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PAPER

Hydrogen Atom Transfer Reactions in Thiophenol: Photogeneration of Two New Thione Isomers

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Photoisomerizations of monomeric thiophenol have been investigated for the compound isolated in low-temperature argon matrices. The initial thiophenol population consists exclusively of the thermodynamically most stable thiol form. The phototransformations were induced by irradiation of the matrices with narrowband tunable UV light. Irradiations at λ>290 nm did not induce any changes in isolated thiophenol molecules. Upon irradiation at 290-285 nm, the initial thiol form of thiophenol converted into its thione isomer: cyclohexa-2,4-diene-1-thione. This conversion occurs by a transfer of H atom from the SH group to a carbon atom in ortho position of the ring. Subsequent irradiations at longer wavelengths (300-427 nm) demonstrated that this UV-induced hydrogen-atom-transfer is photoreversible. Moreover, upon irradiation at 400-425 nm, the cyclohexa-2,4-diene-1-thione product converts, by transfer of a hydrogen atom from ortho to para position, into another thione isomer: cyclohexa-2,5-diene-1-thione. The latter thione isomer is also photoreactive and is consumed if irradiated at λ<332 nm. The obtained results clearly show that H-atom-transfer isomerizations dominate the unimolecular photochemistry of thiophenol confined in a solid argon matrix. A set of low-intensity infrared bands, observed in the spectra of UV irradiated thiophenol, indicates the presence of phenylthiyl radical with H atom detached from the SH group. Alongside the H-atom-transfer and H-atom-detachment processes, the ring-opening photoreaction occurred in cyclohexa-2,4-diene-1-thione by cleavage of the C−C bond in the alpha position with respect to the thiocarbonyl C=S group. The resulting open-ring conjugated thioketene adopts several isomeric forms, differing by orientations around single and double bonds. The species photogenerated upon UV irradiations of thiophenol were identified by comparison of their experimental infrared spectra with the spectra theoretically calculated for the candidate structures at the B3LYP/aug-cc-pVTZ level.

1. INTRODUCTION

Photoinduced hydrogen-atom detachment from the O−H or N−H groups of compounds such as phenol or pyrrole was postulated in 2002 by Sobolewski and co-workers.[1] This detachment should occur on the potential energy surfaces of the excited πσ* states, which have a repulsive character along the O−H or N−H stretching coordinate. Previously, the role of the πσ* states in hydrogen-atom photodetachment processes had not been considered at all. Hence, the postulates of Sobolewski et al.[1] were presented as a new paradigm in photochemistry.

Fast hydrogen atoms, detaching upon UV excitation from phenol, pyrrole and other compounds with O−H or N−H groups, were observed in TKER (total kinetic energy release) experiments.[2] These experiments, concerning the molecules in the gas phase (jet expansions), confirmed the role of the repulsive πσ* states, as it was postulated on the basis of theoretical computations. For compounds bearing O−H or N−H structural elements and isolated in solid noble gas matrices, the photodetached hydrogen atoms usually recombine with the

radical constituting the main body of the molecule. The reason for that is the confinement of the H-atom and the remaining radical in the same cage of a solid matrix. By recombination, the hydrogen atom does not always attach to the atom from which it was abstracted. As a result, tautomeric structures with hydrogen atom transferred from the O−H or N−H groups to other exo- or endocyclic atoms were photo-produced in compounds such as 2-pyridinone, 4-pyrimidinone, cytosine, phenol and others.[3-7] Among the matrix-isolated compounds studied so far, only for several cases radicals generated as a result of H-atom detachment from the O−H group[7-9] (e.g. phenol) or N−H group[9-12] (e.g. adenine) were stabilized in a low-temperature environment and directly observed by stationary IR spectroscopy.

Recently, UV-induced H-atom detachment from the S−H group was observed, for gaseous thiophenol, by photofragment translational spectroscopy,[2, 13-17] and for thiophenol analogues in cyclohexane solutions.[18] Similarly to the case of phenol, also for thiophenol a repulsive state with an electron promoted to the σ* orbital plays a key role in the H-atom detachment process.[19] As far as we are aware, the photochemical behavior of
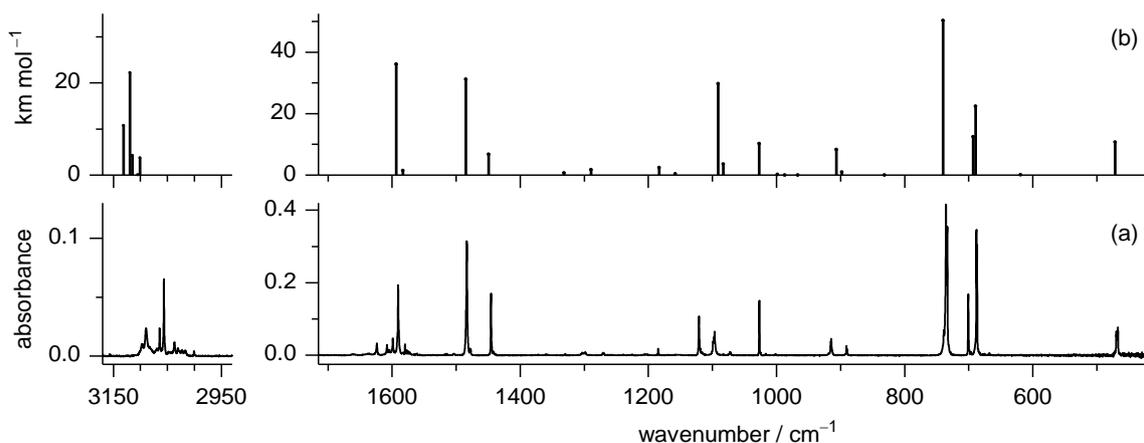
Figure 1. (a) Infrared spectrum of thiophenol monomers isolated in an Ar matrix; (b) the spectrum theoretically calculated at the DFT(B3LYP)/aug-cc-pVTZ level for the **PhSH** structure. The calculated wavenumbers were scaled by a factor of 0.980.

thiophenol monomers isolated in low-temperature inert matrices has never been studied so far. In other matrix-isolated compounds with exocyclic sulfur atom (such as 3-thio-pyridazine, 4-thiopyrimidine, 3,6-dithiopyridazine, 2-thiouracil and 2,4-dithiouracil), the C=S group usually acted as an acceptor of the H-atom photodetached from the vicinal N−H group.[20-23] For these species, the dominating photoreaction was the thione → thiol phototautomerism and the only indication of photoinduced fission of the S−H bond was the observation of a partial reversibility of the thione ↔ thiol phototautomerization.

The current study on photoinduced H-atom-transfer processes in matrix-isolated thiophenol is complementary to the investigations on UV-induced H-atom detachment from thiophenol in the gas phase.[13-17] This is a second case, after the previous studies on phenol,[7] where phototautomerism was observed for a matrix-isolated compound, for which UV-induced detachment of H-atom was detected in the TKER experiments. Hence, the currently reported results are important for establishing a link between the above described experiments: in supersonic molecular beams and in cryogenic matrices. The relationship between obtained results suggests that the observed effects are governed by the same fundamental mechanism.

In the present work, we report the infrared spectrum of monomeric thiophenol, which, to the best our knowledge, is published for the first time. The previous studies provided only the vibrational spectrum of thiophenol as liquid compound.[24] We also investigated the UV-induced transformations of thiophenol monomers isolated in low-temperature argon matrices. Application of a narrowband, tunable source of the excitation light allowed a detailed analysis of the observed photoprocesses. Several isomers of thiophenol were photoproduced and identified by comparison of their infrared spectra with the spectra theoretically predicted for the candidate structures. The isomers of thiophenol, photogenerated in the present study, have never been observed so far.

2. RESULTS

2.1. Structure and IR spectrum of thiophenol isolated in Ar matrices

The infrared spectrum of thiophenol molecules isolated in an Ar matrix is presented in Figure 1a. This spectrum is compared with the spectrum calculated at the DFT(B3LYP)/aug-cc-pVTZ level for the thiol **PhSH** isomer of the compound (Figure 1b and Table 1). The good agreement between the experimental and theoretical spectra shows that in a freshly deposited low-temperature matrix thiophenol exists in the thiol form. The theoretical spectrum was calculated for the optimized geometry that was planar. Therefore, the similarity of the theoretical and experimental patterns of IR bands indicates that the **PhSH**

Table 1. Experimental wavenumbers ($\tilde{\nu}$ / cm^{-1}) and relative integrated intensities (I) of the bands observed in the infrared spectrum of thiophenol (Form **PhSH**) monomers isolated in an Ar matrix compared with wavenumbers ($\tilde{\nu}$ / cm^{-1}) and absolute infrared intensities (A^{th} / km mol^{-1}) calculated at the B3LYP/aug-cc-pVTZ level.[a]

Experiment Ar matrix		Calculation B3LYP/aug-cc-pVTZ			
$\tilde{\nu}$ [b]	I	sym [c]	mode No.	$\tilde{\nu}$ [d]	A^{th}
2610	0.6	A'	Q6	2634	0.4
1591	20	A'	Q7	1593	36
1580	1	A'	Q8	1583	1
1483	39	A'	Q9	1485	31
1446	11	A'	Q10	1449	7
1185	1	A'	Q13	1183	2
1121	11	A'	Q15	1091	30
1097	12	A'	Q16	1083	4
1027	7	A'	Q17	1027	10
915	7	A'	Q21	906	8
891, 890	2	A"	Q22	898	1
735, 733	77	A"	Q24	740	50
701	11	A'	Q25	693	12
688, **687**	33	A"	Q26	689	22
468	12	A"	Q28	471	11

[a] The full version of this table, with assignments, is provided in the ESI, Table S2; [b] more intense components of split bands are shown in bold; [c] sym − symmetry of irreducible representations of the C$_s$ point group; [d] theoretical wavenumbers were scaled by a factor of 0.980.

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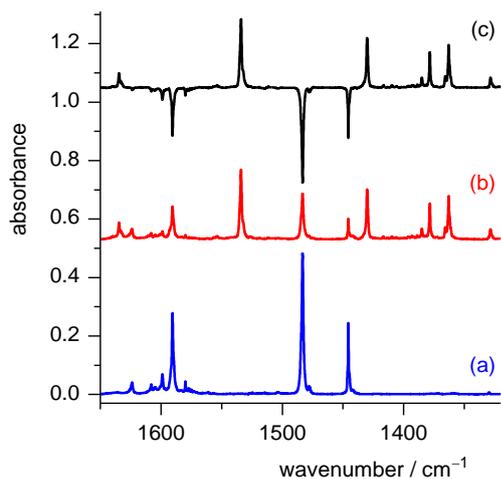
Figure 2. Photogeneration of **24** thione isomer of thiophenol. The infrared spectrum of thiophenol isolated in an Ar matrix: (a) recorded immediately after deposition; (b) recorded after irradiation with monochromatic UV λ=287 nm light; (c) difference spectrum: trace (b) *minus* trace (a).

molecules isolated in solid argon are planar and have C_s symmetry. Microwave experiments, carried out for gaseous thiophenol,[25] demonstrated that thiophenol molecules are planar also in the gas phase. High-level theoretical CCSD(T) and CASPT2//CASSCF calculations also confirm that the planar conformation is the minimum-energy structure.[26]

The comparison of the experimental IR spectrum of thiophenol isolated in an Ar matrix with the theoretical spectrum computed for **PhSH** monomers allowed an assignment of the observed IR bands to the calculated normal modes. The interpretation of the infrared spectrum of thiophenol monomers is presented in Table S2 in the ESI.

2.2. UV-induced transformation of thiol form into cyclohexa-2,4-diene-1-thione

The matrix containing monomers of thiophenol was subjected to a series of irradiations. By each of them the matrix was exposed to monochromatic UV light tuned at a specific wavelength. After every irradiation the matrix was monitored by recording its IR absorption spectrum. Irradiations at wavelengths longer than 291 nm did not induce any transformations of matrix-isolated thiophenol. First indications of photoprocesses consuming the thiol **PhSH** form of monomeric thiophenol were detected after irradiations at 291 and 290 nm. This observation is in a good correlation with the experimentally found long-wavelength absorption limit (~290 nm) of thiophenol in the gas phase.[13]

Upon irradiations at 290 nm, the absorptions due to the initially deposited **PhSH** started to decrease and new bands due to photoproducts started to appear in the infrared spectrum. By irradiation at 287 nm, the photoprocess consuming the thiol form of thiophenol was quite effective (Figure 2). The IR spectrum emerging upon UV (λ = 287 nm) irradiation was compared with theoretical spectra computed for several structures of possible photoproducts. The spectrum calculated for cyclohexa-2,4-diene-1-thione (**24**, Scheme 1) reproduces well the experimental spectrum that appeared after irradiation at 287 nm (see Figure 3, Table 2 and Table S4 in the ESI). A few

Scheme 1. Photoinduced transformations of matrix-isolated thiophenol.
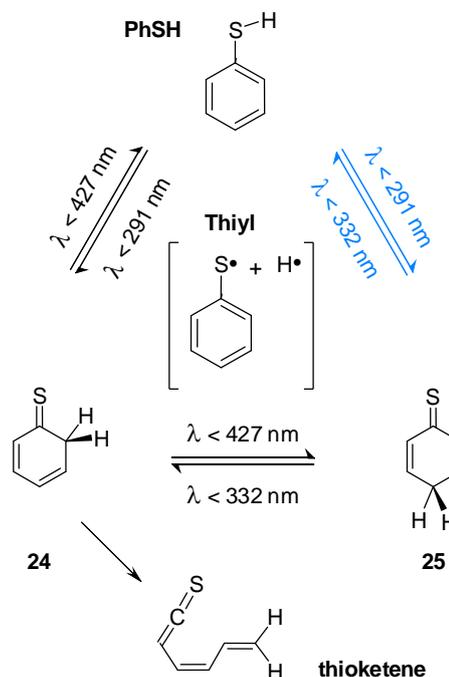
Abbreviations: **PhSH** - thiol form of thiophenol; **24** (reads: "two-four") - cyclohexa-2,4-diene-1-thione; **25** (reads: "two-five") - cyclohexa-2,5-diene-1-thione; **Thiyl** - phenylthiyl radical. In blue: direct **PhSH↔25** photoisomerization, the process which in the present experiment cannot be confirmed or discarded, see discussion in section **3.1**.

low-intensity bands, not ascribable to **24** were also observed. It will be shown below that these bands can be attributed to the infrared signature of the phenylthiyl radical, **PhS•**. A similar UV-induced generation of phenylthiyl radical, and recombination of the radical with the photodetached hydrogen atom at *ortho* position, leading to a **24** isomer, was reported for a thiophenol analogue in cyclohexane solution.[18]

The observed **PhSH → 24** transformation concerns the hydrogen-atom photodetachment from the S−H group, followed by attachment of this atom to the carbon atom in the ortho position of the ring. The photogenerated **24** product is a thione form of thiophenol. As such, it should absorb in UV at longer wavelengths than the initial thiol tautomer.[21] Upon subsequent irradiation of the matrix at 310 nm (where **PhSH** does not absorb), **24** thione form partially converted back into the thiol **PhSH** tautomer (Figure 4). This demonstrated the photoreversibility of the thiol ↔ thione (**PhSH ↔ 24**) hydrogen-atom transfer in thiophenol.

2.3. Phototransformation of cyclohexa-2,4-diene-1-thione into cyclohexa-2,5-diene-1-thione

In a dedicated experiment, a part of the initial thiol **PhSH** population was transformed (by irradiation at λ = 285 nm) into the thione **24** form. Then the matrix was subjected to a series of subsequent irradiations at significantly longer UV-vis wavelengths. The first of these irradiations was carried out using light with λ = 440 nm. After each irradiation the matrix was monitored by recording its IR spectrum. By performing successive irradiations, each next at a
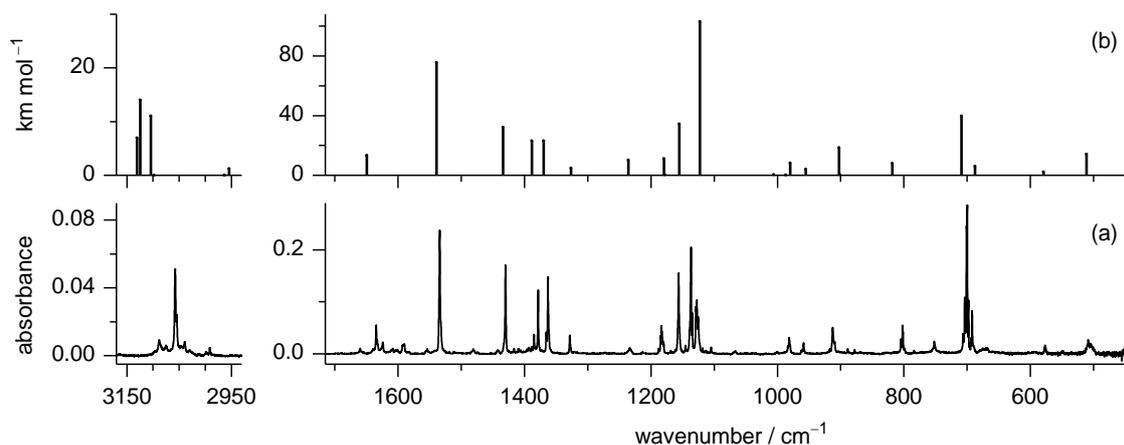
Figure 3. Identification of the **24** thione photoproduct. (a) The extracted infrared spectrum of the photoproduct generated upon irradiation of thiophenol with monochromatic UV λ=287 nm light [it was obtained by subtraction of the spectrum recorded after deposition (and multiplied by 0.33) from the spectrum recorded after UV λ=287 nm irradiation]; (b) the spectrum theoretically calculated at the DFT(B3LYP)/aug-cc-pVTZ level for the cyclohexa-2,4-diene-1-thione structure (see Scheme 1). The calculated wavenumbers were scaled by a factor of 0.98.

Table 2. Experimental wavenumbers ($\tilde{\nu}$ / cm^{-1}) and relative integrated intensities (I) of the bands observed in the infrared spectrum of cyclohexa-2,4-diene-1-thione (Form **24**) monomers isolated in an Ar matrix compared with wavenumbers ($\tilde{\nu}$ / cm^{-1}) and absolute infrared intensities (A^{th} / km mol^{-1}) calculated at the B3LYP/aug-cc-pVTZ level.[a]

Experiment Ar matrix		Calculation B3LYP/aug-cc-pVTZ			
$\tilde{\nu}$ [b]	I	sym [c]	mode No.	$\tilde{\nu}$ [d]	A^{th}
1635	10	A'	Q7	1649	13
1534	50	A'	Q8	1539	76
1430	31	A'	Q9	1434	32
1385, **1378**	15	A'	Q10	1388	23
1363	28	A'	Q11	1370	23
1328	6	A'	Q12	1326	5
1233	5	A'	Q13	1236	10
1184	18	A'	Q14	1179	11
1156	36	A'	Q16	1155	34
1136, 1128	89	A'	Q17	1123	103
981	8	A'	Q20	980	8
959	4	A'	Q21	955	4
912	17	A'	Q22	902	18
802	12	A"	Q24	818	8
700	66	A"	Q25	709	40
692	13	A'	Q26	688	6
577	3	A'	Q27	579	2
506	17	A"	Q28	511	14

[a] The full version of this table, with assignments, is provided in the ESI, Table S4; [b] more intense components of split bands are shown in bold; [c] sym – symmetry of irreducible representations of the C$_s$ point group. [d] theoretical wavenumbers were scaled by a factor of 0.980.

wavelength shorter by 1 nm, it was found that exposure of the matrix to UV light from the range 440 – 428 nm causes no consumption of **24**. Phototransformations consuming **24** started to occur upon excitation at 427 nm and they were occurring also upon irradiation at shorter wavelengths (λ < 427 nm). Irradiations at 425 - 410 nm caused efficient consumption of **24**, accompanied by generation of not only **PhSH**, but also of other products. This was revealed by appearance of new bands in the IR spectrum (Figures 5 and 6). The new IR spectrum emerging upon λ = 410 nm irradiation is so well reproduced (Figure 7, Table 3 and Table S6) by the spectrum
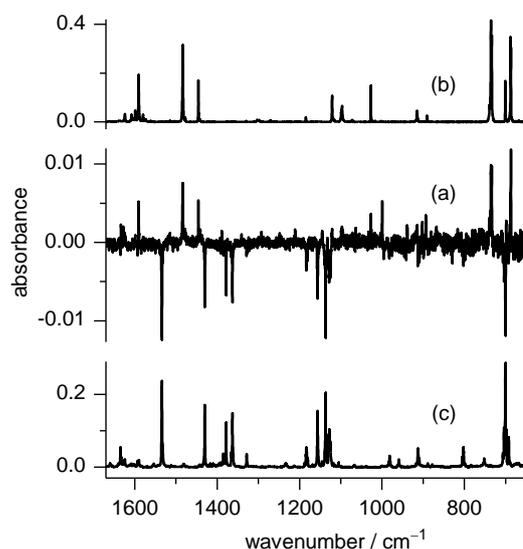
Figure 4. Reversibility of the **PhSH** ↔ **24** phototautomerism. (a) Difference spectrum obtained by subtraction of the spectrum recorded after irradiation at 287 nm from the spectrum recorded after the subsequent irradiation at 310 nm; (b) the spectrum of thiophenol recorded immediately after deposition of an Ar matrix; (c) the extracted spectrum (see Figure 3) of cyclohexa-2,4-diene-1-thione product generated upon irradiation at 287 nm.

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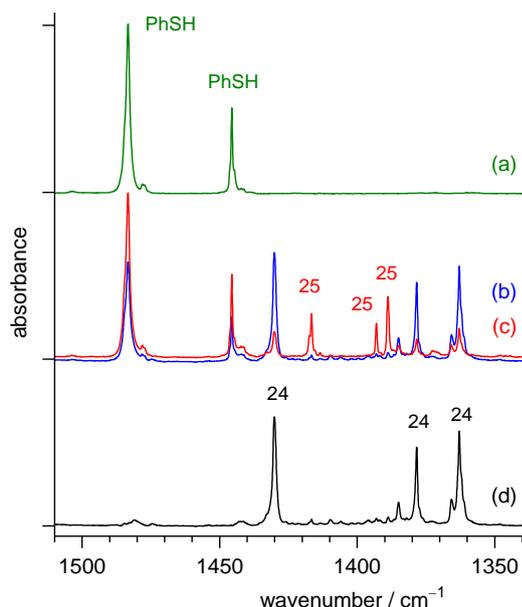
Figure 5. Photogeneration of **25** thione isomer of thiophenol. Spectra recorded: (a, green) immediately after deposition of an Ar matrix; (b, blue) after irradiation at 287 nm; (c, red) after subsequent irradiation at 410 nm, new bands appearing upon this latter irradiation are marked with **25**; (d, black) the extracted spectrum (see Figure 3) of cyclohexa-2,4-diene-1-thione product **24** generated upon irradiation at 287 nm.

Table 3. Experimental wavenumbers ($\tilde{v}$ / cm^{-1}) and relative integrated intensities (I) of the bands observed in the infrared spectrum of cyclohexa-2,5-diene-1-thione (Form **25**) monomers isolated in an Ar matrix compared with wavenumbers ($\tilde{v}$ / cm^{-1}) and absolute infrared intensities (A^{th} / km mol^{-1}) calculated at the B3LYP/aug-cc-pVTZ level.[a]

Experiment Ar matrix		Calculation B3LYP/aug-cc-pVTZ			
$\tilde{v}$ [b]	I	sym [c]	mode No.	$\tilde{v}$ [d]	A^{th}
1640, **1632**	82	A$_1$	Q7	1650	87
1582	8	B$_2$	Q8	1588	11
1417	30	A$_1$	Q9	1422	26
1389	45	A$_1$	Q10	1393	40
1393	16	B$_2$	Q11	1392	13
1258	3	B$_2$	Q13	1261	2
1213	15	A$_1$	Q14	1211	11
1145	90	A$_1$	Q16	1136	116
980	4	B$_2$	Q20	973	5
961	3	A$_1$	Q21	958	3
917	18	B$_1$	Q22	925	17
878	28	A$_1$	Q23	869	30
784, 783	27	B$_1$	Q24	795	17
593	10	B$_2$	Q27	580	3
550	40	B$_1$	Q28	553	29

[a] The full version of this table, with assignments, is provided in the ESI, Table S6; [b] more intense components of split bands are shown in bold; [c] sym – symmetry of irreducible representations of the C$_{2v}$ point group. [d] theoretical wavenumbers were scaled by a factor of 0.980.
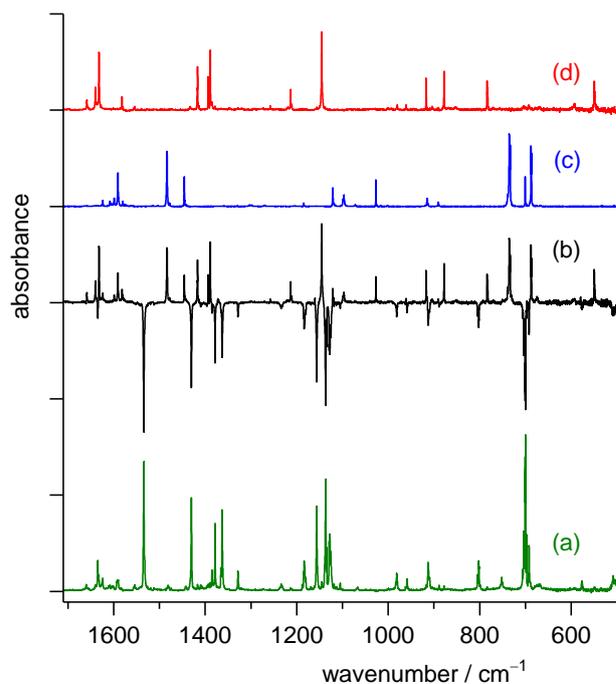
Figure 6. Separation of the infrared spectrum of the photoproduct **25**. (a, green) the spectrum of product **24** (cyclohexa-2,4-diene-1-thione) obtained as described in the caption to Figure 3; (b, black) difference spectrum: the spectrum recorded after irradiation at 410 nm *minus* the spectrum recorded after the previous irradiation at 287 nm; (c, blue) the spectrum of thiophenol recorded immediately after deposition of an Ar matrix; (d, red) the spectrum of product **25** (cyclohexa-2,5-diene-1-thione) obtained by subtraction of the spectra of the initial **PhSH** and of product **24** from the spectrum recorded after irradiation at 410 nm (shown in red in Figure 5).
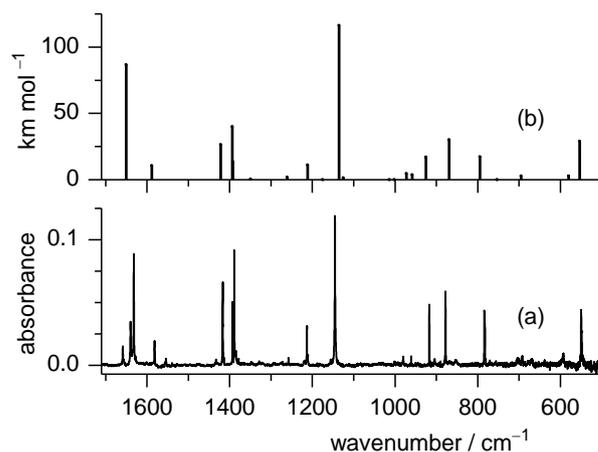
Figure 7. Identification of the **25** thione photoproduct. (a) The experimental spectrum of the new product growing upon irradiation at 410 nm (the spectrum shown in red in Figure 6); (b) the spectrum calculated at the DFT(B3LYP)/aug-cc-pVTZ level for the cyclohexa-2,5-diene-1-thione structure (see Scheme 1). The calculated wavenumbers were scaled by a factor of 0.98.
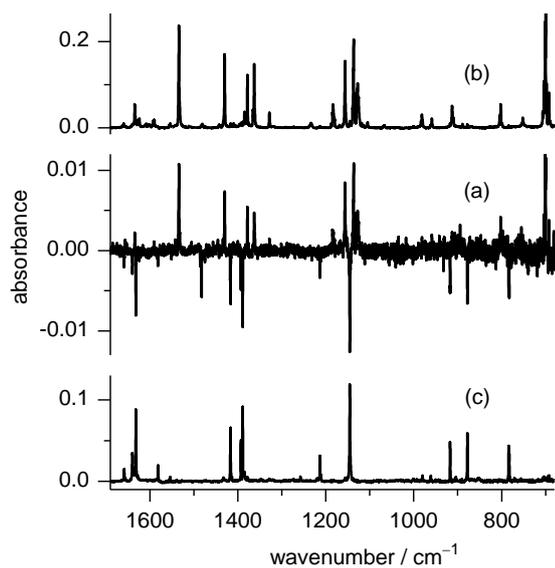
Figure 8. Reversibility of the **24** ↔ **25** phototautomerism. (a) Difference spectrum: the spectrum recorded after irradiation at 380 nm *minus* the spectrum recorded after the previous irradiation at 410 nm; (b) the extracted spectrum of cyclohexa-2,4-diene-1-thione (same as in Figure 3a); (c) the extracted spectrum of cyclohexa-2,5-diene-1-thione (same as in Figure 7a).

calculated for the cyclohexa-2,5-diene-1-thione (**25**, Scheme 1) that identification of this photoproduct leaves no doubts. Because the initial thiol form **PhSH** of thiophenol does not absorb in UV at wavelengths as long as 425-410 nm, the thione **25** form must be produced from the **24** thione tautomer, by photoinduced hydrogen-atom detachment from ortho position and recombination at para position in the ring.

The matrix containing photogenerated **25** was subsequently subjected to a series of irradiations at different wavelengths, changed with a step from 10 to 1 nm. By irradiations at wavelengths in the $333 < \lambda < 427$ nm range, **25** did not react and only **24** was consumed. Photoprocesses consuming **25** occurred upon exposure of the matrix to UV light with $\lambda \leq 332$ nm. As it is shown in Figure 8, upon irradiation at 330 nm of a matrix containing photogenerated **25**, this form transforms to **24**. That demonstrates the photoreversibility of the **24**↔**25** photoreaction, converting one thione form of thiophenol into the other.

2.4. Opening of cyclohexa-2,4-diene-1-thione ring: photo-generation of conjugated thioketene

Alongside the photoinduced hydrogen-atom detachment and hydrogen-atom transfer processes another type of photoisomerization of matrix-isolated thiophenol was observed. This concerns opening of the six-membered ring of the thione **24** form by cleavage of the C−C bond in the α position with respect to the thiocarbonyl C=S group. As a result, open-ring thioketene (Scheme 1) product was photogenerated. The spectral indication of this photoproduct is the IR band, due to the "antisymmetric" stretching vibration of the C=C=S group, emerging at ~1740 cm^{-1} (Figure 9). The band is very structured and the relative intensities of the components of the multiplet depend on the wavelength of the UV excitation light. Analogous behavior was observed for several conjugated ketenes[27] structurally similar to the thioketene photo-
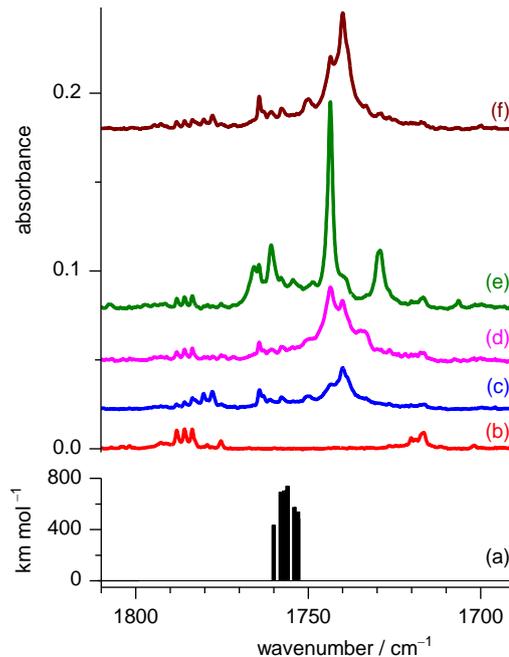
Figure 9. Spectral indication of open-ring thioketene photo-product. Fragment of the infrared spectrum of thiophenol isolated in an Ar matrix recorded: (b) after deposition of the matrix; (c) after irradiation at 285 nm; (d) after subsequent irradiation at 400 nm; (e) after subsequent irradiation at 320 nm; (f) after subsequent irradiation at 275 nm; (a) the fragment of the overlapped spectra theoretically calculated for possible conformers of open-ring conjugated thioketene (Scheme 1). The calculated wavenumbers were scaled by a factor of 0.98.

generated from thiophenol. The structured shape of the band at ~1740 cm^{-1}, is most likely related with different possible conformers of the conjugated thioketene (see ESI, Tables S10 and S11).

The open-ring thioketene was photoproduced not only upon irradiation of the matrix at 287 nm, but also at 320 - 420 nm. We have experimentally proven that irradiations at 320 - 420 nm of freshly deposited matrices, containing only the thiol form of thiophenol, do not induce any photochemical transformations. This indicates that not the initial thiol form of thiophenol, but the thione **24** tautomer is the reactant that converts into the open-ring thioketene isomer (Scheme 1). In fact, the photogeneration of the open-ring species was most pronounced by irradiations consuming effectively the cyclohexa-2,4-diene-1-thione.

Throughout many decades, the photochemical cleavage of an α-bond was believed not to occur for thiocarbonyl compounds, with the C=S bond directly attached to a six-membered ring.[28] However, several years ago, the first experimental observation of such a photoprocess, occurring in matrix-isolated 2*H*-pyran-2-thione, was reported.[29,30] For that compound, photoinduced cleavage of the C−O α-bond in the heterocyclic ring led to generation of an open-ring aldehyde-thioketene product. The present study provides a first example of an α-bond-cleavage photoreaction occurring in a thiocarbonyl compound (**24** thione tautomer of thiophenol) with a six-membered carbon ring that does not contain any heteroatoms. This demonstrates that, though the reported cases are still rare, the photoinduced α-bond cleavage processes in thiocarbonyl compounds do occur.

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3. DISCUSSION

3.1. UV-induced thiol-thione phototautomeric processes

The results described above demonstrate that the photochemical transformations observed for matrix isolated thiophenol are strongly dominated by the hydrogen-atom-transfer processes. Two thione tautomers of thiophenol [cyclohexa-2,4-diene-1-thione (**24**) and cyclohexa-2,5-diene-1-thione (**25**)] were generated upon UV excitations of matrix-isolated thiol **PhSH** form of the compound. These thione isomers of thiophenol are very high in energy (both over 80 kJ mol^{-1}, with respect to **PhSH**)[31] and have never been observed so far. The **24** and **25** photoproducts were identified by comparison of their experimental IR spectra with the spectra calculated for **24** and **25** structures. Nearly all the IR bands increasing or decreasing upon irradiations of thiophenol at different UV wavelengths belong to the spectra of three **PhSH**, **24** and **25** tautomers.

In an additional experiment, the changes in relative amounts of **PhSH**, **24** and **25** tautomers of thiophenol were followed as functions of UV wavelength and time of irradiation. The obtained results are summarized in Figure 10. In the first sequence of irradiations (stage A), the matrix was exposed to UV light with λ = 285 nm. During the period of irradiations at this wavelength, the population of **PhSH** was decreasing, while the **24** thione isomer was produced (see Figures 10A and 11A). Then the matrix was irradiated at longer wavelengths, in the 425 - 390 nm range (stage B). At these wavelengths **PhSH** is not photoexcited, hence it is not consumed. Irradiation at 425 - 390 nm leads to decrease of population of the **24** thione isomer, accompanied by partial repopulation of **PhSH** and generation of the **25** thione form (Figures 10B and 11B). Next, the matrix was subjected to a series of irradiations at 330-320 nm (stage C). Irradiations at such wavelength cause a decrease of the **25** population. This form photoconverts to **24** and into the thiol **PhSH** form (Figures 10C and 11C). The population of **PhSH** increases
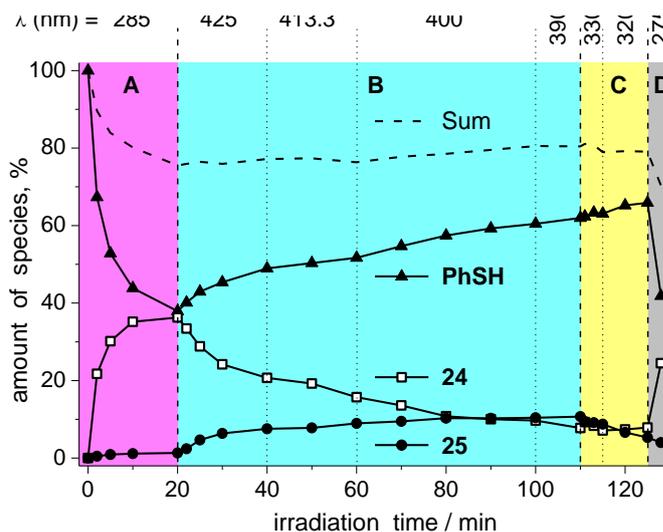
Figure 10. Amounts of thiol and thione isomers of thiophenol in the course of UV irradiations of thiophenol isolated in an Ar matrix, and their sum (**Sum**=**PhSH**+**24**+**25**). For details of amounts determination see Section 5.3. Applied wavelengths are specified on top. A change in wavelength is designated by vertical lines. Dotted lines separate sections where the reactivity is qualitatively the same (same background color). Dashed lines separate stages of the experiment where a qualitative change in reactivity occurs (different background color). The effects of irradiations upon stages A (pink), B (blue), C (yellow), and D (gray) correspond to traces A, B, C, and D in Figure 11. Zero on the time scale corresponds to the freshly deposited matrix.

during stages B and C. Upon irradiations at λ > 290 nm the thiol form is not excited and only produced at cost of decreasing populations of the thione tautomers. A control irradiation at λ = 275
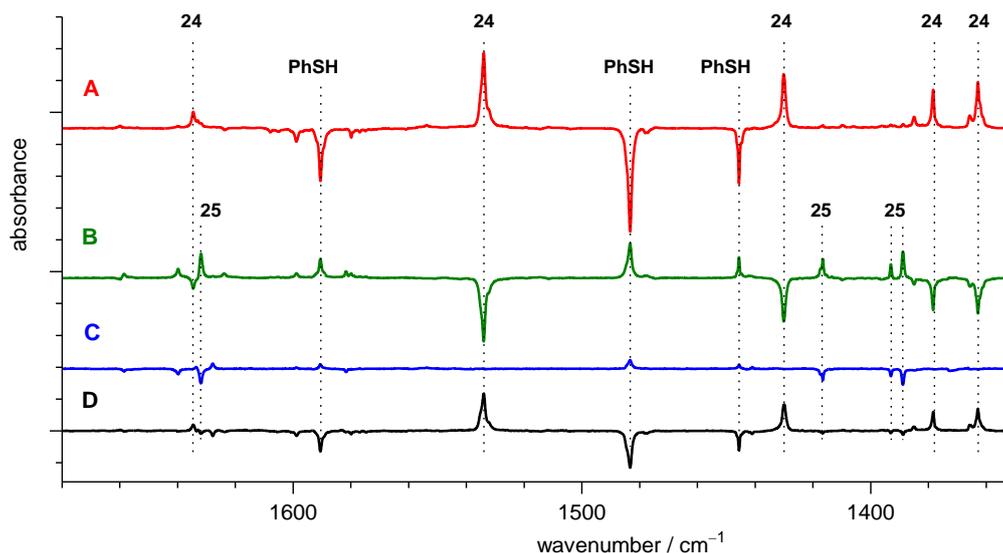
Figure 11. Spectral indications of the hydrogen-atom-transfer processes induced by UV irradiations of thiophenol isolated in an Ar matrix: (A) spectrum recorded after irradiations at 285 nm *minus* spectrum recorded after deposition of the matrix; (B) spectrum recorded after the series of subsequent irradiations at wavelengths in the 425 - 390 nm range *minus* spectrum recorded after the previous irradiation at 285 nm; (C) spectrum recorded after consecutive irradiations at 330 and 320 nm *minus* spectrum recorded after the previous irradiation at 390 nm; (D) spectrum recorded after irradiation at 275 nm *minus* spectrum recorded after the previous irradiation at 320 nm.

nm (stage D) resulted in similar changes (Figures 10D and 11D) as those observed during stage A, i.e. rapid consumption of the **PhSH** thiol form, and rapid population of the **24** thione form.

Of the three C_6H_6S isomers, only the **24** thione form could be excited selectively, by applying irradiations in the visible range, where **PhSH** and **25** forms do not absorb. By irradiations with λ < 332 nm, inducing photochemical transformations in **25** or **PhSH**, also tautomer **24** is excited. Hence, exposure of matrix-isolated thiophenol to UV λ < 332 nm light leads to photochemical equilibria involving all three **PhSH**, **24**, and **25** forms.

The obtained results clearly show that the **24** thione species is readily photoproduced directly from the most stable thiol **PhSH** tautomer of thiophenol, whereas the **25** thione isomer is mostly generated upon subsequent irradiation of **24** at longer wavelengths. It is also clearly demonstrated that both **PhSH↔24** and **24↔25** photo-tautomeric reactions are photoreversible. The observation of the **PhSH↔24** and **24↔25** photoisomerizations provides experimental evidence supporting a stepwise mechanism of the **PhSH↔25** phototransformation, involving **24** as an intermediate. This, however, does not mean that a direct **PhSH↔25** photoisomerization is impossible. A direct **PhOH↔25** photoisomerization was experimentally observed for matrix-isolated phenol,[7] and an analogous process may also occur in thiophenol.

3.2. Spectral indications of phenylthiyl radical

The primary photochemical act consuming the initial thiol form of thiophenol is the hydrogen-atom detachment from the S−H group. In the experiments carried out within the current work, the lowest-energy threshold for this S−H bond fission (leading to consumption of the thiol reagent) was established at energies corresponding to excitation at 290 nm. The same was the threshold for S−H bond fission in gaseous thiophenol, previously assessed by the photofragment translational spectroscopy.[13, 14]

In the previous studies on photochemical transformations of matrix-isolated phenol,[7,32] alongside the oxo tautomers photoproduced from the initial hydroxy form, the phenoxyl radical **PhO•** was unquestionably detected. In order to verify if the phenylthiyl (**PhS•**) radical can be detected for UV-irradiated thiophenol, we carefully analyzed the IR spectra recorded after UV irradiations of the matrix-isolated compound. Theory predicts that there should be only 5 bands in the fingerprint range of the infrared spectrum of phenylthiyl radical with the calculated infrared intensities higher than 5 km mol^{-1}, with just only three strongest bands having intensities between 15 and 40 km mol^{-1} (Table S8 in the ESI). For comparison, in the calculated infrared spectra of the **24** and **25** isomers, the strongest bands have intensities higher than 100 km mol^{-1} (Tables S4 and S6).

Moreover, one of the five potentially detectable **PhS•** bands is predicted to be coincident with a strong absorption due to **24** (the predicted radical band at 1434 cm^{-1} with infrared intensity 12 km mol^{-1} falls exactly at the same frequency as the predicted 1434 cm^{-1} band of **24**, with infrared intensity 32 km mol^{-1}, see Tables S4 and S8 in the ESI). Therefore it is clear that detection of phenylthiyl radical, based on its IR spectrum, is a serious experimental challenge.

Nevertheless, the experimental IR spectra of the UV-irradiated matrices do show four photoproduct bands at the positions (1557/1554, 1067, 752, 670 cm^{-1}) where phenylthiyl radical is expected to absorb (see Figure 12, and Figures S1-S4 in the ESI). Absorptions at similar frequencies (in particular, at 1551, 1073, 724 cm^{-1}) were observed in Raman spectra of phenylthiyl radical obtained after pulse radiolysis of thiophenol in aqueous solution.[33] Besides the characteristic spectral positions, all these four observed infrared bands have distinctive kinetic behavior, different from

kinetics of the **24** and **25** isomers. Once produced by the 285 nm irradiation (at the expense of **PhSH**), intensities of these bands do not change during irradiations at longer wavelengths used in this work.[34] This is consistent with lack of absorption bands in the 330-420 nm range in the experimental optical absorption spectrum of **PhS•** radical.[35] This photochemical behavior suggests phenylthiyl radical as the carrier of these absorptions.[36, 37]

The formation of the **PhS•** radical from the aromatic thiol tautomer **PhSH** is well supported by theory, which explains that it should occur on the repulsive πσ* potential energy surfaces of the excited states, along the S−H stretching coordinate.[18] However, we are not aware of theoretical studies elucidating on the photochemically induced CH bond fission at the sp^3 carbon atom in the **24** and **25** isomers. Such theoretical studies could provide further insight for the mechanisms underlying phototautomeric reactions observed in this work. Finally, formation of the **24** and **25** isomers, in addition to the **PhS•** radical, in the photochemistry of the gaseous thiophenol appears to us also experimentally testable.[38] We very much hope that further theoretical and experimental studies could be stimulated by the present work.
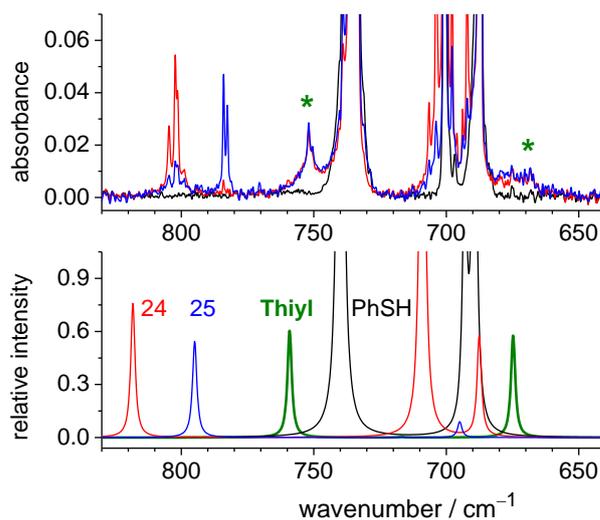
Figure 12. Spectral indication of the phenylthiyl radical. Top panel: black − spectrum of the freshly deposited matrix; red − spectrum recorded after subsequent 10 min of UV irradiation at 285 nm; blue - spectrum recorded after subsequent 80 min of UV irradiations at wavelengths in the 425 - 400 nm range; green asterisks − bands assigned to the phenylthiyl radical (note their distinct behavior). Bottom panel: black, red, blue, green − simulated spectra of **PhSH**, **24**, **25**, and **PhS• (Thiyl)** species, respectively. See section 5.4 for details of simulation and the ESI (Figures S1-S4) for more spectral regions.

4. CONCLUSIONS

Vapors of gaseous thiophenol were trapped in cryogenic argon matrices and characterized spectroscopically. Monomeric matrix-isolated thiophenol was shown to exist exclusively in its thiol form **PhSH**. The photochemistry of thiophenol was studied using narrowband UV and visible light generated in a tunable optical para-metric oscillator. Products emerging upon UV irradiation of matrix-isolated thiophenol have been characterized by IR spectroscopy. On the basis of the analysis of the collected data, H-atom detachment from the SH group of the compound was shown to be the primary photochemical act following the UV excitation. Spectral indications of photogeneration of the phenylthiyl radical **PhS•** were established,

despite this species exhibits only a few medium-intensity infrared absorptions. Once produced by the initial UV irradiation of thiophenol, traces of the **PhS•** absorptions were continually present in the experimental spectra.

The linearly conjugated cyclohexa-2,4-diene-1-thione (**24**) tautomer was identified as the dominating photoproduct of the unimolecular $\lambda < 290$ nm photochemistry of thiophenol. This **24** thione form was found to be photoreactive at much longer wavelengths, extending the reactivity to the violet range of the visible spectrum (up to $\lambda = 427$ nm). Visible light excitation of **24** in the $400 < \lambda < 427$ nm range consumed this form selectively in three different channels: (i) back into the thiol tautomer **PhSH**; (ii) into an open-ring conjugated thioketene (**TK**); (iii) into another thione tautomer, cyclohexa-2,5-diene-1-thione (**25**). No indication of photochemical channels leading to the Dewar isomer was detected. The cross-conjugated **25** thione form was found to be photostable against excitations with visible light. UV excitation of the samples ($\lambda < 332$ nm) consumed the **25** thione form and partially regenerated the **24** thione form.

The application of tunable UV-visible excitation source, allowed us to establish the upper wavelength thresholds of reactivity for three tautomeric forms of thiophenol. These thresholds equal to 291 nm for the **PhSH** thiol form, 427 nm for the **24** thione form, and 332 nm for the **25** thione form. Using the different reactivity thresholds, the **PhSH↔24** and **24↔25** phototautomeric reactions were shown to be photoreversible. Due to the distinct kinetic behavior, the individual infrared signatures of the three thiophenol tautomers **PhSH**, **24,** and **25** could be extracted and fully characterized in this work for the first time.

5. METHODS

5.1. Experimental procedures

Commercial thiophenol (Merck 98%) was used in the present study. Due to its foul and disagreeable odor,[39] the compound was transferred from the factory packing into an effusive cell using a breathing gas mask in a separate room with air extraction system. The effusive cell[40] was equipped with a SS-4BMRG (NUPRO) needle valve with a shut-off possibility which prevented the sample coming into contact with the atmosphere (thiophenol is hygroscopic) or releasing its smell in the laboratory before and during the experiments. Prior to the experiment, the cell was connected to the vacuum system of the cryostat and the compound was additionally purified from dissolved gases and water impurity by pumping through the cryostat. The temperatures of two parts of the effusive cell, the valve nozzle and the sample compartment, were stabilized separately. During deposition of argon matrices, the sample compartment was cooled to 0°C by immersing the ampoule with the compound in a bath with melting water-ice mixture. This reduced the saturated vapor pressure over the compound and improved the metering function of the valve. The valve nozzle was kept at the room temperature (298 K).

In order to prepare a low-temperature matrix, the thiophenol vapors were deposited together with a large excess of argon (purity N60, supplied by Air Liquide) onto a CsI window cooled to 15 K. The IR spectra were recorded in the 4000–400 cm^{-1} range, with 0.5 cm^{-1} resolution, using a Thermo Nicolet 6700 Fourier-transform infrared spectrometer equipped with a KBr beam splitter and a DTGS detector. Matrices were irradiated through the outer quartz window of the cryostat with monochromatic UV light from the 440−230 nm range. Frequency-doubled idler or signal beam of the Quanta-Ray MOPO-SL pulsed (10 ns) optical parametric oscillator

(full width at half-maximum ~0.2 cm^{-1}, repetition rate 10 Hz, pulse energy ~2 mJ) was applied for this purpose. The optical parametric oscillator was pumped with a pulsed Nd:YAG laser.

5.2. Computational methods

The geometries of thiophenol and the candidate structures of photogenerated products were fully optimized with the tight optimization criteria, using the density functional theory method (DFT) with Becke's three-parameter exchange functional,[41] the gradient-corrected functional of Lee, Yang, and Parr,[42] and the Vosko, Wilk, and Nusair correlation functional[43] (B3LYP). The standard aug-cc-pVTZ basis set was used in these calculations. At the optimized geometries, the harmonic vibrational frequencies and IR intensities were calculated at the same DFT(B3LYP)/aug-cc-pVTZ level. The nature of stationary points as true minima was confirmed by the analysis of the corresponding Hessian matrices. All the calculations were performed with the Gaussian program package.[44]

The theoretical normal modes were analyzed by carrying out potential energy distribution (PED) calculations. Transformations of the force constants with respect to the Cartesian coordinates to the force constants with respect to the molecule-fixed internal coordinates allowed the PED analysis to be carried out as described by Schachtschneider and Mortimer.[45, 46] The internal coordinates used in this analysis are listed in Tables S1, S3, S5 and S7 in the ESI. The elements of the computed PED matrices greater than 10% are presented in Tables S2, S4, S6 and S8. The calculated harmonic frequencies were scaled with a uniform scale factor 0.980. The theoretically predicted spectra were used to assist the analysis of the experimental spectra and are shown in Figures 1, 3, 7, and 9 as stick spectra. Cartesian coordinates of all stationary points are provided in the ESI (Tables S9 and S10).

5.3. Data processing

After we had established the spectral signatures of thiophenol **PhSH** (Figure 1), and its thione isomers, **24** (Figure 3) and **25** (Figure 7), we ran dedicated experiments where the amounts of the initially present **PhSH** thiol form as well as the photoproduced **24** and **25** thione forms were followed as functions of the irradiation time and wavelength (Figure 10). Amounts of thiophenol and the photoproducts were obtained using the following procedure. Initially, the integrated absorptions of selected bands (**PhSH** thiol form: 1483.3; 1445.6; 1026.8; 735.6 cm^{-1}; **24** thione form: 1534.1, 1430.0, 1365.7/1362.9, 1156.2, 804.7/802.3 cm^{-1}; **25** thione form: 1417.3/1416.6, 1213.2, 1145.5, 877.9, 784.0/782.6, 549.7/548.3 cm^{-1}), non-overlapping with absorptions due to the other isomers, were measured. At the next step, the experimental intensities of these bands were divided by the corresponding calculated infrared intensities (i.e., were "reduced").[47] After that, the results for each compound were averaged. At the final step, the amounts of every species (in "reduced" arbitrary units) were multiplied by a common unique scaling factor chosen so that the amount of **PhSH** prior to the irradiation would be equal to 100% (i.e., "normalized"). Figure 10 includes reduced and normalized amounts of thiophenol and its photoproducts.[48]

5.4. Modeling of the spectra

For the purpose of modeling IR spectra, we also used simulated "band" spectra. After scaling the B3LYP/ aug-cc-pVTZ calculated frequencies by a factor of 0.980, the resulting frequencies, together with the calculated infrared intensities, served to simulate the spectra shown in Figure 12 and Figures S1-S4 in the ESI by convoluting

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each peak with a Lorentzian function with a full width at half-maximum (fwhm) of 2 cm^{-1}, so that the integrated band intensities correspond to the calculated infrared absolute intensity.[49] In Figure 12, intensities of the simulated spectra of **PhSH**, **24**, **25**, and **PhS•** were scaled by 0.38, 0.30, 0.10, and 0.05, respectively.

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Notes

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† Electronic Supplementary Information (ESI) available: [Tables S1-S8 presenting the interpretation of the infrared spectra of **PhSH**, **24**, **25** and **PhS•**, based on the analysis of the calculated normal modes; Figures S1-S4 showing spectral indications of the phenylthiyl radical; Table S9 showing Cartesian coordinates for the optimized geometries of **PhSH**, **24**, **25**, and **PhS•**; Table S10 presenting the optimized geometries of eight open-ring thioketene forms; Table S11 with calculated spectra for eight open-ring thioketene forms]. See DOI: 10.1039/b000000x/

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Graphical Abstract for:

Hydrogen Atom Transfer Reactions in Thiophenol: Photogeneration of Two New Thione Isomers

by Igor Reva, Maciej J. Nowak, Leszek Lapinski, and Rui Fausto

The photochemistry of thiophenol monomers confined in cryogenic argon matrices is dominated by hydrogen atom transfer reactions and leads to formation of two new thione isomers, which were characterized in this work by infrared spectroscopy and theoretical calculations.

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