Alkoxy isothiocyanates, RO–N=C=S†

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Methoxy isothiocyanate has been identified as a product of pyrolysis of the silver salt of *N*-methoxydithiocarbamic acid. It is also formed on FVT of 1-(*N*-methoxythiocarbamoyl)imidazole and 1-(*N*-methoxythiocarbamoyl)-1,2,4-triazole. Methoxy isothiocyanate was identified by IR spectroscopy in argon matrices at 10 K supported by good agreement with the *ab initio* and DFT calculated spectrum. Isopropoxy isothiocyanate was generated from the corresponding silver salt in a similar manner. The oligomerization of MeONCS to trithiolanes and tetrathianes is also described.

Introduction

Alkoxy and aryloxy isothiocyanates, RO-N=C=S, constitute a hitherto unknown class of compounds, and only a few attempts at their preparation have been reported in the literature. The reaction of N-methoxyamine with carbon disulfide was reported by Traube et al. in 1920.1 The reaction product was reasonably stable at 0 °C but decomposed at higher temperatures and was not isolable in a pure state. In analogy with the well known reaction of carbon disulfide with amines,² the compound formed was most probably the methoxyammonium salt, CH₃ONHCSS⁻, ⁺H₃NOCH₃. Treatment of this salt with silver nitrate afforded a yellow compound to which the structure $[CH_3ON=CS_2]^{2-}$, $2Ag^+$ (1) was ascribed on the basis of the elemental analysis.1 It was reported that this silver salt evolved "pungent smelling fumes" upon heating to temperatures exceeding 40 °C. The nature of these fumes was not investigated. In analogy with the well known synthesis of alkyl and aryl isothiocyanates by heating metal salts of N-alkyl- or N-aryldithiocarbamic acids,3 it is reasonable to assume that the pungent smelling fumes could have been due to methoxy isothiocyanate (2).

$$[CH_3ON=CS_2]^{2-}, 2Ag^+ \xrightarrow{heat} CH_3ONCS + Ag_2S$$
1
2

It is known that 5-alkyl-, 5-aryl-, and the corresponding 5-alkyl(aryl)oxy-1,2,3,4-thiatriazoles decompose thermally and photochemically to nitriles (cyanates), nitrogen, and sulfur together with varying amounts of isothiocyanates, R–N=C=S.⁴ However, no alkoxy isothiocyanates, RONCS, were detected during the decomposition of 5-alkoxythiatriazoles to alkyl cyanates.⁵ Attempts to prepare such compounds from *O*-alkyl-

hydroxylamines and thiophosgene were also unsuccessful.⁵ The analogous methoxy isocyanate, MeONCO, was generated by Teles and Maier⁶ by pyrolysis of *N*-methoxycarbonyl-*O*-methylhydroxylamine. They found that methoxy isocyanate was stable only below 90 K. It may be expected that alkoxy isothiocyanates will also be rather unstable compounds. We have embarked on an investigation using gas phase mass spectrometry and flash vacuum thermolysis (FVT) with matrix isolation IR spectroscopy in an effort to identify alkoxy isothiocyanates. The existence of the neutral molecules in the gas phase, at least on the microsecond time scale, has been demonstrated by neutralization–reionization–collisional activation mass spectrometry.⁷ Here we report the FVT–matrix IR spectroscopic study as well as the isolation of oligomers of MeONCS.

Results and discussion

Pyrolysis of the silver salt of *N*-methoxydithiocarbamic acid 1

On repeating Traube's pyrolysis of the silver salt 1, we noticed that when the salt was heated slowly on a Kofler hot bench, it darkened and decomposed but gave rise to only a small amount of fumes. However, if the salt was allowed to drop onto the Kofler bench above 140 $^{\circ}$ C, it deflagrated with evolution of white fumes with a smell similar to that of methyl isothio-cyanate.

The silver salt 1 was placed in the sublimation oven of an apparatus for flash vacuum thermolysis (FVT) with the oven set at a temperature of *ca.* 100 °C to avoid condensation. On heating the sublimation oven to 140 °C as rapidly as possible and isolating the products in an argon matrix at 10 K, the IR spectrum shown in Fig. 1 was obtained. This shows clearly a strong, broad band at 1888 cm⁻¹, which is in the region for ordinary isothiocyanates. Other major bands that can be ascribed to 2 are at 1075 and 756 cm⁻¹. *Ab initio* and DFT calculations for 2 are in very good agreement with these experimental values (Table 1). When the product was isolated neat, without Ar, the same three major bands were observed with some displacements: 1874, 1055 and 750 cm⁻¹. On subsequent incremental heating of the sample on the BaF₂ window, the three bands

[†] Calculated frequencies and cartesian coordinates of the computed structures of **2** and **9** are available as supplementary data. For direct electronic access see http://www.rsc.org/suppdata/p2/1999/1869, otherwise available from BLDSC (SUPPL. NO. 57617, pp. 4) or the RSC Library. See Instructions for Authors available *via* the RSC web page (http://www.rsc.org/authors).

Table 1 Calculated IR spectra of MeO–N=C=S and iso-PrO–N=C=S^{a,b}



^{*a*} Frequency in cm⁻¹ and intensity (given in parentheses) in km mol⁻¹. Frequencies with intensity value less than 22 km mol⁻¹ at the B3LYP/6-31G* level are not reported here. ^{*b*} B3LYP and MP2 frequencies were scaled by 0.9613,¹⁶ and 0.9427,¹⁷ respectively.



Fig. 1 Ar matrix IR spectrum of MeONCS 2 obtained from silver salt 1. Bands marked A are at 1888, 1075, and 756 cm^{-1} .

remained unchanged until 120 K and then gradually disappeared between 120 and 160 K. If in a similar experiment the salt was heated slowly, the IR spectrum of the thermolysis products was much more complicated, and the 1888 cm^{-1} peak was either absent or very weak in accordance with the Kofler bench experiments.

The lead salt analogous to **1** was prepared in the same way as the silver salt. However, this lead salt gave no NCS band upon pyrolysis and was therefore not investigated further.

It was attempted without success to trap the methoxy isothiocyanate from a preparative thermolysis of the silver salt by treating the thermolysis products with an amine to give an *N*-alkyl-*N'*-alkoxythiourea. Isolation of the neat thermolysis products on a cold finger at 77 K gave rise to a yellow oil which did not show any NCS band in the IR spectrum. GC-MS analysis revealed that it consisted of three products with nearly identical retention times, all of which had the molecular ion at m/z210, corresponding to a mixture of trithiolanes **3–5**. A smaller peak with m/z 242, corresponding to a tetrathiane (6 or 7) was



Fig. 2 Collisional activation spectrum (He) of the m/z 210 ions derived from the trithiolane mixture 3–5. The structure assigned to the m/z 75 ion is tentative.



also present. The same products were also observed on direct monitoring of the FVT reaction by mass spectrometry. The m/z 242 ion gives a prominent fragment peak at m/z 153. The three peaks with m/z 210 had identical mass spectra, which means that they are either closely related isomers, or they interconvert in the mass spectrometer. The identity of the trithiolanes was further confirmed by the CA mass spectra of the three products (Fig. 2) and by the ¹³C NMR spectrum of the mixture. Here, three narrowly spaced methoxy signals are observed at 63.65, 63.71, and 63.75 ppm. Further, three smaller signals at 153.3, 152.4 and 150.3 ppm correspond to the three trithiolanes **3–5**. Smaller singlets at 63.7 and 154.1 ppm are ascribed to the tetrathianes **6** or **7**, corresponding to the m/z 242 species.

For further proof, the tetrathiane–trithiolane mixture 3–7 was prepared from carbon disulfide, methoxyamine and hydrogen peroxide in a manner similar to that described for the analogous phenylhydrazono derivatives.⁸ The same mixture of compounds was obtained, the only difference being that the trithiolanes were the main products in the pyrolysis experiment, whereas the tetrathiane was the main product of the oxidative preparation. It was observed by Gambi⁸ that, upon reflux in acetone solution, tetrathianes lose one sulfur atom to give the corresponding trithiolane; this may explain why the trithiolanes are the main products in the thermal reactions.

When the decomposition of the silver salt 1 was carried out in an oven mounted in the source housing of a mass spectrometer,⁹ the main product observed had m/z 210, corresponding to the trithiolanes, of which at m/z 89 (methoxy isothiocyanate) is a fragment ion. If the pyrolysis was carried out directly on the heated probe in the ion source, signals due to S_n (n = 1-8) appeared first, followed by intense signals at m/z 89 (base peak), 153, 185, 210, and 242. Here, m/z 210 and 242 correspond to the abovementioned trithiolanes and tetrathianes 3–7. The value m/z 185 corresponds to methoxyiminotetra-

thiolane; a CAMS of this ion gave m/z 89 as the base peak. The peak m/z 153 is the base peak in the mass spectrum of the tetrathiane (m/z 242), and a CAMS of m/z 153 again gives m/z 89 as the base peak. In the mass spectrum of the pyrolysis product, the signal at m/z 89 remained the base peak at low voltage (10-12 eV), thus suggesting that this may be due, in part, to the thermally produced monomer, MeONCS, 2. However, because the trithiolanes, tetrathiane, and other compounds are also present, it cannot be ascertained that the m/z 89 signal is not, wholly or in part, due to the summation of fragment ion intensities derived from the other products. The CA spectrum of the m/z 89 ion derived from the pyrolysis mixture was identical with the one investigated previously under dissociative ionization conditions and ascribed to MeONCS⁺.⁷ Neutralization-reionization mass spectrometry of the m/z 89 peak showed an abundant recovery signal, thus verifying the inherent stability of the neutral molecule.

FVT of the tetrathiane–trithiolane mixture did not result in peaks at 1888 cm⁻¹ in the matrix IR spectra. FVT of *N*-alkoxy-thioureas also did not produce any such bands but instead gave rise to phenylcyanamide, PhNHCN.¹⁰

Pyrolysis of the silver salt of N-isopropoxydithiocarbamic acid

N-Isopropoxyamine was treated with carbon disulfide in the same way as *N*-methoxyamine, and the reaction product was converted into a silver salt, which was not, however, obtained in an analytically pure state. When the impure salt was pyrolysed by rapid heating as above, it gave rise to an IR matrix spectrum



with major absorptions at 1886, 1115, 1028, and 783 cm⁻¹, again in good agreement with *ab initio* and DFT calculations (Table 1). In the absence of Ar, this species was stable until 150 K and then disappeared in the course of further warming to 200 K. In analogy with the results for the methoxy compound, mass spectrometry of the pyrolysis product showed masses at m/z 266 and m/z 298 corresponding to trithiolanes **8** and tetrathianes **9**.

FVT of N-thiocarbamoyl azolides

It was of importance to find a second precursor for alkoxy isothiocyanates. It has been shown that thiocarbonyl diimidazoles such as **10** react with primary amines to give isothio-



cyanates.¹¹ Thermolysis of analogous diimidazoles has been used for the preparation of N,N-dialkylamino isothiocyanates¹² but was not successful for the preparation of benzyloxy isothiocyanate.¹¹

Methoxyamine reacts readily with both thiocarbonyl diimidazole and thiocarbonyl-1,2,4-triazole to give the corresponding diazoles. The methoxyimino imidazole **11** was prepared according to the literature, although it was difficult to obtain the neutral compound from the primarily formed imidazolium salt in the yield described.¹³ No such problem was encountered in the preparation of the triazole derivative **12**.

$$H^{+}N \underbrace{\searrow} N-C \underbrace{\bigvee}_{S^{-}} H^{+}N \underbrace{\bigvee}_{S^{-}} N-C \underbrace{\bigvee}_{S^{-}} H^{+}N \underbrace{\bigvee}_{S^{-}} N-C \underbrace{\bigvee}_{S^{-}} H^{+}N \underbrace{\bigvee}_{S^{-}} H$$

FVT of both the imidazolide **11** and the triazolide **12** at 400 °C with Ar matrix isolation of the products gave rise to the peaks at 1888, 1076, and 754 cm⁻¹ in the IR spectra, thereby confirming the assignment of MeONCS **(2)**. Signals due to imidazole (triazole), HNCS (3508, 1982 cm⁻¹), CH₂O (2864, 2798 cm⁻¹), and *N*-cyanoimidazole¹⁴ (2267 cm⁻¹) were also present.

FVT-MS experiments with pyrolysis in the ion source of the mass spectrometer again afforded the m/z 89 peak. However, m/z 89 is also formed as a fragment ion from both azolides upon dissociative ionization.⁷ In order to probe whether m/z 89 was formed both thermally and dissociatively, the FVP-MS experiment was carried out at different ionization potentials. The triazolide showed m/z 89 as the base peak under all conditions (room temperature to 250 °C; 10–70 eV). For the imid-azolide, the intensity of the m/z 89 peak increased from *ca.* 30% at room temperature (10–70 eV), to *ca.* 60% at 250 °C (10 eV), thereby indicating that this peak is due, at least in part, to the ionization of thermally produced MeONCS (2).

Theoretical calculations

Standard DFT and *ab initio* calculations¹⁵ of the IR spectra of MeONCS (2) and iPrONCS (9) are presented in Table 1. The B3LYP/6-31G* structures of the two compounds are also given in the Table. A complete listing of calculated frequencies (including weak bands) and the cartesian coordinates of the computed structures are available as supplementary data.† It is seen that the bands observed experimentally (*vide supra*) are in very good agreement with the strongest calculated bands, thereby strongly supporting the experimental identifications.

Conclusions

Methoxy isothiocyanate 2 is formed from three different precursors (1, 11, 12) on FVT and identified by its Ar matrix IR spectrum in conjunction with *ab initio* and DFT calculations. The corresponding isopropoxy isothiocyanate 9 is generated from the silver salt 8. These alkoxy isothiocyanates are stable until *ca.* 120 and 150 K, respectively, and oligomerise to produce mixtures of bis(alkoxyimino)trithiolanes and -tetrathianes.

Experimental

General

The FTIR and argon matrix isolation apparatus employing a quartz thermolysis tube (150 mm length and 8 mm internal diameter) has been described earlier.¹⁸ BaF₂ optics were used. The FVP-MS equipment based on a six-sector tandem mass spectrometer (Micromass AutoSpec 6F) fitted with a quartz thermolysis tube (50 mm length, 3 mm inner diameter) directly connected to the outer ion source was as previously described.^{9,19,20} CA spectra were recorded by scanning the field of the second electric sector and collecting the ions with the first off-axis photomultiplier detector, the collision gas being helium. Low ionization voltage mass spectra were recorded on a Kratos MS25RFA instrument with direct insertion and pyrolysis on the heatable solid insertion probe tip. Routine EI

mass spectra were recorded on a Varian MAT 311A spectrometer. NMR spectra were recorded on Varian Gemini 300 MHz and Bruker AC 250 MHz spectrometers. HPLC was performed on a Waters Delta Prep 3000 with Waters 600E System Controller and Waters 484 Tunable Absorbance Detector with an RP18 column with Delta Pak C18, 300 Å, 15 μ .

Pyrolysis of the silver salts of N-alkoxydithiocarbamic acid

The silver salt was placed in the sublimation oven of the FVT apparatus, and the temperature was adjusted to 140 °C. The compound deflagrated. It may be necessary to place a little quartz wool between the sublimation oven and the pyrolysis oven to prevent solid material being deposited on the cryostat target.

Pyrolysis of sublimable compounds

The compounds were placed in the sublimation oven and sublimed into the pyrolysis oven. The pyrolysis products were codeposited with ca. 200 mbar of Ar on a BaF₂ window in ca. 20 min.

Materials

Methoxyamine and isopropoxyamine were prepared according to literature procedures.²¹

Silver N-methoxydithiocarbamate 1. 1 was prepared by a modification of the method used by Traube.¹ O-Methoxyamine (0.47 g, 0.01 mol) in ethanol (10 ml) was cooled to -10 to -15 °C with exclusion of water, and carbon disulfide (0.76 g, 0.01 mol) in ethanol (10 ml) was added during 10 min. The mixture was left with stirring at the same temperature for 1 h, when silver nitrate 10% (6 ml) was added. A yellow compound precipitated and was isolated by centrifugation, washed with water (2 × 10 ml), and then with ethanol (10 ml) and dry ether (10 ml). The compound was dried in a desiccator over conc. sulfuric acid in the dark. Yield (0.64 g, 38%). Found: C, 7.47; H, 0.88; N, 4.30; ref. 1: C, 6.56; H, 1.0; N, 4.63. C₂H₃NOS₂Ag₂ requires C, 7.13; H, 0.90; N, 4.16%.

Lead N-methoxydithiocarbamate. This was prepared in the same way as the silver salt. Yield (0.70 g, 43%). Found: C, 7.35; H, 0.80; N, 4.13. $C_2H_3NOS_2Pb$ requires C, 7.32; H, 0.92; N, 4.27%.

Silver *N*-isopropoxydithiocarbamate 8. This was prepared from *N*-isopropoxyamine in the same way as 1. Yield 24%. Found: C, 11.33; H, 1.50; N, 4.20. $C_4H_7NOS_2Ag_2$ requires C, 13.16; H, 1.93; N, 3.84%. As it was not possible to obtain a satisfactory analysis, the compound was used as such in the pyrolyses.

3,6-Bis(N-methoxyimino)-1,2,4,5-tetrathiane. The method was analogous to that used for the preparation of the corresponding bis(phenylhydrazono)tetrathiane.⁸ To O-methoxyamine (1.43 g, 0.03 mol) in ethanol (96%; 70 ml) was added carbon disulfide (6.86 g, 0.09 mol) during 10 min with cooling in ice under argon. After stirring for a further 2 h at 0 °C (pH = 5–6), hydrogen peroxide 35% (5.83 g, 0.06 mol) was added during 10 min. The yellow-green solution was stirred for a further 75 min, when chloroform (200 ml) was added. The chloroform phase was washed with water $(3 \times 50 \text{ ml})$ and dried over sodium sulfate. After evaporation of the chloroform, a yellow oil was left (1.46 g). GC-MS showed three narrowly spaced peaks and a fourth larger peak corresponding to 3,5bis(N-methoxyimino)-1,2,4-trithiolane and 3,6-bis(N-methoxyimino)-1,2,4,5-tetrathiane, respectively. These could not be separated by column chromatography. The tetrathiane was isolated by HPLC. Found: C, 21.76; H, 2.79; N, 11.13; S, 53.3.

 $C_4H_6N_2O_2S_4$ requires C, 19.82; H, 2.50; N, 11.56; S, 52.92%. It was not possible by HPLC to obtain it absolutely pure. IR (KBr neat) v = 2976, 2936, 2895, 2816, 1529, 1460, 1068, 959, 872, 640 cm⁻¹; IR (Ar matrix 10 K) v = 2991, 2953, 2909, 2828, 1538, 1467, 1442, 1354, 1079, 969, 881 cm⁻¹; NMR δ_H (300 MHz; CDCl₃; Me₄Si) 4.04 (s, OMe); δ_{13C} (250 MHz; CDCl₃; Me₄Si) 63.67 (OCH₃), 154.11 (C=N–). MS(EI) *m/z* 242 (M⁺, 88%), 153 (100), 122 (2), 95 (13), 89 (15), 76 (2), 64 (7), 46 (2).

1-(*N***-Methoxythiocarbamoyl)imidazole 11. 11** was prepared according to a literature procedure¹³ from methoxyamine and *N*,*N*-thiocarbonyldiimidazole.

1-(*N***-methoxythiocarbamoyl)-1,2,4-triazole 12. 12** was prepared according to a literature procedure.²² 1,1'-Thiocarbonyl-di(1,2,4-triazole) (1.8 g, 0.01 mol) was dissolved in dry THF freshly distilled (10 mL) and *O*-methoxyamine (0.94 g, 0.02 mol) was added under nitrogen during 90 minutes, the colour changing from orange to yellow. The white compound which had precipitated was isolated by centrifugation, washed with dry THF (4 × 10 mL), dried in a desiccator over conc. sulfuric acid. Yield: (0.5 g, 28%). Mp 126–128 °C. Mass spectrum: *m*/*z* 158 (M⁺, 23%), 128 (4), 89 (100), 59 (12), M⁺ 158.026777, calc. for C₄H₆N₄OS 158.026233; NMR δ_H (300 MHz; DMSO; Me₄Si) 3.68 (s, 3H, OCH₃), 7.30 (s, 1H, NH), 7.89 (s, 1H, triazole CH); 8.89 (s, 1H, triazole CH); NMR δ₁₃_C (250 MHz; DMSO; (triazole *C*), 159.83 (*C*NOCH₃).

N-Alkoxythioureas. These were prepared from alkoxyamines and isothiocyanates.^{16,17}

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