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2-Nitrophenyl Aryl Sulfides Undergo Both Intramolecular and Electrospray-Induced Intermolecular Oxidation of Sulfur: An Experimental and Theoretical Case Study

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Abstract

Aromatic sulfides bearing a nitro group undergo sulfur oxidation upon electrospray ionization in the positive-ion mode. For example, 2-nitrophenyl phenyl sulfide, its *para* nitro isomer, and its chloro and methyl substituted analogs pick up an oxygen atom to afford $[M + H + O]^+$ and $[M + Na + O]^+$ ions upon ESI. Elemental-composition determination and tandem mass spectrometry confirm the reactions. Another oxidation of the sulfur, by the *ortho* nitro group of the $[M + H]^+$ ions, occurs as intramolecular oxygen-transfer processes, evidenced by characteristic losses of SO, SO₂ and SO₂H⁺, the latter yielding the carbazole radical cation, and the generation of the aryl-SO⁺ product ion. The intramolecular oxidation via oxygen transfer from the nitro group to the sulfur was corroborated by molecular modeling. The results substantiate both inter- and intramolecular oxidation and provide more evidence that care must be taken when analyzing not only methionine-containing peptides but also small sulfides.

Introduction

Electrochemical processes occurring in electrospray ionization (ESI) continue to generate considerable interest among mass spectrometrists and ion chemists [1-3]. The generation of oxidizing agents, likely OH radicals and oxygen molecules, occur in the spray as a consequence of the electrolysis of water molecules [4,5]. Electrochemical processes also perturb solution pH and consequently the abundances of positive ions generated in the gas phase [3]. The electrochemically-induced oxidative processes can be advantageous, for example, in the generation of fullerene radical cations in the gas-phase, allowing investigation of their ion/molecule reactions [6]. Other examples include the formation of $[M - H]^+$ ions from easily oxidizable benzofuran derivatives [7], the generation of higher oxidation states of metal ions in dithiocarbamates [8], and the production of closed-shell ions in the ESI of stable aromatic

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radicals [9]. The yield of oxidation products impacts ionization efficiency and become greater when the conditions of ESI are modified so as to exploit the inherent electrochemistry by using a porous flow-through electrode emitter [10].

The most troublesome oxidation in proteomics occurs where the methionine sulfur in peptides and proteins is converted to a sulfoxide, yielding an $[M + H + O]^+$ at 16 m/z higher than expected [11,12]. Experiments conducted by using ^{18}O labeled water as solvent revealed that the source of oxygen to form the methionine sulfoxide is water [11]. We note that some of the example oxidative processes appear to involve the direct abstraction of an electron [6,8,9], whereas others [7,11] involve a process whereby the oxidation number of functional group is raised [13]. For example, in the case of methionine oxidation, the oxidation number of the functional group containing sulfur is raised by an oxygen transfer.

We report here two different oxidation reactions of the sulfur atoms in the 2-nitrophenyl aryl sulfides (the aryl sulfides **1** to **4** investigated here are given in Scheme 1) observed in these molecules ionized by electrospray. The first class of oxidation of sulfur occurs by oxygen addition, which results from electrochemical oxidation inherent in positive-ion ESI, to form presumably a sulfoxide $[M + H + O]^+$ species. A second, more subtle oxidation of sulfur takes place as an intramolecular process, where upon activation either in the ionization process itself or by collisional activation (CA), the sulfur is oxidized and the nitro group is reduced via oxygen transfer between these moieties. Evidence for this latter process comes from accurate mass measurements, studies of reference compounds, MS/MS, and molecular modeling. The results complement our continuing studies of nitro aromatic compounds [14]. Uniting the two processes are fragmentations that raise the oxidation state of the sulfur atom.

Indeed, aromatic sulfides are susceptible to oxidation under mild conditions on the timescale of minutes under microwave irradiation [15]. Intramolecular oxidation of sulfur via oxygen transfer from a proximal nitro group [16] occurs for radical cations, leading to surprising fragmentations (e.g., loss of SO_2 from protonated 2-nitrophenyl-4-tolyl sulphide in EI MS [17] and the formation from $C_6H_5SO_2^+$ from protonated 2-phenylthio-3-nitropyridine [18]). (In addition, oxidation of selenium analogs via hydroxyl transfer from a protonated proximal nitro moiety was reported [17]). A mechanism of elimination of SO_2 involving both oxygen and phenyl migration without further cyclization was proposed and buttressed with rudimentary calculations using DFT theory [19]. The purpose of this research is to see if both inter and an analogous intramolecular oxidation occurs for ESI-generated, closed-shell $[M + H]^+$ ions and to explore the mechanisms for the reactions.

2. Experimental

Synthesis

Sulfides **1** to **4** (Scheme 1) were synthesized from the appropriate chloronitrobenzenes and thiophenol by using reported procedures [19]. Purity of the samples was checked by TLC, and the structures were confirmed by NMR, IR, and mass-spectrometric analyses, as described earlier [14]. Carbazole used for this study was purchased from Aldrich Chemical Co. (Milwaukee, WI) and used without further purification.

Mass Spectrometry

ESI experiments were conducted by using a Micromass Q-ToF-*Ultima* (Waters, Manchester, UK) instrument operated in the positive-ion mode. The metallic needle voltage was 3 kV, and the cone voltage was 90 V. The temperatures of the source block and for desolvation were 90 and 150 °C, respectively. The samples were dissolved in 1:1 mixture of acetonitrile and water containing 1% formic acid. The samples were introduced by direct infusion at a flow rate of 10 $\mu L/min$. All parameters (i.e., aperture to the TOF, transport voltage, offset voltages) were

optimized to achieve maximum sensitivity and a mass resolving power of 15,000 in the “w” mode (full width at half maximum). The CAD experiments were carried out by mass selecting the precursor ion by using the quadrupole analyzer and collisionally activating the selected ion in a quadrupole collision chamber that follows; the product ions were recorded by using the time-of-flight analyzer. Collision voltages for fragmenting the precursor ions were in the range of 7 to 10 V. Accurate masses of the product ions were determined by using the precursor ion as the internal mass standard.

Some ESI MS and low-energy MS/MS and MS³ experiments were performed by using a Thermo Finnigan LCQ Advantage or a Thermo Finnigan LCQ Classic 3D ion-trap mass spectrometers (San Jose, CA).

For high-energy experiments, ions were generated by CI (chemical ionization) using methane as the reagent gas. The CI MI (metastable ion) and high-energy CA experiments were conducted on a VG ZAB-T four-sector mass spectrometer of BEBE design [20]. Samples were introduced through a heated direct-insertion probe with source temperature of 200 °C. MS1 is a standard high-resolving power, double-focusing mass spectrometer (ZAB) of reverse geometry. MS2 possesses a prototype Mattauch-Herzog-type design, incorporating a standard magnet and a planar electrostatic analyzer having an inhomogeneous electric field, followed by single-point and array detectors. Ions were accelerated to 8 kV and subjected to collisions at 4 keV in the third field-free region and detected at the single-point detector. Data acquisition and workup were accomplished by using a VAX 3100 work-station equipped with OPUS software (VG, Manchester, England).

Theoretical Calculations

Initial scans for candidates and connections on potential energy surfaces for protonated 2-nitrophenyl-phenyl sulfide and sulfoxide were performed by using the PM3 [21,22] semi-empirical algorithm (Spartan '02 for Linux, Wave function, Inc.) for computational efficiency. Additional scans of the potential surface were performed by using density functional theory (B3LYP). Geometric optimization of candidate minima and transition states were performed by using density functional theory (DFT; B3LYP/6-31G(d, p) level), which requires less computational overhead than do formal *ab initio* methods and yet incorporates dynamic correlation, has little spin contamination [23-25], and usually performs adequately giving proper geometries, energies, and frequencies [26]. DFT was part of the Gaussian 03/98 suites (Gaussian, Inc.) [27,28]. The optimized minima and transition states were confirmed by vibration frequency analysis. Connections of transition states to minima were analyzed by combination of inspection, projection along normal reaction coordinates, or reaction-path calculations as needed; also discovered by the reaction-path calculations were ion-dipole complexes. Final single-point energies were calculated at the B3LYP/6-311+G(2d,p)//B3LYP/6-31G(d,p) level, scaled thermal-energy corrections for standard conditions derived from the frequency calculations were applied [29], and reported as relative enthalpies in kcal/mol.

3. Results and Discussion

ESI-induced intermolecular oxidation

The ESI mass spectrum of 2-nitrophenyl phenyl sulfide **1** shows an [M + H]⁺ ion of *m/z* 232 and another ion of *m/z* 248, 16 *m/z* higher (Fig. 1). The measured accurate mass for the ion of *m/z* 248 is 248.0381, which agrees within 2 ppm of the accurate mass calculated for the [M + H + O]⁺ ion, C₁₂H₁₀NO₃S (Table 1). That ion of *m/z* 248, [M + H + O]⁺, is likely the [M + H]⁺ ion of the sulfoxide generated by an oxygen-transfer process initiated by generation of intermediate oxidizing species at the emitter electrode of the ESI source [4,5]. The ions of *m/z* 254, 270, and 286 are the analogous [M + Na]⁺, [M + Na + O]⁺ likely contaminated with

minor isobaric $[M + K]^+$, and $[M + K + O]^+$ ions, respectively, of **1** (Table 1) where Na^+ or K^+ has replaced the proton as the ionizing agent.

To confirm the structure assigned for the ion of m/z 248, its CAD mass spectrum (Fig. 2a) was compared with that of the authentic sulfoxide of sulfide **1** (Fig. 2b). That standard was produced by a standard oxidation procedure of sulfide **1** by using sodium periodate and introduced to the spectrometer by ESI [30]. The two spectra are virtually identical, confirming the proposed structure produced by ESI-induced electrochemical oxidation of sulfide **1** in the ion source. The elemental compositions of the fragment ions were assigned based on high mass resolving power ($\sim 15,000$), accurate-mass data (Table 1) obtained in the MS/MS mode, taking the precursor ion as the mass standard.

Calculations by DFT reveal that the preferred site of protonation to form the $[M + H]^+$ of the mono-oxidized species is at the oxygen on the sulfur (Scheme 2), in contrast to one of the nitro-group oxygens as is the case for the $[M + H]^+$ of the unoxidized species [14]. Indeed, the SO site is preferred over the oxygens of the nitro group by > 30 kcal/mol. Major fragment ions, observed in the CAD spectra, are of m/z 217, $[M + H - HNO]^+$; 184, $[M + H - SO_2]^+$; 170 $[M + H - C_6H_6]^+$; and 167 $[M + H - (SO_2 + OH)]^+$. Note that the losses of SO_2 and $(SO_2 + OH^\bullet)$ would require a transfer of an oxygen from the nitro group to the sulfur atom. The overall envelop of fragments is distinct from that observed for the protonated sulfides (Fig. 3), indicating that the sulfoxide, because of a different site for initial protonation, has available to it different routes of fragmentation.

The ESI mass spectra of sulfides **2-4** (Fig. 1b-d, Table 1) show similar features to that for 2-nitrophenyl phenyl sulfide **1** including the ESI-induced oxidation in all cases. The measured accurate masses of the proposed $[M + H + O]^+$ ions (Table 1) agree closely with the expected elemental compositions; also produced by ESI were the adducts, $[M + Na]^+$, $[M + Na + O]^+$, and $[M + K + O]^+$ ions (Table 1). The CAD mass spectra of the ESI-generated $[M + H + O]^+$ ions (Table 2) show that sulfides **1, 3, 4** fragment similarly; whereas, sulfide **2**, which has a *para* nitro group instead, does not undergo the prominent losses of HNO , SO_2 and $(SO_2 + OH^\bullet)$ but instead loses $OH^\bullet$ (to give an ion of m/z 231) and $NO_2^\bullet$ (to give an ion of m/z 202). Thus, the losses of HNO , SO_2 and $(SO_2 + OH^\bullet)$ require the proximal *ortho* nitro group, and the losses SO_2 and $(SO_2 + OH^\bullet)$ additionally require the transfer of an oxygen, which we view as an intramolecular oxidation. In addition, the $[M + H + O]^+$ ions generated from sulfides **1-3** dissociate by the elimination of a molecule of C_6H_6 whereas that of sulfide **4**, having a methyl group at the 4'- position, expels a molecule of $C_6H_5CH_3$, consistent with the assignment that they are indeed sulfoxides.

Intramolecular oxidation

ESI-protonated 2-nitrophenyl phenyl sulfide **1** produces, upon collisional activation, fragment ions of m/z 215, 214, 202, 186, 184 168, 167, 154, 125, 123 (Fig. 3) and m/z 109 (not shown). The ions of m/z 215 and 214 arise by the losses of an OH radical and H_2O , respectively; we described the mechanisms of these fragmentations earlier [13]. The unusual ions of m/z 202, 168 and 167 are formed by eliminations of $NO^\bullet$, SO_2 and $SO_2H^\bullet$, respectively, from the $[M + H]^+$. The product ions of m/z 154, 125, 123, and 109 are $C_6H_4NO_2S^+$, $C_6H_5SO^+$, $C_6H_5NO_2^+$, and likely $C_6H_5S^+$, respectively. The isobaric fragment ions of m/z 184 arise by the expulsion of either SO or the elements of H_2NO_2 from the $[M + H]^+$ ion; selection of m/z 234 as the $[M + H]^+$ ion, using the native ^{34}S isotope, reveals both are major losses. The m/z 186 ion arises from the sequential loss of H_2O and CO from the $[M + H]^+$ ion, as previously reported [13]. Furthermore, MS^3 studies of the product ions of m/z 184 and 168 reveal further dissociations by losses of OH and H radicals, respectively, to generate m/z 167. Moreover, the CAD mass spectrum of the m/z 167 fragment is virtually identical to that of the radical cation of carbazole, indicating that m/z 167 product ion is indeed the carbazole radical cation and is

formed in violation of the even-electron ion rule. Accurate mass measurements of the fragment ions, obtained under high-mass resolving power as described in **Experimental** Section, verify the formulae of the product ions and losses in the eliminations (Table 3).

For comparison, we produced protonated 2-nitrophenyl phenyl sulfide **1** by CH₄ CI (**Experimental**); this ionization does not produce the [M + O + H]⁺ ion. The MI spectrum of the CI-generated [M + H]⁺ ion is shown in Fig. 4; the CAD spectrum of the same precursor is similar but shows enhanced abundances of lower *m/z* fragment ions (not shown). No matter the ionization mode, CAD produces the same series of fragment ions but in somewhat different abundances. In addition, it appears that the CH₄ CI ions are produced with more internal energy than the ESI produced ions.

The abundances of ions from the losses of NO[•], SO, SO₂, and SO₂H[•] are summarized in Table 3 for the CAD spectra for the ESI-produced [M + H]⁺ ions of sulfides **1-4**. We note that losses of SO, SO₂, and SO₂H[•] are absent in the CAD spectra for the ESI-produced [M + H]⁺ ion of sulfide **2**, which has a *para* rather than an *ortho* nitro group. Consistent also with oxidation of S are the aryl-SO⁺ ions formed upon CAD of the [M + H]⁺ ions of sulfides **1, 3, 4**. On this basis, we surmise that the expulsions of SO, SO₂, and the SO₂H radical from the [M + H]⁺ ions arise after transfer of one or two oxygen atoms from the nitro group to the sulfur atom rather than by an abstraction in the final elimination step. In addition, given that the *m/z* 167 ion is the tricyclic carbazole radical cation, it is likely that cyclization takes place as a consequence of this intramolecular oxidation of sulfur, and is driven by the internal energy of the ions. The structure of the *m/z* 184 ions, which arise by losses of both SO and the elements of NO₂H₂ (likely H₂O + NO), were unresolved with respect to model ions because of lack of necessary precursor ion resolving power. To elucidate further the mechanism of the necessary rearrangements and subsequent eliminations of SO, SO₂ and SO₂H radical, we carried out molecular orbital calculations by using DFT, as described in **Experimental**.

Theoretical Calculations

We discovered in scanning the potential energy surface at both low level and DFT that there exists a web of potential routes for the intramolecular oxidation of the sulfur by the nitro group and the formation of characteristic product ions. We selected for presentation the ‘best’ of the potential routes based on lowest required energy to surmount the greatest transition-state barriers. We report the calculated enthalpies of formation for the intermediates, products and transition states, relative to that of the previously reported [M + H]⁺ ion [14] in kcal/mol.

Proposed mechanism for intramolecular oxidation of sulfur by two sequential oxygen transfers is shown on Scheme 3. The first step involves the transfer of an OH group from the nitro group to the sulfur atom, affording intermediate **I** (**A₃**). This first step is presumably rate limiting in that it presents the greatest energetic barrier, **TS(1-2)**, in the scheme. The second round of oxygen transfer involves a stable intermediate, **A₆**, which decomposes followed by cyclization ultimately leading to the tricyclic intermediate **II** (**A₉**), an energetically favorable form ($\Delta^2H_f = -37.1$ kcal/mol) in which both oxygens are now attached to the sulfur, and the nitro group has been consequently reduced to a secondary amine.

The route to the expulsions of SO₂ and the SO₂H radical starts from intermediate **II** (Scheme 4) and proceeds through the metastasis of a carbon-sulfur bond to a carbon-carbon bond yielding a tricyclic intermediate with a five-membered ring, **A₁₃**. We propose that this intermediate, which features a long C-S bond of 2.54 Å, can decompose to yield the heterocyclic fragments of *m/z* 168 and 167 (protonated carbazole and a carbazole radical cation, respectively, the latter being experimentally verified). In addition, the intermediate **I**, formed by the transfer of one oxygen atom from the nitro group to sulfur, is also the starting point for the formation of the *m/z* 125 ion (C₆H₅SO⁺), as shown in Scheme 5. A critical and significant

feature of this route to the product ion involves sequential NO[•] migrations that are more energetically favorable than any H or OH migration we discovered. Additionally, the exit channel features a prominent ion-neutral complex between the phenyl-SO⁺ product ion and nitrosobenzene.

Proposed route for SO loss is analogous to that for SO₂ loss and involves an intramolecular transfer of oxygen from the protonated nitro moiety to the sulfur via a cyclic intermediate, **A**₂₀, which is just a shoulder on the transfer pathway (Scheme 6). This is followed by cyclization and proton transfer to form an energetically favorable tricyclic intermediate, **A**₂₃ ($\Delta^2H_f = -29.0$ kcal/mol). The expulsion of SO commences from intermediate **A**₂₃ via the metastasis of a carbon-sulfur bond to a carbon-carbon bond, yielding a tricyclic intermediate with a five-membered ring, **A**₂₄, which decomposes by SO loss (Scheme 6) through an ion-dipole complex. We note that in all the proposed schemes, the maximum barrier at a transition state is ~ 40 kcal/mol, which is also consistent with previously proposed mechanisms for other fragmentations of these sulfides (14).

4. Conclusion

ESI of 2-nitrophenyl phenyl sulfide, the chloro and methyl substituted analogs, and its *para* nitro isomer all undergo oxygen atom addition in an ESI source during ionization. The products formed are sulfoxides, as characterized by tandem mass spectrometric experiments and accurate mass measurements. Additionally, those ESI-protonated aromatic sulfides containing *ortho* nitro groups also show oxidation of sulfur by internal oxygen transfer. Evidence includes the characteristic expulsions of SO, SO₂ and the SO₂H radical, and the production of aryl-SO⁺. We view this chemistry as a second class of oxidation, an intramolecular oxidation of the sulfur atom with reduction of the nitro group via transfer of oxygen atoms. The mechanisms for transfer and consequent fragmentation were substantiated by molecular modeling using DFT theory.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Fig. 1. ESI mass spectra of (a) sulfide **1** (b) sulfide **2** (c) sulfide **3** (d) sulfide **4**. The figures show $[M + H]^+$, $[M + H + O]^+$ and $[M + Na + O]^+$ ions

Fig. 2. The CAD mass spectra of ions of m/z 248 **(a)** oxidation product of sulfide **1** **(b)** $[M + H]^+$ of sulfoxide

Fig. 3.
CAD mass spectrum of ESI produced $[M + H]^+$ ion of sulfide **1**.

Fig. 4. MI mass spectrum of CH_4 CI produced $[\text{M} + \text{H}]^+$ ion of sulfide **1** (BEBE instrument)

Scheme 1.
Structures of the sulfides

Scheme 2.
Preferred structure of m/z 248

Scheme 3.

Proposed mechanism for intramolecular oxidation and cyclization.

All values for relative heats of formation and reaction are given in kcal/mol.

Zero point for relative heats of formation is the **A₀** conformer for consistency with and from a previous publication [13].

Scheme 4. Proposed mechanism for elimination of SO_2 and $SO_2H^\bullet$.

Scheme 5. Proposed mechanism for formation of $C_6H_5SO^+$ (m/z 125 ion).

Scheme 6.
Proposed mechanism for elimination of SO.

Table 1

Measured accurate masses of the ESI oxidation products from sulfides **1-4**.

Compound	Ion	Molecular formula for ion	Measured mass	Calculated mass	Deviation (ppm)
1	[M + H + O] ⁺	C ₁₂ H ₁₀ NO ₃ S	248.0377	248.0381	-2
2	[M + H + O] ⁺	C ₁₂ H ₁₀ NO ₃ S	248.0387	248.0381	2
3	[M + H + O] ⁺	C ₁₂ H ₉ NO ₃ SCl	281.9991	281.9992	-0.4
4	[M + H + O] ⁺	C ₁₃ H ₁₁ NO ₃ SCl	296.0143	296.0148	-2
1	[M + Na] ⁺	C ₁₂ H ₉ NOSNa	254.0253	254.0246	2.6
1	[M + Na + O] ⁺ [M + K] ⁺	C ₁₂ H ₉ NO ₃ SNa C ₁₂ H ₉ NO ₃ SK	270.0175	270.0195 269.9986	-7.5 70.5
2	[M + Na + O] ⁺	C ₁₂ H ₉ NO ₃ SNa	270.0182	270.0195	-4.9
3	[M + Na + O] ⁺	C ₁₂ H ₈ NO ₃ SClNa	303.9811	303.9808	0.8
4	[M + Na + O] ⁺ [M + K] ⁺	C ₁₃ H ₁₀ NO ₃ SClNa C ₁₃ H ₁₀ NO ₃ SK	317.9898	317.9962 317.9752	-20.1 45.9
1	[M + K + O] ⁺	C ₁₂ H ₉ NO ₃ SK	285.9940	285.9948	-2.7
2	[M + K + O] ⁺	C ₁₂ H ₉ NO ₃ SK	285.9940	285.9947	-2
3	[M + K + O] ⁺	C ₁₂ H ₈ NO ₃ SClK	319.9583	319.9545	11.8
4	[M + K + O] ⁺	C ₁₃ H ₁₀ NO ₃ SClK	333.9703	333.9701	0.449

Table 2

Partial CAD mass spectra of $[M + H + O]^+$ ions derived by ESI of sulfides 1-4.

Precursor	Measured accurate masses of fragment ions due to loss of X, elemental composition and abundances in parenthesis.				Other ions
	X = HNO	X = SO ₂	X = C ₆ H ₆	X = SO ₂ + OH ⁺	
Sulfoxide 1 <i>m/z</i> 248	217.0325 C ₁₂ H ₉ O ₂ S (52)	184.0767 C ₁₂ H ₁₀ NO (12)	169.9906 C ₆ H ₄ NO ₃ S (68)	167.0725 C ₁₂ H ₉ N (100)	<i>m/z</i> 183 (18) 168 (25)
Sulfoxide 2 <i>m/z</i> 248	ND	ND	169.9906 C ₆ H ₄ NO ₃ S (35)	ND	<i>m/z</i> 202(100) 231(75)
Sulfoxide 3 <i>m/z</i> 282	250.9930 C ₁₂ H ₆ O ₂ SCl (50)	218.0357 C ₁₂ H ₆ NOCl (10)	203.9512 C ₆ H ₃ NO ₃ SCl (90)	201.0340 C ₁₂ H ₈ NCI (100)	<i>m/z</i> 183(42) 167(65)
Sulfoxide 4 <i>m/z</i> 296	265.0098 C ₁₃ H ₁₀ O ₂ SCl (12)	232.0494 C ₁₃ H ₁₁ NOCl (70)	203.9520 C ₆ H ₃ NO ₃ SCl (100)	215.0499 C ₁₃ H ₁₀ NCI (65)	<i>m/z</i> 214(75) 180(90)

Table 3

Partial CAD mass spectra of $[M + H]^+$ ions produced by ESI from sulfides 1-4.

Precursor	Measured accurate masses of fragment ions due to loss of X, elemental composition and abundances in parenthesis.				Other ions
	X = NO [•]	X = SO	X = SO ₂	X = SO ₂ H [•]	
Sulfide 1 m/z 232	202.0463 C ₁₂ H ₁₀ OS (66)	184.0769 C ₁₂ H ₁₀ NO (66)	168.0815 C ₁₂ H ₁₀ N (100)	167.0732 C ₁₂ H ₉ N (40)	184.0343 C ₁₂ H ₈ S (<1%) [M+H-NO ₂ H ₂] ⁺
Sulfide 2 m/z 232	202.0463 C ₁₂ H ₁₀ OS (65)	ND	ND	ND	184.0349 C ₁₂ H ₈ S (3) [M+H-NO ₂ H ₂] ⁺
Sulfide 3 m/z 266	236 C ₁₂ H ₉ OSCl (10)	218 C ₁₂ H ₉ NOCi (13)	202 C ₆ H ₃ NO ₂ Cl (9)	201 C ₁₂ H ₈ NCl (15)	m/z 167 (100) [M+H-SO ₂ -Cl] ⁺
Sulfide 4 m/z 280	250 C ₁₃ H ₁₀ O ₂ SCl (5)	232.0494 C ₁₃ H ₁₁ NOCi (18)	214. C ₆ H ₃ NO ₃ SCl (13)	215 C ₁₃ H ₁₀ NCl (25)	m/z 181 (100) [M+H-SO ₂ -Cl] ⁺