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Alkoxy Isothiocyanates as Intermediates in the Flash Vacuum Pyrolysis of Alkoxythioureas

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Methoxy isothiocyanate MeO–NCS **2b** was detected by matrix isolation IR spectroscopy following flash vacuum pyrolysis (FVP) of *N*-methoxythioureas, *N*-*tert*-butyl-*N*′-methoxythiourea **1d** being the best precursor. Isothiocyanates **3**, amines, and aldehydes are also generated by FVP of several substituted *N*-alkoxythioureas **1** in the temperature range 400–800°C. The formation of these products can be explained either by secondary pyrolysis of initially formed alkoxy isothiocyanates **2**, or by an initial cleavage of the O–N bond in **1** via a free-radical mechanism. *N*-Cyanoamines **4** and/or the tautomeric carbodiimides **5** are formed by another pathway. The pyrolyses were monitored by IR spectroscopy and online mass spectrometry or tandem mass spectrometry, and the reaction mechanisms are supported by theoretical calculations.

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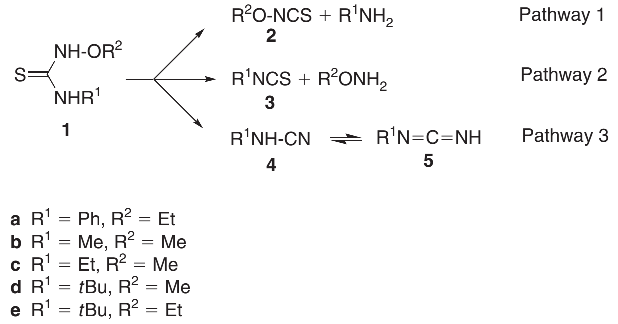
Introduction

Alkoxy isothiocyanates, RO–N=C=S, constitute a rare and elusive class of molecules having the characteristics of reactive intermediates.[1,2] It is known that *N*-alkyl- and *N*-arylthioureas can undergo thermal fragmentation into amines and isothiocyanates.[3,4] Therefore, the title compounds **1** could be considered as possible sources of alkoxy isothiocyanates. Larsen et al. studied the fragmentation of 3-ethoxy-1-phenylthiourea **1a** on heating in the inlet system of a mass spectrometer but did not obtain any definitive evidence for the formation of ethoxy isothiocyanate **2a**.[5] In previous work, we have reported the detection of methoxy and isopropoxy isothiocyanates. Here we report an investigation of various monosubstituted alkoxythioureas **1** (Scheme 1) by flash vacuum pyrolysis (FVP) coupled with matrix-isolation IR spectroscopy and online mass spectrometry.

Results and Discussions

Three fragmentation pathways, 1–3, were considered for the thermal reactions of the *N*-alkoxythioureas **1a**–**e** (Scheme 1). Pathway 1 involves fragmentation to an alkoxy isothiocyanate **2** and an amine. Pathway 2 generates an aryl or alkyl isothiocyanate **3** and an alkoxyamine. Pathway 3 involves the formation of an *N*-cyanoamine **4**. Several of the *N*-alkoxythioureas decompose to alkyl- or arylcyanamides and elemental sulfur already at room temperature.[6] Therefore, in all likelihood, the cyanamides observed in the present work are formed in the solid phase and are not the results of FVP reactions. The mechanism of the solid phase reaction is unknown. Cyanamides can tautomerize to *N*-monosubstituted carbodiimides, $R^1N{=}C{=}NH$ **5**,[7] and either of these tautomers may be observed in the IR and mass spectra.



Scheme 1. Thermolysis reactions of thioureas **1**.

*1-Phenyl-3-ethoxythiourea **1a***

The FVP of **1a** at 700°C with Ar matrix isolation of the products at 10 K afforded isothiocyanic acid HNCS as a prominent product, readily identified by strong absorptions at 1982 (NSC) and 3508 (NH) cm^{-1} in the IR spectrum (Fig. 1).[8] Another prominent peak at 2255 cm^{-1} was assigned to PhNHCN **4a**.[9] It was not possible to obtain a pure matrix spectrum of the thiourea **1a**, because decomposition giving rise to PhNHCN takes place below the sublimation temperature (Pathway 3; see above).

A small doublet corresponding to PhNCS was observed at 2045 and 2051 cm^{-1}. Additional peaks at 2124, 1596, and 752 cm^{-1} were also assigned to this compound based on comparison with previously reported spectra.[10] Further peaks at 1742, 1727, 1428, 1348, and 1111 cm^{-1} correspond to acetaldehyde,[11] as ascertained by comparison with an authentic Ar matrix IR spectrum. Acetaldehyde can be formed together with ammonia by secondary pyrolysis of $C_2H_5ONH_2$, i.e. the

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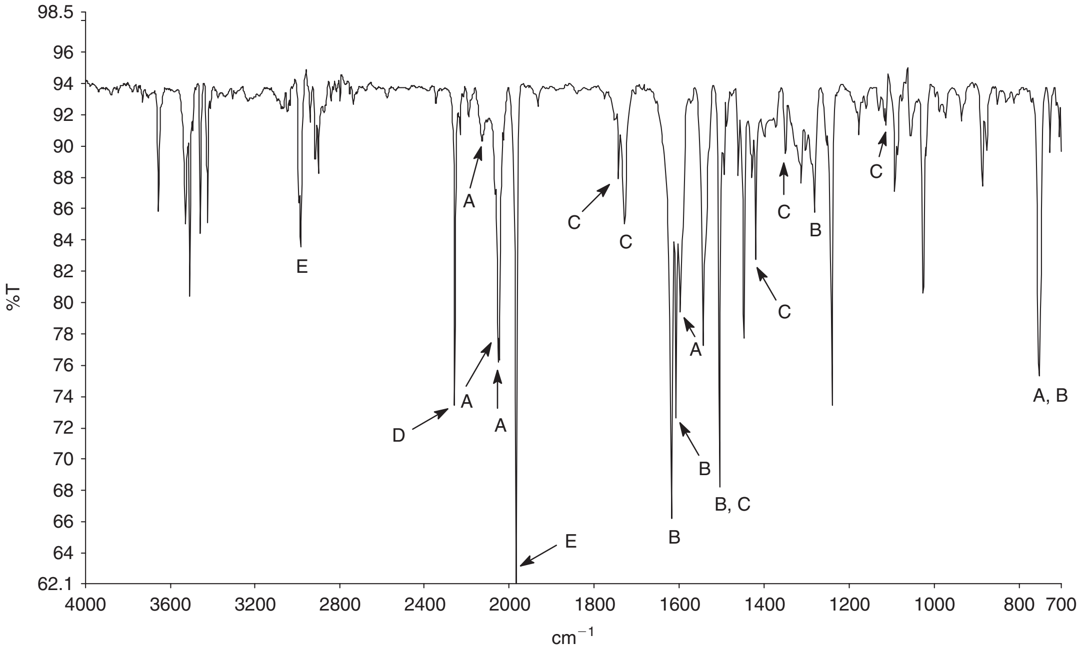
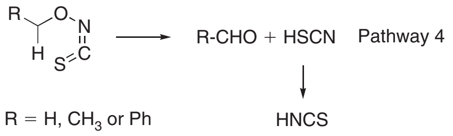


Fig. 1. IR spectrum (10 K, Ar matrix) of the pyrolysis products of compound **1a** at 700°C. (A) Bands due to PhNCS: 2124, 2051, 2045, 1596, 752 cm^{-1}. (B) Bands due to $PhNH_2$: 1619, 1607, 1503, 1288, 752 cm^{-1}. (C) Bands due to CH_3CHO: 1742, 1727, 1348, 1111 cm^{-1}. (D) Band due to PhNHCN: 2255 cm^{-1}. (E) Bands due to HNCS: 3508, 1982 cm^{-1}.



Scheme 2. Pericyclic formation of aldehydes and HNCS.

amine by-product expected to be formed together with PhNCS in Pathway 2 (Scheme 1). Authentic $C_2H_5ONH_2$ was found to pyrolyze at 500°C to give a strong IR spectrum due to acetaldehyde. An increase of the temperature in the FVP of **1a** caused the phenyl isothiocyanate and *N*-cyanophenylamine signals to increase; at 800°C, their intensities were of the same order.

Direct evidence for Pathway 1 (Scheme 1), the possible formation of ethoxy isothiocyanate EtONCS **2a**, remained elusive in this case. The calculated spectrum of **2a** at the *B3 LYP/ 6–31G*** level has the strongest absorption at 1989 cm^{-1}. Scaling by a factor 0.96 gives an expected absorption at ~1909 cm^{-1}. No peak was observable in this region. This is likely to be due to the high temperature required to pyrolyze **1a** (>700°C). The by-product of Pathway 1, aniline, was detected by its IR spectrum (1619vs, 1607m, 503s, 1288m, and 752s cm^{-1}). As shown below, alkoxy isothiocyanates *can* be observed directly in the pyrolyses of **1c** and **1d**, which take place at lower temperatures.

The aforementioned formation of acetaldehyde in the FVP of **1a** could also be due to a pericyclic reaction involving ethoxy isothiocyanate **2a** formed as an intermediate (Pathway 4, Scheme 2). This process also explains the formation of HNCS, as the primarily formed thiocyanic acid (HSCN) would tautomerize to the more stable isothiocyanic acid (Scheme 2).

The formation of acetaldehyde, aniline, and isothiocyanic acid could, however, also be a consequence of an initial homolytic cleavage of the O–N bond in the thiourea. The mechanistic alternatives will be addressed below in the computational section.

The formation of acetaldehyde (*m/z* 44), aniline (*m/z* 93), ethanol (*m/z* 46), ammonia (*m/z* 17), HNCS (*m/z* 59), phenyl isothiocyanate (*m/z* 135), and phenylcyanamide/ phenylcarbodiimide (*m/z* 118) was confirmed by online FVP-MS and collisional activation mass spectrometry (CAMS) experiments on the corresponding molecular ions.

*1-Methyl-3-methoxythiourea **1b***

The FVP of **1b** proceeded in much the same way as described for **1a** (see Fig. S1, Accessory Publication). However, in this case, we have the advantage that we know the Ar matrix IR spectrum of methoxy isothiocyanate **2b** as formed by FVP of 1-(*N*-methoxythiocarbamoyl)-1,2,4-triazole.[1]

Thanks to the lower sublimation temperature of **1b** compared with **1a**, we were able to obtain a matrix IR spectrum of undecomposed **1b**. Very little pyrolysis took place at temperatures below 400°C, but it was nearly complete at 500°C. Between 450 and 500°C, a very weak peak was observed at 1888 cm^{-1}, which corresponds to the strongest peak in the spectrum of methoxy isothiocyanate, MeONCS **2b**.[1] It has the same shape as previously observed,[1] and it is absent at pyrolysis temperatures higher than 500°C, thus indicating the thermal decomposition to HNCS and formaldehyde as described above. Yet, the weakness of this band makes it desirable to find a better precursor. This was achieved with **1d** (see below). Signals due to methylamine[12] (the potential by-product of Pathway 1) were also present in the IR spectrum.

Similarly to the case of **1a**, HNCS, methyl isothiocyanate **3b**, and formaldehyde were formed as evidenced by the corresponding strong signals in the IR and mass spectra. Authentic methyl isothiocyanate **3b** has strong absorptions at 2125 and 2237 cm^{-1}. The better spectral resolution achieved in a pulsed pyrolysis

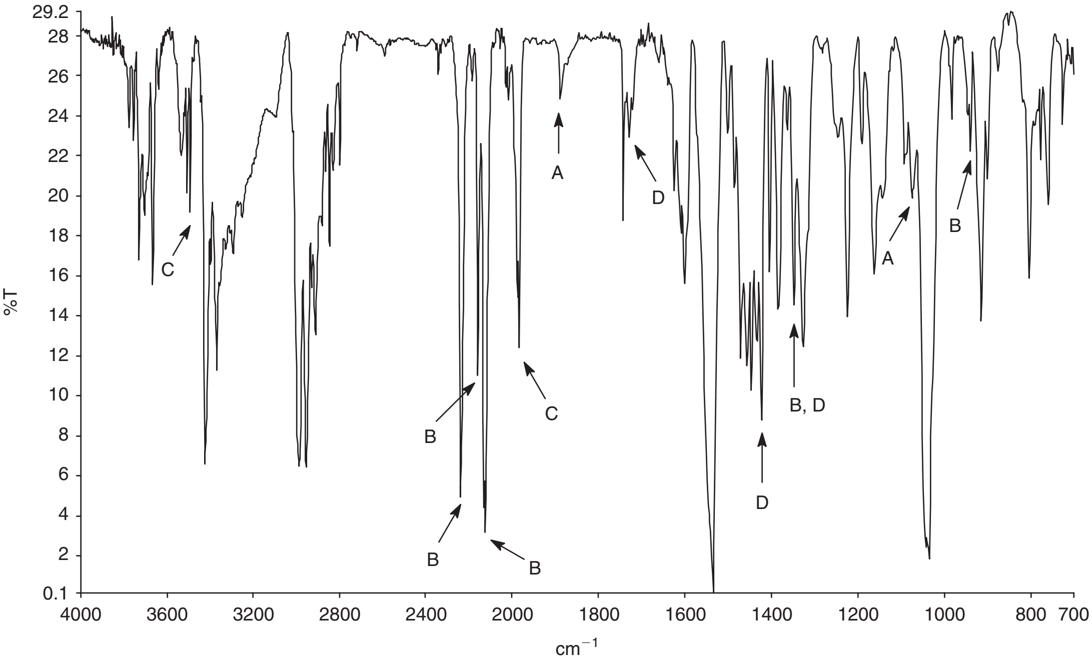


Fig. 2. IR spectrum (10 K, Ar matrix) of the pyrolysis products of compound **1c** at 400°C, showing (A) bands due to MeONCS **2b** at 1887 and 1074 cm^{-1}; (B) bands due to EtNCS at 2237, 2157, 2122, 1347, and 939 cm^{-1}; (C) bands due to HNCS at 3508 and 1982 cm^{-1}; (D) bands due to MeCHO at 1726, 1430, 1347, and 970 cm^{-1}.

experiment[13] revealed the presence of a further compound absorbing at 2232 cm^{-1} – the typical region for cyanoamines. The calculated IR spectra of methylcyanoamine CH_3NHCN **4b** and the isomeric methylcarbodiimide $CH_3N{=}C{=}NH$ **5b** feature strong absorption at 2258 and 2173 cm^{-1}, respectively (*B3 LYP/6–31G***; wavenumbers scaled by a factor 0.9613). The 2232 cm^{-1} band is ascribed to cyanoamine **4b**. A corresponding, prominent peak was observed at *m/z* 56 in the mass spectrum of the pyrolysis products.

1-Ethyl-3-methoxythiourea ***1c***

The FVP reactions of this compound were similar to those described for **1b**, except that weak bands ascribed to MeONCS were now clearly observed at 1887 and 1074 cm^{-1} following FVP at 400°C (Fig. 2). Bands due to ethyl isothiocyanate, HNCS and acetaldehyde were also present.

*1-*tert*-Butyl-3-methoxythiourea* ***1d*** *and 1-*tert*-Butyl-3-ethoxythiourea* ***1e***

The FVP of thiourea **1d** finally afforded more substantial amounts of the elusive methoxy isothiocyanate **2b**. Thus, FVP of **1d** at 400°C gave rise to a significant IR band at 1887 cm^{-1}, together with the accompanying bands at 1073 and 755 cm^{-1}, in excellent agreement with the previously reported spectrum[1] of methoxy isothiocyanate, MeONCS **2b** (Fig. 3). *tert*-Butylamine, the by-product of Pathway 1, was also observed in the IR spectrum (2966, 1366, 1223, 818 cm^{-1}; Fig. 3). In contrast, FVP of **1e** did not afford any band in the 1900 cm^{-1} region where calculations show EtONCS to have its strongest band. Otherwise, the reactions of **1d** and **1e** were analogous.

One could expect the formation of *tert*-butyl isothiocyanate **3d** as one of the reaction products of the pyrolysis of **1d** and **1e** via Pathway 2 (Scheme 1). *tert*-Butyl isothiocyanate has three significant absorptions at 2068, 2076, and 2084 cm^{-1}, but these bands were not observed. Instead, a series of significant bands due to 2-methyl-2-propene are noted. It has previously been observed that *N*-*tert*-butyl groups can be eliminated on FVP.[10] Here, the *tert*-butyl group may be eliminated as 2-methyl-2-propene from **1d** and **1e** to form the thiourea **6** (Scheme 3). A strong band at 2129 cm^{-1} is assigned to *tert*-butylcarbodiimide **5d**, which was also observed in the FVP-MS at *m/z* 98 (Pathway 3).

Bands due to formaldehyde (from **1d**) or acetaldehyde (from **1e**) were also observed. This is in line with an intense HNCS band (1982 cm^{-1}) and could be due to either Pathway 1 or Pathway 2 (Scheme 3), but Pathway 2 is unlikely in this case because of the absence of *tert*-butyl isothiocyanate **3d**. Control experiments showed that *tert*-butyl isothiocyanate does not decompose to 2-methyl-2-propene at 700°C. Thus, alkoxy isothiocyanates **2** could be formed by elimination of 2-methyl-2-propene followed by a Pathway 5 reaction of compound **6** (Scheme 3). Further fragmentation by the pericyclic Pathway 4 affords acetaldehyde and HNCS. In summary, methoxy isothiocyanate **2b** may be formed by either Pathway 1 or Pathway 5 (Scheme 3).

The formation of methoxy isothiocyanate **2b** was confirmed by FVP-MS. The real-time analysis of the CAMS of the *m/z* 89 ions (already present without pyrolysis) indeed reveals the appearance near 450°C of new peaks at *m/z* 74, 59, 32, 30, 29 during the pyrolysis of **1d** (see Fig. 4). These telltale peaks were identical with those observed in the CAMS of the *m/z* 89 ions originating from the FVP of 1-(*N*-methoxythiocarbamoyl)-1,2,4-triazole.[2]

Theoretical Calculations

Activation energies ($\Delta E^{\neq}$) and reaction energies (ΔE_0) for selected key processes in the FVP of **1b** were calculated at the *B3 LYP/6–31G*** and *MP2/cc-pVDZ* levels of theory and are indicated in Scheme 4, where values in parentheses

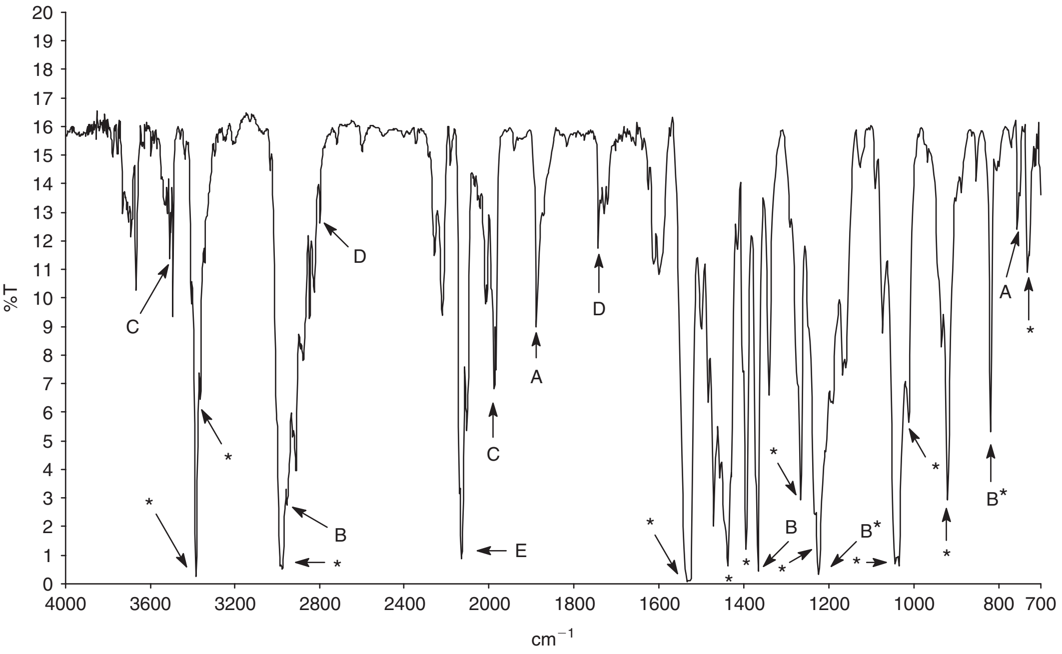
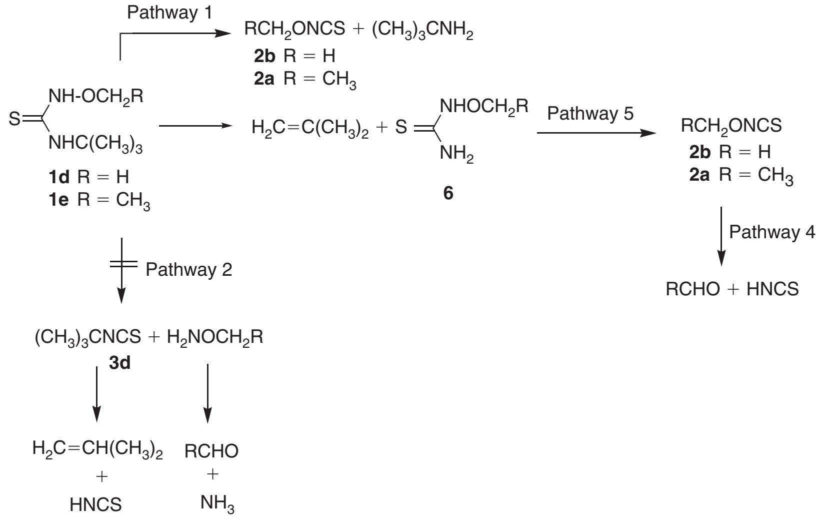


Fig. 3. IR spectrum (10 K, Ar matrix) of the pyrolysis products of compound **1d** at 400°C. (A) Bands due to MeONCS **2b**: 1887, 1073, and 755 cm^{-1}. (B) Bands due to *t*BuNH$_2$: 2966, 1366, 1223, and 818 cm^{-1}. (C) Band due to HNCS: 1982 cm^{-1}. (D) Bands due to HCHO: 2797 and 1741 cm^{-1}. (⋆) Bands due to unpyrolyzed starting material **1d**. (E) Band ascribed to *t*BuNCNH: 2129 cm^{-1}.



Scheme 3. Thermolysis of the *N*-*tert*-butyl-*N*′-alkoxy thioureas.

correspond to the *MP2* results. The fragmentations to MeONCS **2b** + MeNH$_2$ (**TS1**) and to MeNCS **3b** + H$_2$NOMe (**TS2**) have calculated activation energies of 163 (146) and 171 (156) kJ mol^{-1}, respectively. These estimates of activation barriers suggest that both these processes are readily accessible under FVP conditions, and the formation of the methoxy isothiocyanate **2b** is clearly a favourable process. Fragmentation reactions leading to formaldehyde, HNCS and MeNCS **3b** via thiourea derivatives **7** and **8** have calculated barriers on the order of 134–191 kJ mol^{-1}; therefore, all these reactions can take place at or near the temperature where MeONCS **2b** is formed.

The pericyclic decomposition of MeONCS **2b** to HSCN and formaldehyde (Pathway 4) is a favourable process with an activation barrier of 134 (111) kJ mol^{-1} (**TS8**, Scheme 4). Similar values were calculated for the decomposition of **2a** to HSCN and acetaldehyde (131 (105) kJ mol^{-1}). As expected, the direct formation of HNCS from **2b** has an ~100 kJ mol^{-1} higher calculated barrier (233 kJ mol^{-1}) (**TS9**, Scheme 4).

The cleavage of the O–N bond in **1b** to form the methoxy radical and thiourea radical **9** (Scheme 5) is predicted to have a barrier of 196 kJ mol^{-1} at the *B3 LYP/6–31G*** level, and 199 kJ mol^{-1} at the *CCSD(T)/cc-pVDZ* level, in excellent agreement with experimental bond dissociation energies of O–N bonds of ~200 kJ mol^{-1},[14] whereas the *MP2* method overestimates this bond energy (234 kJ mol^{-1}; Scheme 5). Thus, all the calculations predict that the free-radical pathway (Scheme 5) has a significantly higher activation barrier than the molecular processes in Scheme 4. Nevertheless, some participation of free

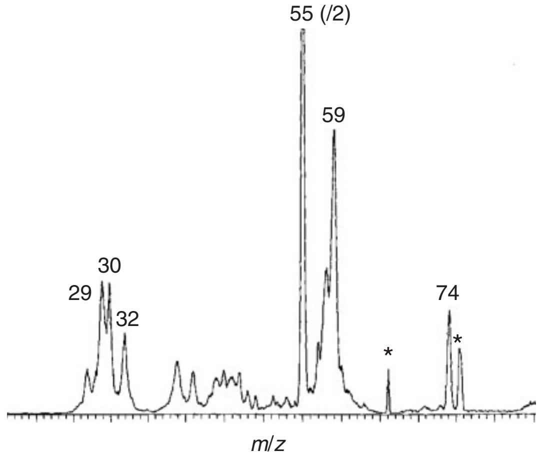
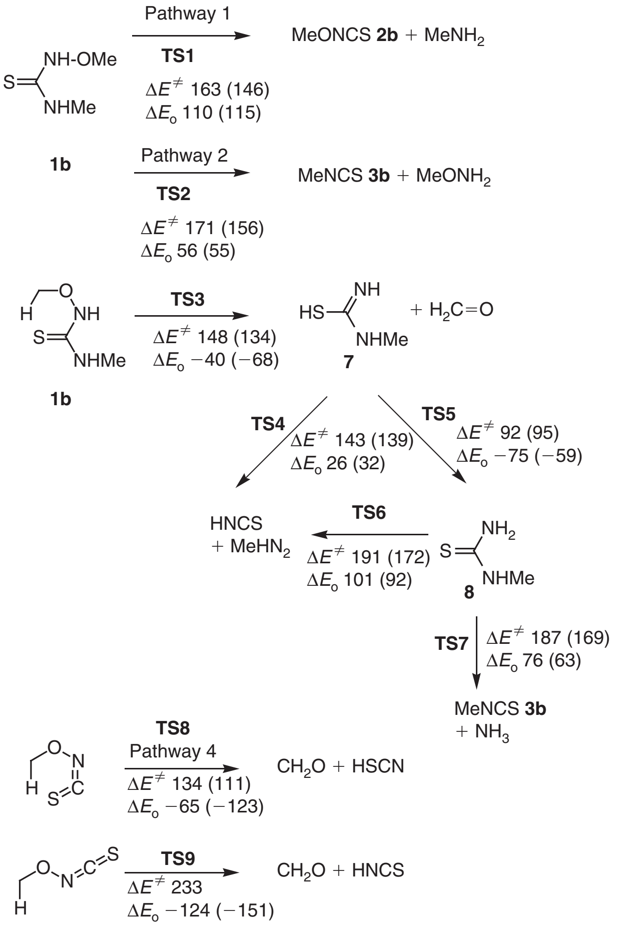
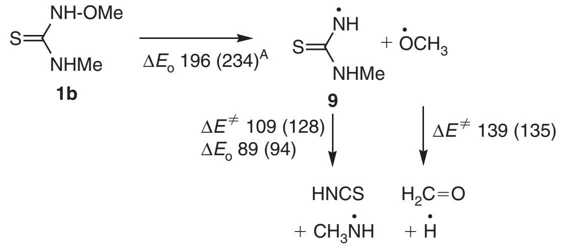


Fig. 4. Collisional activation mass spectrum (CAMS) of *m/z* 89 ions (MeONCS **2b**) generated after flash vacuum pyrolysis of **1d** at a temperature of ~450°C; ⋆ refers to artefact peaks.



Scheme 4. Calculated activation barriers $\Delta E^{\neq}$ and energies of reaction ΔE_0 at the *B3 LYP/6–31G*** (*MP2/cc-pVDZ*) levels of theory in kJ mol^{-1}.

radical processes cannot be excluded. If Scheme 5 were followed, then formaldehyde could be formed from the methoxy radical $CH_3O^{\bullet}$ with a barrier of 139 (135) kJ mol^{-1}, and HNCS and methylamine could be formed from the thiourea radical **9** with an activation barrier of ~109 (128) kJ mol^{-1} (Scheme 5).



Scheme 5. Calculated activation barriers $\Delta E^{\neq}$ and energies of reaction ΔE_0 at the *B3 LYP/6–31G*** (*MP2/cc-pVDZ*) levels of theory in kJ mol^{-1}. $^{A}\Delta E_0 = 199$ kJ mol^{-1} is obtained at the *CCSD(T)/cc-pVDZ* level.

Similar activation energies have been calculated for the reactions of thiourea **1a** analogous to Schemes 4 and 5. However, a very notable difference is that the **TS1** reaction ($\Delta E^{\neq} = 178$ (161) kJ mol^{-1}) leading to EtONCS **2a** is now less favourable than the **TS2** reaction ($\Delta E^{\neq} = 167$ (153) kJ mol^{-1}) leading to PhNCS **3a**, in agreement with the fact that it is experimentally very difficult to observe **2a**. Changing the R^1 group from methyl to phenyl thus alters the calculated ~10 kJ mol^{-1} preference for reaction via **TS1** to a ~10 kJ mol^{-1} preference for reaction via **TS2**.

Free radical reactions involving initial dissociation of either of the N–H bonds in **1a** and **2a** have very high calculated barriers (NH bond dissociation energies 344–387 (358–493) kJ mol^{-1}) and are therefore not likely to be involved.

Conclusions

Methoxy isothiocyanate MeONCS **2b** has been identified as a product of FVP of the corresponding *N*-alkoxythiourea **1d** by means of its Ar matrix IR spectrum. Weaker and therefore less securely identified signals due to MeONCS **2b** were also observed in the FVP of **1b** and **1c**. Theoretical calculations support the formation of **2b** from thiourea **1b** with an activation barrier of 140–160 kJ mol^{-1}. Ethoxy isothiocyanate **2a** is possibly formed in the FVP reactions of thioureas **1a** and **1e** but was not directly observable, either because it was formed in too low concentration, or because it decomposed under the high-temperature FVP conditions. The formation of aldehydes and isothiocyanic acid, HNCS, as secondary fragmentation products may take place via pericyclic reactions of the alkoxy isothiocyanates or by free radical reactions involving primary cleavage of the O–N bond of the alkoxythioureas.

Computational Methods

Calculated IR spectra were obtained at the *B3 LYP* level of theory[15] with the *6–31G*** basis set.[16] Energies of ground and transition structures were obtained from fully optimized geometries at the *B3 LYP/6–31G*** and *MP2/cc-pVDZ* levels of theory. All calculations were performed using the *Gaussian 03* program package.[17] Transition structures were located using the default optimization algorithm in the *Gaussian 03* program, and verified by frequency calculations and tracing the intrinsic reaction coordinate in cases where the normal mode associated with the imaginary frequency did not clearly connect the two minima.

Experimental

General Methods

The Fourier-transform (FT)-IR and argon matrix isolation apparatus employing a quartz thermolysis tube (150 mm length and

8 mm internal diameter) has been described earlier.[18] BaF_2 optics were used. For some of the pyrolyses, e.g. **1d** and **1e**, a modified oven was used, in which the hot tube extends to within a few mm from the cold BaF_2 disk. 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 previously described.[19]

The pulsed pyrolysis apparatus[13] employed a solenoid valve (General Valve Corp. Series 9) operating at a frequency of four pulses per min and a pulse duration of 10 s. The sample was evaporated at 100°C in a stream of Ar passed through the sample chamber at a stagnation pressure of 100 Pa. The sample chamber was attached directly to the valve, and both were held at the same temperature. The exit aperture of the valve led into an electrically heated quartz capillary (60 mm long, inner diameter 0.9 mm). The pyrolysis temperature in the oven was measured by optical pyrometry through a quartz window. Temperatures between 1000° and 1200°C were used.

Materials

The thioureas were prepared from alkoxyamines and isothiocyanates according to known procedures.[20,21] *O*-Methoxyamine and *O*-ethoxyamine are commercially available as hydrochlorides.

Matrix IR Spectra of Authentic Samples

Ar matrix, 10 K, ν/cm^{-1}: *Benzaldehyde* 3063(w), 2825(m), 2743(m), 1716(v), 1654(m), 1597(s), 1584(s), 1455(m), 1392(m), 1311(m), 1205(s), 1166(m), 1073(w), 828(s), 748(s).

Aniline 3498(w), 3411(w), 3048(w), 1702(vw), 1619(v), 1503(m), 1281(m), 1176(w), 1090(w), 875(w), 755(s).

Formaldehyde 2863(w), 2797(m), 1741(s), 1498(w), 1245(vw).

Methyl Isothiocyanate 2237(m), 2156(m, sh), 2125(v), 1592(w), 1527(m), 1452(vw), 1420(m), 1105(vw).

Ethyl Isothiocyanate 2228(v), 2203(v), 2155(v), 2132(v), 1453(m), 1347(s), 1269(m), 1064(m), 939(m).

Acetaldehyde 2750(w), 2737(w), 1749(m), 1726(s), 1431(m), 1348(m), 872(w).

Accessory Publication

Electronic supplementary information showing computational data (Cartesian coordinates, absolute energies, and IR spectra) for calculated species is available from the journal's website.

Acknowledgements

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