $\lambda_{max}$ ) at 300 and 450 nm.<sup>35</sup> Recently, a transient absorption at 460 nm was observed in the photolytic C–S bond cleavage of the aryl benzyl sulfoxide radical cation.<sup>31-33</sup> More recently, PhSO• has been detected by EPR spectroscopy in functionalizing nanostructured SBA-15 silicas with diazene precursors.<sup>36</sup>





Similar to other sulfinyl radicals (CH<sub>3</sub>SO•,<sup>37</sup> CF<sub>3</sub>SO•,<sup>38</sup> and *t*-BuSO•<sup>6</sup>), computations of PhSO• at the B3LYP/6-31+G(d,p) level suggest that the spin density is almost entirely localized on the sulfur and oxygen atoms with equal contribution.<sup>35</sup>

However, unlike the spontaneous oxidation of CH<sub>3</sub>SO• by molecular oxygen in a solid Ar matrix under cryogenic conditions,<sup>13</sup> the reactivity of PhSO• with <sup>3</sup>O<sub>2</sub> in solution at room temperature is very low, and no oxidation product was identified.<sup>35</sup> Furthermore, solution studies demonstrate that PhSO• in the <sup>2</sup>A" ground state is a relatively inefficient singlet oxygen quencher due to the absence of a low-lying <sup>1</sup>A' state.<sup>39</sup>

In comparison to the thermally persistent sulfinyl radicals R-SO•, computational studies conclude that the isomeric oxathiyl radicals R-OS• have lower stability, which are the lowest among the related radicals R-SO• > R-SS• > R-OO• > R-OS•.<sup>40-42</sup> Nevertheless, the exceptionally high activation barriers associated with the interconversion between R-SO• and R-OS• (e.g., H, CH<sub>3</sub>, CF<sub>3</sub>, > 40 kcal mol<sup>-1</sup>) allowed isolation of an oxathiyl radical CF<sub>3</sub>OS• during UV light irradiation (266 or 254 nm) of the sulfinyl radical CF<sub>3</sub>SO• in solid noble gas matrices.<sup>38</sup> In sharp contrast, the oxathiyl radical PhOS• remains barely known, although the structurally related phenylperoxy radical PhOO•<sup>43-45</sup> and other phenyl-substituted sulfur-centered radicals like PhS•<sup>11</sup> and PhSO2•<sup>46</sup> have already been intensively studied in the last decades.

In continuation of our interest in the photochemistry of sulfur-containing radicals (e.g.,  $CH_3SO_3^{\bullet}$ ,<sup>14</sup>  $CH_3SO_2^{\bullet}$ ,<sup>12</sup> and  $CF_3SO^{\bullet 38}$ ), we herein report the first gas-phase generation of the phenylsulfinyl radical PhSO $\bullet$ , its photochemistry including isomerization and ring-opening, and the oxidation with molecular oxygen (Scheme 2), which is achieved by combining matrix isolation spectroscopy (IR and UV/Vis) with quantum chemical computations.

# Scheme 2. Generation, photochemistry, and oxidation of PhSO•.



## EXPERIMENTAL AND COMPUTATIONAL DETAILS

**Sample Preparation.** The commercially available PhS(O)CF<sub>3</sub> and 2-hydroxybenzenethiol were checked by <sup>13</sup>C NMR and gas-phase IR spectroscopy. Sulfinyl chloride PhS(O)Cl was prepared according to the published protocol,<sup>47</sup> and the purity was checked by using NMR spectroscopy (<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, tetramethylsilane (TMS))  $\delta$  = 7.55 (m, 5H) ppm, <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, TMS)  $\delta$  = 123.35, 129.14, 133.38, 148.18 ppm) with a Bruker Avance III HD400 spectrometer at 25 °C.

Matrix-isolation IR Spectroscopy. Matrix IR spectra were recorded on a FT-IR spectrometer (Bruker 70V) in a reflectance mode by using a transfer optic. A KBr beam splitter and liquid-nitrogen cooled MCT detector were used in the mid-IR region (4000–400 cm<sup>-1</sup>). Typically, 200 scans at a resolution of 0.5 cm<sup>-1</sup> were co-added for each spectrum. The gaseous PhS(O)CF<sub>3</sub>, PhS(O)Cl, and 2-hydroxybenzenethiol were mixed by Ar (1 : 1000) through a U-trap containing ca. 20 mg of corresponding samples at -28, 18, and -10 °C, respectively. The mixtures were passed through an aluminum oxide furnace (o.d. 2.0 mm, i.d. 1.0 mm), which was heated over a length of ca. 25 mm by a tantalum wire (o.d. 0.4 mm, resistance 0.4  $\Omega$ ), deposited (2 mmol  $h^{-1}$ ) in a high vacuum (~106 pa) onto the Rh-plated Cu block matrix support (2.8 K for PhS(O)CF<sub>3</sub> and PhS(O)Cl, 15 K for 2-hydroxybenzenethiol) using a closedcycle helium cryostat (Sumitomo Heavy Industries, SRDK-408D2-F50H) inside the vacuum chamber. Temperatures at the second stage of the cold head were controlled and monitored using a LakeShore 335 digital cryogenic temperature controller a Silicon Diode (DT-670). The voltage and current used in the pyrolysis experiments are 5.1 V and 3.34 A, respectively. Photolysis was performed using ArF excimer laser (Gamlaser EX5/250, 3 Hz) and UV flashlight (365 nm, Boyu T648, 20 W).

Matrix-isolation UV/Vis Spectroscopy. The cryostat used was an APD Cryogenics HC-2 closed-cycle refrigerator system with KBr windows for IR and BaF2 windows for UV/Vis measurements. IR spectra were recorded with a Bruker IFS 55 FT-IR spectrometer (spectral range of 4000–350 cm<sup>-1</sup> with a resolution of 0.7 cm<sup>-1</sup>, 50 scans per measurement accumulated), UV/Vis spectra with a Jasco V670 spectrometer (spectral range of 190–850 nm with a scanning speed of 1 nm s<sup>-1</sup>). For the combination of HVFP with matrix isolation, a small, home-built, water-cooled oven directly connected to the vacuum shroud of the cryostat was used. The pyrolysis zone consisted of a completely empty quartz tube (inner diameter 8 mm, length of heating zone 50 mm) resistively heated by a coax heating wire. The temperature was controlled through a Ni/CrNi thermocouple. A gas mixture PhS(O)CF<sub>3</sub> and Ar (1:1000) was prepared in a 2 L storage bulb and evaporated at room temperature into the quartz pyrolysis tube. Immediately after leaving the tube, at a distance of ca. 50 mm, all pyrolysis products were condensed (typically 30 to 60 mbar in one hour) on the surface of the 12.0 K matrix window. For irradiation, a high-pressure mercury lamp (HBO 200, Osram) with a monochromator (Bausch & Lomb) or a low-pressure mercury spiral lamp (Gräntzel) with interference filter (254, 365, and 436 nm) was used.

**Computational Details.** Molecular structures and IR frequencies of stationary points were computed using DFT UB3LYP/def2-TZVPP<sup>48</sup> and UCCSD(T)/aug-cc-pV(D+d)Z.<sup>49-<sup>51</sup> Local minima were confirmed by vibrational frequency analysis, and transition states were further checked by intrinsic reaction coordinate (IRC) computations.<sup>52,53</sup> Time-dependent (TD) DFT (B3LYP/def2-TZVPP) calculations.<sup>54,55</sup> were performed for the prediction of vertical excitations. The natural spin densities were computed at UB3LYP/def2-TZVPP level with the Natural Bond Orbital (NBO) method..<sup>56</sup> These computations were performed using the Gaussian 09 software package.<sup>57</sup> The CCSD(T) calculations were performed using the MOLPRO 2015 package..<sup>58</sup></sup>

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#### **RESULTS AND DISCUSSION**

Generation and photochemistry of PhSO• and PhOS•. The generation of PhSO• was achieved first by high-vacuum flash pyrolysis (HVFP) of the sulfoxide PhS(O)CF<sub>3</sub> (1, Figure 1A) at about 1000 K. The IR spectrum of the pyrolysis products (Figure 1B) isolated in solid Ar-matrix at 2.8 K suggests that nearly 80% of the sulfoxide decomposes and yields the expected fragmentation species •CF<sub>3</sub> (2) with characteristic IR bands at 1250.5, 1086.4, and 703.3 cm<sup>-1.59</sup> In addition, the formation of a new species is evidenced by the presence of the IR bands (3) mainly at 1472.2, 1444.7, 1088.9, 1059.5, 737.6, and 681.4 cm<sup>-1</sup>. In order to aid the assignment, the IR spectrum for the remaining fragment PhSO• (Figure 1D) was computed, showing good agreement with the experimental observations (Table 1).



**Figure 1.** (A) IR spectrum of Ar-matrix isolated PhS(O)CF<sub>3</sub> (1). (B) IR spectrum of Ar-matrix isolated HVFP products of 1. (C) IR difference spectrum reflecting the change of the Ar-matrix isolated HVFP products of 1 upon 10 min UV light irradiation (365 nm); (D) Simulated IR difference spectrum based on the computed IR spectra of PhSO• (3) and PhOS• (4) at the B3LYP/def2-TZVPP level. The IR bands of CF<sub>3</sub>• (2) and H<sub>2</sub>O (\*) are labeled.

Considering the computed (TD-B3LYP/def2-TZVPP) intense vertical transitions at 398 (oscillator strength f = 0.0179) and 377 nm (f = 0.0086) for PhSO• (Table S1), the matrix containing the pyrolysis products of 1 was subjected to UV light (365 nm) irradiation. The resulting IR difference spectrum (Figure 1C) demonstrates the sole depletion of PhSO• and the formation of a new species (4) with strong IR bands at 1483.8, 1185.2, 1135.9, 895.3, and 752.3 cm<sup>-1</sup>. These band positions nicely coincide with the computed IR frequencies for the isomeric oxathiyl radical PhOS• (Table 1 and Figure 1D). Similar RSO•  $\rightarrow$  ROS• isomerization has been previously observed only for CF<sub>3</sub>SO• under the 266 nm laser irradiation conditions,<sup>38</sup> whereas, the most frequently computationally explored HSO•  $\rightarrow$  HOS• isomerization remains experimentally unobserved.<sup>60-62</sup>

Gas-phase generation of PhSO• was also observed when sulfinyl chloride PhS(O)Cl (5, Figure 2A) was used as the precursor under the same pyrolysis conditions with PhS(O)CF<sub>3</sub>. The IR spectrum of the pyrolysis products (Figure 2B) suggests that the only byproduct is atomic chlorine (IR inactive). The fully reproducible PhSO•  $\rightarrow$  PhOS• photoisomerization (Figure 2C) enables the unambiguous identification of the very weak IR bands associated with both radicals. According to the

computed vibrational displacement vectors for PhSO•, the S-O stretching vibration couples asymmetrically with the C-S stretching mode and occurs at 1088.9 cm<sup>-1</sup> (calcd. 1097 cm<sup>-1</sup>, B3LYP/def2-TZVPP) as the strongest IR band, which exhibits a discernible isotopic shift of 4.7  $\text{cm}^{-1}$  (calcd. 5.7  $\text{cm}^{-1}$ ) for the naturally abundant <sup>34</sup>S. The symmetrically coupled stretching vibration appears at 1059.5 cm<sup>-1</sup> (calcd. 1069 cm<sup>-1</sup>) with an isotopic shift of 4.5 cm<sup>-1</sup> (calcd. 5.1 cm<sup>-1</sup>). These two band positions are close to those of the S-O stretching vibrations found in CF<sub>3</sub>SO• (1072.6 cm<sup>-1</sup>, Ar-matrix)<sup>38</sup> and CH<sub>3</sub>SO• (1068.2 cm<sup>-1</sup>, Ar-matrix).<sup>63</sup> The C–S stretching mode appears at 704.9 cm<sup>-1</sup> (calcd. 711 cm<sup>-1</sup>) as a very weak band, which is between those in CF<sub>3</sub>SO• (751.9 cm<sup>-1</sup>) and CH<sub>3</sub>SO• (669.9 cm<sup>-1</sup>). The COS deformation in PhSO• locates at 470.4 cm<sup>-1</sup> (calcd. 475  $\text{cm}^{-1}$ ) and is higher in frequency that that in  $CF_3SO$ • (340.8 cm<sup>-1</sup>). In PhOS•, the IR fundamentals for the C–O and O–S stretching modes occur at 1135.9 cm<sup>-1</sup> (calcd.  $1147 \text{ cm}^{-1}$ ) and 895.3 cm<sup>-1</sup> (calcd. 906 cm<sup>-1</sup>), and the latter is associated with a weak band at 891.7 cm<sup>-1</sup> for the naturally abundant <sup>34</sup>S.



**Figure 2.** (A) IR spectrum of Ar-matrix isolated PhS(O)Cl (5). (B) IR spectrum of Ar-matrix isolated HVFP products of **5**. (C) IR difference spectrum reflecting the change of the Ar-matrix isolated HVFP products of **5** upon 10 min UV light irradiation (365 nm). The IR bands of  $H_2O$  (\*) are labeled.

Attempts to convert PhOS• back to PhSO• were made by using visible (560-400 nm) and UV light irradiations (365 and 266 nm), however, no interconversion took place. Instead, the UV light slowly depleted both radicals simultaneously (Figure 3A). By following the changes of the IR spectra obtained at different photolysis time, at least three new species can be distinguished among the photolysis products. In the corresponding IR difference spectrum (Figure 3B), one prominent band at 2133.5  $\text{cm}^{-1}$  (labeled with 8), which is very close to the characteristic asymmetric C=C=O stretching vibrations observed in ketenes such as H<sub>2</sub>CCO (2141.8 cm<sup>-1</sup>, Armatrix).<sup>64</sup> Therefore, it is very likely that ring-opening occurs in PhOS• during the photolysis, resembling the known photoinduced ring-opening of the closely related phenylperoxy radical PhOO• to a ketoketene radical, for which the asymmetric C=C=O stretching vibration was observed in the range of 2150-2050 cm<sup>-1</sup> in solid Ar-matrix.<sup>43</sup>

Table 1. Observed and com	puted vibrational frequencies	$(1700-400 \text{ cm}^{-1})$	) of PhSO• isomers. <sup>a</sup>
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PhSO• (3)			PhOS• (4)			ortho-HOPhS• (6)		
Observed	Computed		Observed	Computed		Observed	Computed	
Ar-matrix <sup>b</sup>	B3LYP <sup>c</sup>	$\operatorname{CCSD}(\mathrm{T})^d$	Ar-matrix <sup>b</sup>	B3LYP <sup>c</sup>	$\text{CCSD}(\mathbf{T})^d$	Ar-matrix <sup>b</sup>	B3LYP <sup>c</sup>	$CCSD(T)^d$
	1616 (<1)	1599.8	1600.2 (6)	1634 (4)	1623.4	1586.3 (40)	1621 (55)	1633
1573.1 (2)	1610(1)	1595.0	1590.6 (12)	1625 (3)	1611.3	1546.7 (15)	1583 (37)	1595
1472.2 (9)	1508 (5)	1462.6	1483.8 (59)	1516 (30)	1476.0	1450.8 (100)	1484 (139)	1486
1444.7 (15)	1477 (10)	1431.7	1460.8 (17)	1493 (4)	1448.2		1477 (46)	1473
1326.2 (2)	1354 (2)	1333.4		1351 (<1)	1337.0	1365.2 (23)	1386 (45)	1389
1300.1 (3)	1325 (1)	1296.7	1304.1 (1)	1333 (<1)	1298.6	1335.4 (17)	1341 (43)	1338
	1201 (<1)	1178.1	1185.2 (38)	1207 (12)	1184.7	1312.9 (19)	1270 (59)	1279
1184 (<1 1104 (3)	1184 (<1)	1162.2		1182 (<1)	1153.7	1234.5 (13)	1213 (83)	1205
	1104 (3)	1136.9	1135.9 (52)	1147 (10)	1142.0	1213.6 (13)	1185 (3)	1162
1088.9 (100)	1097 (64)	1082.8	1071.0 (10)	1101 (8)	1078.9	1158.5 (52)	1142 (11)	1125
1059.5 (19)	1069 (13)	1070.5	1023.8 (7)	1044 (5)	1024.3	1113.3 (10)	1085 (8)	1062
1020.6 (3)	1044 (4)	1021.8		1021 (<1)	987.2	1066.7 (6)	1038 (6)	1127
	1023 (<1)	975.8		1010 (<1)	921.9		997 (<1)	938
993.4 (2)	1014 (1)	937.1		994 (<1)	903.4		978 (2)	931
	1000 (<1)	914.0		940 (6)	876.5		878 (2)	842
907.8 (2)	945 (2)	883.1	895.3 (100)	906 (29)	861.0	839.1 (21)	851 (5)	833
	865 (<1)	832.4		849 (<1)	811.1	750.1 (13)	774 (47)	755
737.6 (56)	767 (47)	720.3	752.3 (80)	780 (56)	737.0	728.5 (4)	752 (8)	694
704.9 (3)	711 (1)	690.7		760 (6)	730.9	699.2 (4)	707 (7)	661
681.4 (27)	707 (32)	604.5	682.1 (24)	703 (26)	600.4	620.8 (38)	678 (75)	626
	628 (<1)	560.2	. ,	627 (<1)	583.0	~ /	560 (6)	547
470.4 (28)	475 (23)	460.7		555 (3)	540.4		524 (5)	503
` '	466 (6)	430.9	488.3 (8)	505 (7)	470.6		512 (4)	495

<sup>*a*</sup> Full list of the computed IR fundamentals are given in the Supporting Information. <sup>*b*</sup> Band positions in Ar-matrix at 2.8 K, relative integrated intensities (%) in parentheses. <sup>*c*</sup> Harmonic frequencies (unscaled) at the def2-TZVPP basis set, IR intensities (km mol<sup>-1</sup>) in parentheses. <sup>*d*</sup> Harmonic frequencies (unscaled) at the UCCSD(T)/aug-cc-pV(D+d)Z level.

The tentative assignment is also supported by the agreement with the computed strongest IR fundamental at 2198 cm<sup>-1</sup> (IR intensity: 1880 km mol<sup>-1</sup>) for the thioketoketene radical **8** in the most favorable conformation (Scheme 2, Table S3). In the ring-opening of PhOO• (Scheme S1),<sup>43</sup> a seven-membered ring intermediate, 2-oxepinoxy radical, bearing characteristic C=O stretching vibration at 1726.9 cm<sup>-1</sup> is involved. By analogy, 2-thiepinoxy radical should be also formed via the ringexpansion of **4**. However, no distinguishable IR band at around 1700 cm<sup>-1</sup> in the IR spectrum (Figure 3A) for the characteristic C=O stretching vibration (calcd. 1711 cm<sup>-1</sup>, Table S3) could be observed, which might be due to the photolability of 2-thiepinoxy radical towards the light (365 nm) applied in photolysis of **4**.

Among the photolysis products of PhOS• (4), another new species exhibits IR bands (6) at 1586.3, 1546.7, 1450.8, 1365.2, 1335.4, 1312.9, 1234.5, 1213.6, 1158.5, 750.1, and 620.8 cm<sup>-1</sup>. These band positions coincide with the computed IR fundamentals for 2-hydroxyphenylthiyl radical (6, Table 1), an isomer of PhOS• (4). Given the known photo-induced hydrogen-elimination in phenol PhOH ( $\rightarrow$  PhO• + H•, 248 nm)<sup>65</sup> and PhSH ( $\rightarrow$  PhS• + H•, 285–290 nm) in solid Ar-matrices,<sup>66</sup> the photochemistry of 2-hydroxybenzenethiol (7) in solid Armatrix with an ArF excimer laser (193 nm) was also studied. The corresponding IR difference spectrum (Figure 3B) shows the formation of both 2-hydroxyphenylthiyl radical (6) and the acyclic thioketoketene radical (8). Notably, a broad and weak band centered at 1667.8 cm<sup>-1</sup> keeps increasing its intensity during photolysis, it can be tentatively assigned to the C=C

stretching vibrations in thione isomers produced via recombination of  $\mathbf{6}$  and hydrogen atoms in Ar-matrix cages.



**Figure 3.** (A) IR difference spectrum reflecting the change of the Ar-matrix isolated PhOS (**4**)• upon UV light irradiation (365 nm, 30 min). (B) IR difference spectrum reflecting the change of the Ar-matrix isolated 2-hydroxybenzenethiol (**7**) upon ArF laser irradiation (193 nm, 50min). IR bands of 2-hydroxyphenylthiyl radical (**6**), the thioketoketene radical (**8**), and unknown species (#) are labeled.

The photochemistry of PhSO• (3) in solid Ar-matrix was also followed by UV/Vis spectroscopy (Figure 4). Consistent

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with the TD-B3LYP/def2-TZVPP computed vertical transitions at 521 (f = 0.0006), 398 (f = 0.0179), and 377 nm (f = 0.0086) for PhSO• (Table S1), the HVFP products of Ph(O)CF<sub>3</sub> (1) shows very weak absorption starting at around 475 nm and terminating at 410 nm, which is also in agreement with the previously observed transient absorptions at around 450 nm for PhSO• in solution.<sup>31-33,35</sup> In line with the computed intense absorptions at around 300 nm (311 nm, f = 0.0554; 295 nm, f = 0.0432), a much stronger absorption centered at 300 nm with superimposed vibrational fine structures vanishes upon the 365 nm irradiation, hence, it should also belong to the same carrier PhSO•. Apparently, the  $n \rightarrow \pi^*$  transition in PhSO• ( $\lambda_{max} = 465$  nm) is significantly blue-shifted in comparison with those in CH<sub>3</sub>SO• (530 nm)<sup>63</sup> and CF<sub>3</sub>SO• (550 nm).<sup>38</sup>



**Figure 4.** (A) UV/Vis spectra of the HVFP products of Ph(O)CF<sub>3</sub> in solid Ar-matrices at 12 K with 30 min deposition. (B) UV/Vis spectra of the HVFP products of Ph(O)CF<sub>3</sub> in solid Ar-matrices at 12 K with 90 min deposition. (C) Ten-fold expansion of the spectra (B).

After the UV light irradiation (365 nm) of PhSO• (3), two weak but distinguishable absorptions at 502 and 433 nm appear in the UV/Vis spectrum (Figure 4), which reasonably account for the computed transitions at 522 (f = 0.0775) and 450 nm (f = 0.0131) for the expected isomer PhOS• (4). Furthermore, the theoretically predicted absorptions at 693 nm (f= 0.0131) for the photolysis products 2-hydroxyphenylthiyl radical (6) and thioketoketene radical (8) at 570 nm (f =0.0127) were also observed at 632 and 576 nm, respectively.

Oxidation of PhSO• and PhOS•. The facile gas-phase generation of PhSO• radicals allows the study of its oxidation with molecular oxygen by pyrolysis a 1:50:1000 mixture of Ph(O)Cl (5), O<sub>2</sub>, and Ar. The IR spectrum of the pyrolysis products isolated at 2.8 K is shown in Figure 5a. Unlike the efficient trapping reaction of CH<sub>3</sub>SO• with  $O_2$  ( $\rightarrow$ CH<sub>3</sub>S(O)OO•) in the gas phase,<sup>13</sup> most PhSO• (3) radicals survive under the pyrolysis conditions. Interestingly, traces of SO<sub>2</sub> (9, 1354.5 cm<sup>-1</sup>) and OSOO (10, 1231.1, 1045.1, and 597.1 cm<sup>-1</sup>)<sup>67</sup> form, the presence of the latter implies the likely formation of the unstable complex PhS(O)OO• followed by fragmentation into Ph.68 and OSOO. This is consistent with the observation of OS18O18O as the sole 18O-labeled species among the HVFP products of a 1:50:1000 mixture of Ph(O)Cl (5), <sup>18</sup>O<sub>2</sub>, and Ar (Figure S1). However, none of the IR bands for phenyl radical Ph<sup>68</sup> or its O<sub>2</sub>-trapping complex PhOO<sup>41</sup>

could be identified in the IR spectrum (Figure 5A) probably due to low IR intensities.



**Figure 5.** (A) IR spectrum of Ar-matrix isolated HVFP products of a mixture of PhS(O)Cl (5), O<sub>2</sub>, and Ar (1:50:1000). (B) IR difference spectrum reflecting the change of the Ar-matrix isolated HVFP products of a mixture of PhS(O)Cl (5) and O<sub>2</sub> (1:50) upon 130 min UV light irradiation (365 nm). IR bands of PhSO• (3), PhOS• (4), SO<sub>2</sub> (9), OSOO (10), and PhO• (11) are labeled.

Upon irradiation with UV light (365 nm, Figure 5B), depletion of PhSO• (3) occurs and yields PhOS• (4), SO<sub>2</sub> (9), and PhO• (11, 1553.1, 1491.3, 787.2, and 633.3 cm<sup>-1</sup>).<sup>65</sup> The absence of the IR bands for the O<sub>2</sub>-trapping product of PhSO• (3) or derivatives suggests that no photooxidation happens. Instead, PhSO• (3) prefers isomerization to PhOS• (4), and the latter combines O<sub>2</sub> in the same matrix cages to furnish PhOSOO• with immediate photofragmentation to PhO• (11) and open-chain SOO, and the last species isomerizes to SO<sub>2</sub> under the irradiation conditions (Figures S2-S3).<sup>69</sup>

**Quantum chemical computations.** By referring to the intensively explored mechanism for the decomposition of PhOO $\cdot$ ,<sup>42</sup> the pathways for the isomerization of PhSO $\cdot$  were computationally investigated (Figure 6).

In line with the general higher thermal stability of the sulfinyl (RSO•) than the oxathiyl form (ROS•, R = H,<sup>48</sup> CH<sub>3</sub>,<sup>40</sup> F,<sup>70</sup> and CF<sub>3</sub><sup>38</sup>), PhSO• (**3**) is lower in energy than PhOS• (**4**) by 12.8 kcal mol<sup>-1</sup> at the CCSD(T)/cc-pVTZ//B3LYP/def2-TZVPP level of theory. Importantly, the activation barrier (TS1) associated with the conversion from **3** to **4** is formidable (69.1 kcal mol<sup>-1</sup>). Considering the large C–S bond dissociation energy (88.3 kcal mol<sup>-1</sup>), **3** should be thermally persistent in the gas phase, which is consistent with the absence of any isomerization or fragmentation species of **3** at the HVFP condition (1000 K). Whereas, the 365 nm UV light (78.3 kcal mol<sup>-1</sup>) enables the isomerization even under the matrixisolation condition (2.8 K).



Figure 6. Computed potential energy profile for the isomerization of PhSO• (3) at the CCSD(T)/cc-pVTZ//B3LYP/def2-TZVPP and B3LYP/def2-TZVPP (in parentheses) levels.

Similar to the isomerization of the phenylperoxy radical to an epoxide radical, the photochemically generated oxathiyl radical PhOS• (4) may further isomerize to a thiirane radical (13) by overcoming a barrier (TS2) of 44.4 kcal mol<sup>-1</sup>. The absence of this elusive species in the photolysis of 4 indicates further reactions, including either ring-expansion (TS4) to a sevenmembered ring intermediate (14) or formation of an elusive 2thiolphenoxy radical (15) via hydrogen-shift (TS3). The latter is slightly more favorable; however, the initially generated intermediate 15 is unstable due to facile rearrangement to the lower-energy 2-hydroxyphenylthiyl radical (6) by surmounting a small barrier (TS6) of 4.8 kcal mol<sup>-1</sup>, which reasonably explains the experimental observation of  $\mathbf{6}$  as the main photolysis product of 4. Despite that a seven-membered ring intermediate (2-oxepinoxy radical) has been identified during the photolysis (> 400 nm) of PhOO,<sup>41</sup> the analogous sulfur intermediate 14 was not observed probably due to its sensitivity to the applied 365 nm UV light (calcd. 363 nm, f = 0.0022). Instead, its ringopening product 8 was tentatively identified according to the characteristic IR band at 2133.5 cm<sup>-1</sup> (Figure 3), although 8 is significantly higher in energy than the ring species 14. Unlike the formation of CO and CO<sub>2</sub> elimination products in the photochemistry of PhOO•,<sup>43</sup> no IR bands for fragmentation species CO, CS, or OCS were observed in the photolysis of PhSO.

Natural population analyses (NPA) of the spin densities in the phenyl-substituted sulfur-centered radicals  $PhSO_x \cdot (x = 0-2)$  were computed at the B3LYP/def2-TZVPP level (Figure 7). In accord with the recent computations for PhS• and PhSO<sub>2</sub>•,<sup>11</sup> the densities for the unpaired electron spin in all these species are largely localized on the heteroatoms. Similar to CF<sub>3</sub>SO•,<sup>38</sup> the spin density in PhSO• is almost equally distributed on the S (0.506) and O (0.379) atoms. In contrast the heavier S atom (0.769) carries significantly more spin than the O atom (0.165) in PhOS•.



**Figure 7.** Computed spin densities of  $PhSO_x \cdot (x = 0-2)$  at the B3LYP/def2-TZVPP level.

## CONCLUSIONS

The parent molecule of arylsulfinyl radicals PhSO• (3) has been generated in the gas phase through high-vacuum flash pyrolysis (HVFP) of precursors PhS(O)X (X = CF<sub>3</sub> and Cl). In addition to the IR and UV/Vis spectroscopic characterization, the photochemistry and oxidation reaction with molecular oxygen have been studied in solid Ar matrices. Three novel isomers, phenoxathiyl radical PhOS• (4), 2-hydroxyphenylthiyl radical (6), and an acyclic thioketoketene radical 8 were identified during the UV light (365 nm) photolysis of PhSO• (3). In the gas phase, PhSO• partially combines molecular oxygen to PhS(O)OO as followed by dissociation to Ph• and OSOO. Whereas, the oxidation of PhOS• with  $O_2$  in cryogenic matrix yields PhO• and SO<sub>2</sub> under the UV light irradiation. To account for the observed isomerization reactions of PhSO• (3), the corresponding pathways were computationally explored. The computations suggest that a thiirane radical (13) plays the key role in the formation of both 2-hydroxyphenylthiyl radical (6) and the acyclic thicketoketene radical 8. Comparing to the previous photolytic generation and complex secondary reactions of PhSO• (3) in solution, its facile gas-phase generation will aid further studies on its structure and reactivity. Additionally, the disclosed photoisomerization and oxidation is of importance in understanding its implications in the atmospheric oxidation of volatile organic sulfur compounds.

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## **ASSOCIATED CONTENT**

#### Supporting Information

IR spectra for the <sup>18</sup>O-labeling experiments, the computed vertical transitions, vibrational frequencies, energies and atomic coordinates for PhSO• (3) and isomers (4, 6, 8, 13, and 14). This material is available free of charge via the Internet at http://pubs.acs.org.

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#### Notes

The authors declare no competing financial interest.

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