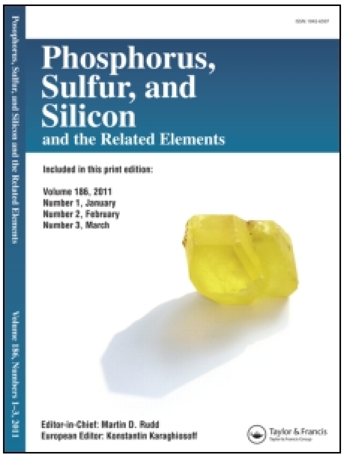

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The Formation of Alkoxyisothiocyanates and Alkoxyisocyanates from *N*-Alkoxy Thioureas and Ureas Studied by Flash Vacuum Pyrolysis

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The Formation of Alkoxyisothiocyanates and Alkoxyisocyanates from *N*-Alkoxy Thioureas and Ureas Studied by Flash Vacuum Pyrolysis

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The formation of alkoxy isothiocyanates from N*-alkoxy-substituted thioureas and alkoxy cyanates from* N*-alkoxy-substituted ureas by flash vacuum pyrolysis has been shown by combined Fourier Transform Infra Red (FTIR)-matrix isolation spectroscopy and online collisional activation mass spectrometry.*

Keywords Alkoxy isothiocyanates; flash-vacuum-pyrolysis; matrix isolation; online-mass spectrometry

We have prepared methoxy and isopropoxy isothiocyanate by pyrolysis of the silver salts of *N*-methoxy- and *N*-isopropoxydithiocarbamic acid.[1,2] In continuation of our interest in alkoxy isothiocyanates we have studied the pyrolysis of *N*-alkoxy-substituted thioureas and ureas. It is known that substituted thioureas fragment into an isothiocyanate and an amine upon GC-pyrolysis.[3] The same is observed in a mass spectrometric study of substituted thioureas.[4] We have therefore studied the pyrolysis of *N*-alkyl and aryl, *N′*-alkoxy thioureas and ureas (Scheme 1), which should give rise to a mixture of isothiocyanates (cyanates) and alkoxy isothiocyanates(cyanates) plus an amine or an *O*-substituted hydroxylamine.

Charles Larsen *et al.*[5] have studied the GC-MS pyrolysis of *N*-phenyl, *N′*-ethoxy thiourea, but were not able to give definite proof of whether ethoxy isothiocyanate was formed during this pyrolysis.

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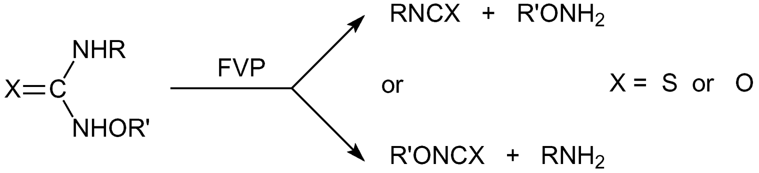


SCHEME 1

The compounds formed from the pyrolysis were in our study identified by a combination of Ar matrix isolation IR spectroscopy and online collisional activation mass spectrotrometry. From our study of methoxy isothiocyanate, we know that alkoxy isothiocyanates are not stable at room temperature. The methoxy compound was found to be stable only below 120K.[1]

However, we were not able to identify the alkoxy isothiocyanates directly from the pyrolysis of the thioureas at 700°C, but only indirectly by the formation of acetaldehyde and isothiocyanic acid (see Figure 1). At low temperature 300°C, the formation of *N*-cyanoamines was observed as the dominant pyrolysis products formed by the loss of hydrogen sulfide from the thiourea.

The formation of isothiocyanic acid and acetaldehyde from ethoxy isothiocyanate can be explained by the following pericyclic reaction

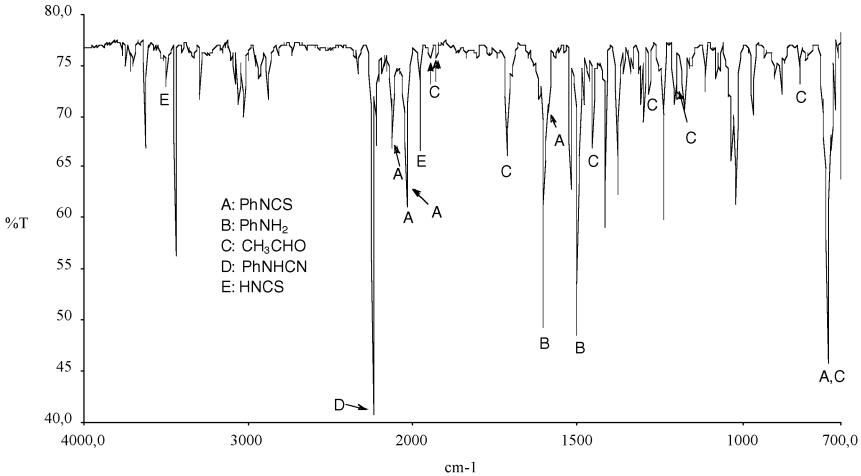
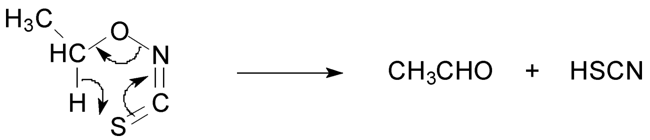


FIGURE 1 IR spectrum (10 K, Ar matrix) of the pyrolysis products of *N*-phenyl, *N'*-ethoxy thiourea at 700°C.



SCHEME 2

(Scheme 2) with subsequent rearrangement of thiocyanic acid to isothiocyanic acid

The electron ionization mass spectra of the thiourea at 200° and 800°C are shown in Figure 2. Without pyrolysis, the molecular ion peak (*m*/*z*196) is present but with a reduced intensity. Upon FVP at 800°, this peak disappeared and pyrolysis products were thus clearly identified at *m*/*z* 150, 135, and 118, and ascribed to phenylcyanamide (*m*/*z* 118) and phenylisothiocyanate (*m*/*z* 135) as evidenced by their collisional activation spectra (CAMS). *M*/*z* 150 ions could be due to the production (loss of EtOH) of 2-aminobenzothiazole; signals resulting from this compound are also observed in the FVP/IR experiment. The CAMS spectrum of the *m*/*z* 118 ions are identical to that obtained from an authentic sample.

Unambiguous identification of other pyrolysis products in the lower mass range was more difficult because of the complexity of the spectrum, but ethanol and ammonia have nevertheless also been characterized.

If alkyl groups are used instead of phenyl, the same result is observed. If *N*-benzyloxy-substituted thioureas are pyrolysed, benzaldehyde is observed instead of acetaldehyde, but in this case, too, we had no direct proof of the existence of benzyloxy isothiocyanate.

The pyrolysis of analogous ureas gave analogous results. In this case, too, we could only get indirect proof of the primary formation of alkoxy

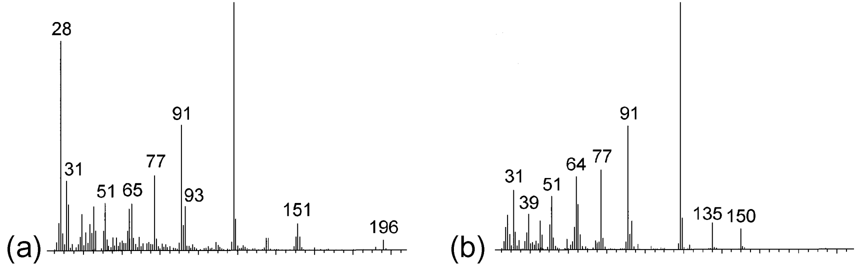


FIGURE 2 EI mass spectra of *N*-phenyl, *N*′-ethoxy thiourea at 200°C (a) and 800°C (b) oven temperature.

cyanates. The pyrolysis of *N*-phenyl-*N′*-ethoxy urea gave rise to the formation of phenyl cyanate, acetaldehyde, and isocyanic acid. In this case the formation of *N*-cyano phenylamine at low temperature 300°C was not observed.

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