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Analysis of thiocyanates and isothiocyanates by ammonia chemical ionization gas chromatography–mass spectrometry and gas chromatography–Fourier transform infrared spectroscopy☆

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ABSTRACT

Under NH_3-chemical ionization (CI) conditions alkyl thiocyanates give mass spectra which show only the adduct ions $(M + NH_4)^+$ (base peak) and $(M + NH_4 \cdot NH_3)^+$. Allyl thiocyanate and aromatic thiocyanates show fragmentation similar to the corresponding isothiocyanates but still produce $(M + NH_4)^+$ as base peak and $(M + NH_4 \cdot NH_3)^+$ as a prominent ion. These properties allow the thiocyanates to be easily distinguished from isothiocyanates whose NH_3-CI mass spectra indicate considerable fragmentation but little, or no, adduct ion formation. The isothiocyanates are further characterized by relatively abundant M^+ and $(M + H)^+$ ions in spectra of the C_1–C_5 alkyl isomers and the ion at m/z 115 as base peak for the longer-chain alkyl isothiocyanates.

Thiocyanates and isothiocyanates can also be differentiated on the basis of their gas-phase Fourier transform (FT) IR spectra. The spectra of isothiocyanates are dominated by a very intense absorption band at *ca.* 2060 cm^{-1} (–NCS) similar to that seen in liquid film spectra. Thiocyanates, in contrast, show only weak absorption at *ca.* 2165 cm^{-1}. Due to their weak interaction with infrared, aromatic thiocyanates are difficult to detect by this technique. Allyl thiocyanate is a special case. Under normal GC–FT-IR conditions it quickly isomerizes to allyl isothiocyanate. Allyl thiocyanate was only detected in admixture with allyl isothiocyanate, with light-pipe temperatures below 100°C.

INTRODUCTION

Isothiocyanates are formed by enzymatic hydrolysis of glucosinolates with myrosinase [1] but occasionally thiocyanates are also produced. Allyl thiocyanate, for example, is the major product from autolysis of *Thlaspi arvense* [2,3], 4-methylthiobutyl thiocyanate is obtained from *Eruca sativa* [4] and benzyl thiocyanate from *Lepidium sativum* and *L. ruderale* [2].

Allyl thiocyanate represents a special situation as it isomerizes readily to the corresponding isothiocyanate [3,5] (reaction 1) and the reverse isomerization also occurs in the hot injector (> 150°C) of a gas chromatograph [3]. The latter isomerization has also been indicated for allyl isothiocyanate isolated from Japanese horseradish (*Wasabi japonica*) [6] and GC–electron impact (EI) MS of a commercial sample of allyl

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isothiocyanate was also shown to contain two products having similar mass spectra [3,6]. Comparison with synthetic compounds [3] showed that the two products in commercial allyl isothiocyanate were in fact allyl thiocyanate and isothiocyanate.

$$CH_2{=}CH{-}CH_2{-}SCN \leftrightarrow SCN{-}CH_2{-}CH{=}CH_2 \quad (1)$$

The EI mass spectra of a number of isothiocyanates [7,8] and the similarity of the spectra of several thiocyanate–isothiocyanate pairs have been reported [9]. The main differences in the EI-MS of the short chain (C_1–C_5) alkyl isomers are the greater relative abundances of M^+ and the ion at *m/z* 72 (CH_2NCS) in spectra of the isothiocyanates. Jensen *et al.* [9] also reported that the mass spectra of alkyl thiocyanate and isothiocyanate isomers become less distinct with increasing chain length. As indicated in Fig. 1a and b, fragmentation of the allyl isomers under EI conditions does not allow unequivocal identification of thiocyanate and isothiocyanate and this is typical of other pairs of these isomeric compounds.

Because the EI mass spectra of allyl [3,6] and alkyl thiocyanates and isothiocyanates [9], do not permit unambiguous identification, it was decided to investigate other mass spectral techniques. Methane- and butane-chemical ionization (CI) MS of the allyl isomers gave identical spectra containing the $(M+1)^+$ ions as base peak together with the relevant adduct ions. However, using NH_3 as reagent gas, it was apparent that differences in the spectra of allyl thiocyanate and isothiocyanate (*cf.* Fig. 1c and d) would permit the identification of these two isomers. Subsequently, a number of alkyl/aryl thiocyanate–isothiocyanate pairs were examined by NH_3-CI-MS and the results are reported in this paper.

A complementary approach to differentiating between thiocyanates and isothiocyanates would be to utilize differences in the IR spectra of these compounds. The IR absorption bands of several thiocyanates and isothiocyanates have been listed by Bellamy [10] as occurring in the range 2174–2137 cm^{-1} and 2106–2045 cm^{-1}, respectively. Nakanishi and Solomon [11] indicated that alkyl thiocyanates have their –SCN bands in

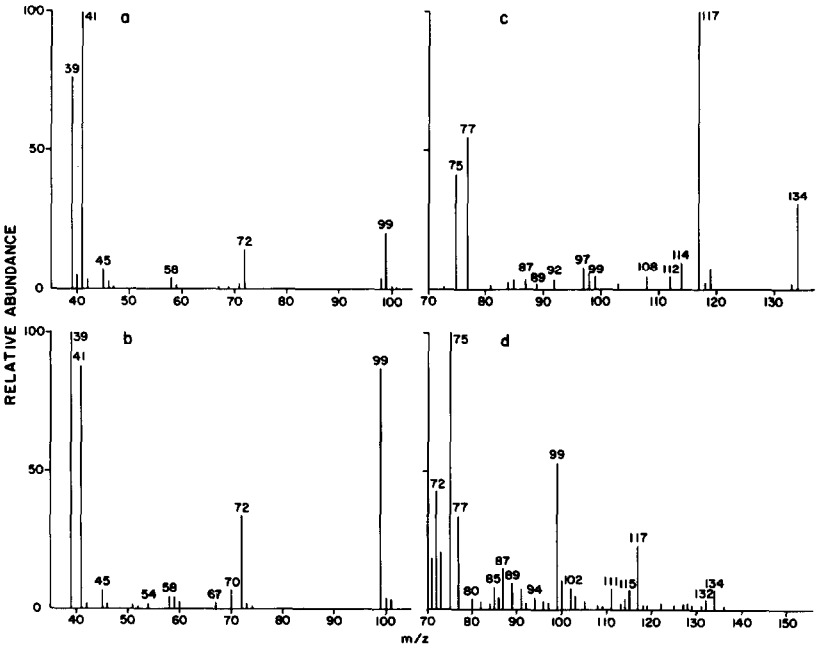

Fig. 1. EI mass spectra of (a) allyl thiocyanate; (b) allyl isothiocyanate; NH_3-CI mass spectra of (c) allyl thiocyanate; (d) allyl isothiocyanate.

the region of 2140 cm^{-1} with aryl thiocyanates showing this absorption at 2175–2160 cm^{-1}, while alkyl isothiocyanates have the–NCS absorption band at 2140–1990 cm^{-1} and aryl isothiocyanates at 2130–2040 cm^{-1}. Previously, Lieber *et al.* [12] reported that several thiocyanates and isothiocyanates could be differentiated on the basis of the vibration frequencies in the region of 2140 cm^{-1} and 2105–2060 cm^{-1}, respectively. The aforementioned citations refer exclusively to room temperature liquid film infrared spectra. Nevertheless, these properties suggest that thiocyanates and isothiocyanates may be distinguishable by GC–FT-IR. Accordingly, several isothiocyanates and thiocyanates were analyzed by GC–FT-IR–flame ionization detection (FID) and the unexpected results observed are included in this report.

EXPERIMENTAL

Chemicals were obtained from Aldrich (Milwaukee, WI, USA), Fairfield (Blythewood, SC, USA) or Dixon (Sherwood Park, Canada).

Allyl thiocyanate was prepared [3] by a modification of the procedure described by Emerson [13] and shown [3] to contain about 0.5% allyl isothiocyanate by GC–FID and GC–MS.

Allyl isothiocyanate free of thiocyanate was prepared [3] by treating allyl amine with 1,1'-thiocarbonyldiimidazole following the procedure of Staab and Walther [14].

The following thiocyanates were prepared by heating the corresponding bromides with NH_4SCN (1.1 equiv.) in ethanol on the steam bath for 4–8 h, adding ice–water and extracting with pentane: *n*-Pr, iso-Pr, *sec.*-Bu, iso-Bu, 3-butenyl, *n*-pentyl, *n*-heptyl, *n*-nonyl, *n*-decyl, 2-phenylethyl. *tert.*-Butyl thiocyanate was prepared by treating the bromide with NH_4SCN in ethanol at 0°C for 1 h followed by 2 h at room temperature. The pentane extract was concentrated by distillation at 45°C and the residual solvent removed by a stream of nitrogen at room temperature. Under these conditions approximately equal amounts of thiocyanate and isothiocyanate were obtained. Phenyl thiocyanate was synthesized from aniline by diazotisation followed by treatment with KSCN [15]. No attempt was made to optimize yields. GC–MS analyses confirmed the identities of the products and, in some cases, the presence of starting material.

3-Butenyl isothiocyanate was a gift from M. Chisholm (Plant Biotechnology Institute) and was prepared by treatment of the corresponding glucosinolate with myrosinase (EC 3.2.3.1).

Volatile products from homogenized stinkweed plants (*Thlaspi arvense*) were collected as described previously [16].

Instrumentation

GC analyses were performed on a Hewlett-Packard (Avondale, PA, USA) 5880 chromatograph fitted with a J & W Scientific DB-5 capillary column [60 m × 0.32 mm I.D., film thickness (d_f) 0.25 μm, Chromatographic Specialties, Brockville, Canada). The following conditions were used, unless stated otherwise: injector, 200°C; detector, 320°C; column, 20°C for 8 min, 4°C/min to 220°C, 10°C/min to 300°C; helium, 30 cm/s at 50°C. All samples were injected in the splitless mode with CH_2Cl_2 as solvent and toluene as internal reference.

A Finnigan 4000 GC–MS system (San Jose, CA, USA) was used for EI- and CI-MS and was operated under identical conditions as for GC analysis. The ammonia was adjusted to 0.40–0.45 Torr (1 Torr = 133.322 Pa) to maximize NH_4^+ and $(NH_4 \cdot NH_3)^+$. High-resolution MS data were obtained with a VG-250 SEQ mass spectrometer (VG Analytical, Altrincham, UK).

The IR spectra of allyl isothiocyanate (Aldrich) and allyl thiocyanate were obtained as liquid films (thickness unknown) on NaCl plates with a Bio-Rad (Mississauga, Canada) FTS 40 spectrometer. The allyl thiocyanate was kept on ice until ready for analysis.

A Hewlett-Packard 5890 gas chromatograph with an Ultra-2 (20 m × 0.22 mm I.D., d_f 0.25 μm, Hewlett-Packard), or Supelcowax-10 capillary column (20 m × 0.32 mm I.D., d_f 0.25 μm, Supelco Canada, Oakville, Canada) and a Nicolet FT-IR 20SXB spectrometer (Nicolet Instrument Canada, Mississauga, Canada) were used for gas-phase IR–FID determinations. The columns were connected directly to the light pipe via a heated transfer line. Unless stated other-

wise, the following conditions were used: column, 60°C for 1 min, 15°C/min to 275°C and hold 5 min; helium, 30 cm/s at 50°C; FID, 295°C. Samples in chloroform were introduced via a duck-bill cool-on-column injector. For most observations the light pipe was maintained at 180°C while the transfer line was held at 200°C. Effluent from the light pipe was transferred via a short megabore fused-silica capillary column to an FID system on the HP 5890 gas chromatograph.

RESULTS AND DISCUSSION

Gas chromatography

Under the chromatographic conditions used, baseline separation of all isothiocyanate–thiocyanate pairs is possible on a DB-5 column with the exception of *sec.*-BuNCS and *sec.*-BuSCN which essentially co-elute (t_R 23.13 and 23.21 min, respectively). In general, on the non-polar DB-5 or Ultra-2 columns, a thiocyanate elutes before the corresponding isothiocyanate with a quite regular difference in retention time. However, the *tert.*-butyl, and *sec.*-butyl isomers are exceptional in that the isothiocyanate elutes first.

Mass spectroscopy

In the ammonia CI-MS of the allyl isomers (Fig. 1c and d) the main distinguishing features are: (1) the base peak in the MS of the thiocyanate corresponds to $(M + NH_4)^+$ but the base peak of the isothiocyanate is at m/z 75; (2) the greater intensity of the ion at m/z 134, corresponding to $(M + NH_4 \cdot NH_3)^+$, in the spectrum of the thiocyanate; (3) the low intensity of M^+ in the spectrum of the thiocyanate; (4) the absence of the ion at m/z 72 in the spectrum of the thiocyanate.

The EI mass spectra of benzyl thiocyanate and benzyl isothiocyanate (not shown) are virtually identical. However, differences in the NH_3-CI-MS again permit distinction between the thiocyanate (Fig. 2a) and the isothiocyanate (Fig. 2b) since the MS of the latter is free of adduct ions (m/z 167, 184). For benzyl thiocyanate, the $(M + 18)^+$ ion is the base peak and is accompanied by the relatively abundant adduct ion at m/z (M + 35) but with no indica-

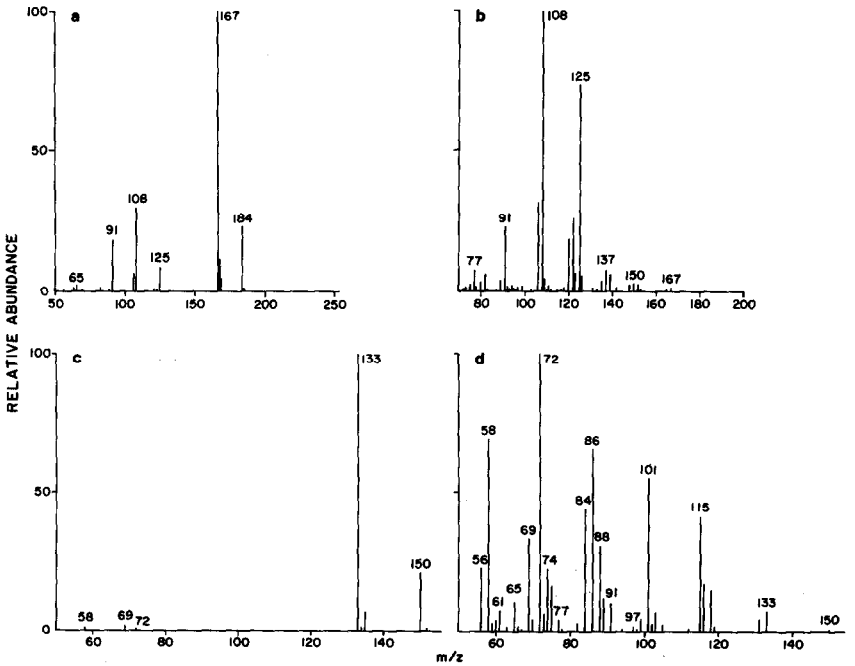

Fig. 2. NH_3-CI mass spectra of (a) benzyl thiocyanate; (b) benzyl isothiocyanate; (c) *sec.*-butyl thiocyanate; (d) *sec.*-butyl isothiocyanate.

tion of M^+ (Fig. 2a). In contrast to allyl isothiocyanate (Fig. 1d), the MS of benzyl isothiocyanate (Fig. 2b) shows only minor amounts of M^+ (*m/z* 149) and $(M+18)^+$ (*m/z* 167). For benzyl isothiocyanate, the base peak at *m/z* 108 is accompanied by a number of other prominent ions, some of which are also in the MS of the thiocyanate (Fig. 2a and b).

Analysis of additional pairs of isomers confirmed that the base peak for all thiocyanates examined occurs at *m/z* (M + 18) and is accompanied by a relatively abundant ion at *m/z* (M + 35) (*cf.* Figs. 1c and 2a and c). In contrast, these adduct ions have minimal abundances in the MS of the isothiocyanates with the exception of allyl isothiocyanate (Fig. 1d) and 2-phenylethyl isothiocyanate (Table I).

Table I contains selected data on representative isothiocyanates. Generally, the NH_3-CI-MS of alkyl (up to C_5) and aromatic isothiocyanates (except benzyl) contain a prominent molecular ion. For 3-butenyl, *tert.*-butyl, 2-methylbutyl, phenyl, *o*-, *m*-, *p*-methylphenyl and 1-naphthyl isothiocyanates, the M^+ is always the base peak but, for the other alkyl isothiocyanates up to C_5, the base peak may be M^+ or a smaller fragment (Table I, Figs. 1d and 2d). The longer-chain alkyl isothiocyanates all give the ion at *m/z* 115

TABLE I

RELATIVE ABUNDANCES OF IONS IN THE AMMONIA CHEMICAL IONIZATION MASS SPECTRA OF ISOTHIOCYANATES

Compound	Relative abundance (%)				
	M^+	$(M+1)^+$	$(M+18)^+$	$(M+35)^+$	Base peak (*m/z*)
MeNCS	100	17	6	–	M
EtNCS	100/46[a]	20	7	2	M/58
AllylNCS	55/21	10	25	5	75/58
iso-PrNCS	38/19	10	3	–	58/72
n-PrNCS	33/45	14	4	–	58/72
3-Butenyl-NCS	100	8	–	–	M
iso-BuNCS	33	26	5	–	78
n-BuNCS	100/89	12	2	–	M/86
sec.-BuNCS	41/18	17	7	–	72/86
tert.-BuNCS	100	–	58[b]	–	M
2-MeBuNCS	100	26	3	–	M
3-MeBuNCS	100/60	25	4	–	M/114
Pentyl-NCS	100/89	32	4	–	M/100
Hexyl-NCS	10	8	1	–	115
Heptyl-NCS	6	6	1	–	115
Octyl-NCS	5	10	1	–	115
Nonyl-NCS	13	11	–	–	115
Decyl-NCS	8	10	–	–	115
Phenyl-NCS	100	10	–	–	M
Benzyl-NCS	3	4	2	–	108
o-Tolyl-NCS	100	7	–	–	M
m-Tolyl-NCS	100	8	–	–	M
p-Tolyl-NCS	100	9	–	–	M
PhEtNCS[c]	20	10	45	–	108
1-Naphthyl-NCS	100	12	–	–	M

[a] Some of the isothiocyanates do not consistently give one particular ion as base peak. This is indicated by alternate values of relative abundance for M^+ and *m/z* values for the base peak.

[b] Relative abundance for ion at *m/z* (M + 17).

[c] PhEt = 2-Phenylethyl.

as the base peak (Table I). Kjaer *et al.* [7] reported that the ion at m/z 115 was prominent in the EI-MS of linear alkyl isothiocyanates with chain lengths greater than C_5. The spectra of the longer-chain (*i.e.* $>C_5$) isothiocyanates are also characterized by moderately abundant M^+ and $(M+1)^+$ ions (Table I). These features help distinguish the isothiocyanates from the isomeric thiocyanates.

The ease of distinction between alkyl thiocyanates and isothiocyanates by NH_3-CI-MS is typified by the spectra of the *sec.*-butyl isomers (Fig. 2c and d). Whereas the spectrum of the thiocyanate (Fig. 2c) contains only adduct ions, considerable fragmentation of the isothiocyanate is apparent (Fig. 2d). In this respect the NH_3-CI-MS of allyl thiocyanate (Fig. 1c) and benzyl thiocyanate (Fig. 2a) are anomalous as they indicate fragmentation similar to the corresponding isothiocyanates (Figs. 1d and 2b, respectively). This anomaly is also seen in the NH_3-CI-MS of phenyl thiocyanate and 2-phenylethyl thiocyanate (not shown) and may indicate that the presence of allyl or aromatic residues stabilizes these ions relative to their alkyl counterparts. Alternatively, this anomaly may be due to partial isomerization of the allyl and aromatic isomers in the ionization source. The tendency of allyl thiocyanate to isomerize to isothiocyanate is well known [3,5,14], and the reverse isomerization by brief exposure to temperatures greater than 150°C has also been demonstrated [3]. However, isomerization of aromatic thiocyanates is less well documented and no isomerization was detected in the present work using injector temperatures up to 200°C.

Isothiocyanates are known to react with ammonia to give thioureas (2) and some of the spectra do show minor ions at m/z $(M+NH_3)$ but this ion is prominent only in the spectrum of *tert.*-butyl isothiocyanate (Table I). However, the NH_3-CI mass spectra of the isomeric butyl thioureas (not shown) are identical and contain the ion at m/z $(M+1)$ {*i.e.* m/z $133 \equiv (M+NH_4)^+$ for the parent isothiocyanate} as the base peak and the adduct ion $(M+NH_4)^+$ at *ca.* 3% relative abundance. The NH_3-CI-MS of other alkyl thioureas, and benzyl thiourea, also give the $(M+H)^+$ ion as base peak and different fragments than the parent isothiocyanates (not shown). These observations suggest that little or no thiourea is formed during NH_3-CI-MS of isothiocyanates.

$$RCH_2\text{–}NCS + NH_3 \rightarrow RCH_2\text{–}NH\text{–}\underset{\displaystyle NH_2}{\overset{\displaystyle |}{C}}\text{=}S \qquad (2)$$

The fragmentation of the isothiocyanates under NH_3-CI conditions can be rationalized by postulating elimination of various neutral species from the adduct ions. For allyl isothiocyanate (Fig. 1d) the ions at m/z 77, 75 correspond to loss of cyclopropene and propylene, respectively, from the adduct $(M+NH_4)^+$. However, high-resolution MS showed the ion at m/z 72 has the same composition (CH_2NCS) as in the EI mass spectrum and is most likely derived from the relatively abundant molecular ion. Similarly, in the spectrum of *sec.*-butyl isothiocyanate (Fig. 2d) the molecular ion and the ion at m/z 72 are also abundant and other ions such as m/z 74, 91 appear to arise by loss of HNCS from the $(M+NH_4)^+$ and $(M+NH_4\cdot NH_3)^+$ adducts, respectively. Similar losses to give the base peak at m/z 108 and the ion at m/z 125 in the spectrum of benzyl isothiocyanate (Fig. 2b) were confirmed by high-resolution MS. The ion at m/z 108 is also the base peak in the spectrum of 2-phenylethyl isothiocyanate and is accompanied by the ion at m/z 125 (Table I). These ions are also prominent in the NH_3-CI mass spectrum of toluene which was used as a retention time reference. For toluene the ions at m/z 108, 125 obviously arise from adduct ions and can be represented by the elimination of H_2 from the $(M+NH_4)^+$ and $(M+NH_4\cdot NH_3)^+$ ions, respectively. The presence of the ions at m/z 108, 125 in the NH_3-CI-MS of these compounds suggests that these fragments are diagnostic for the benzyl group.

Infrared spectroscopy

A series of alkyl and aryl thiocyanates and isothiocyanates were examined by GC–FT-IR–FID (Table II). Fig. 3a shows the FID response and Fig. 3c the corresponding Gram–Schmidt reconstructed FT-IR chromatograms, respective-

TABLE II

THIOCYANATES AND ISOTHIOCYANATES EXAMINED BY GC–FT-IR

Peak No.	R	RNCS (ng)	RSCN (ng)	RSCN:RNCS
1	CH_3	68	2474	36
2	Et	60	2105	35
3	iso-Bu	62	2105	34
4	*n*-Bu	55	2000	36
5	*n*-C_5	50	363[a]	7
6	Ph	70	2500	36
7	*n*-C_7	53	1868	35
8	$PhCH_2$	56	2500	45
9	*n*-C_{10}	51	1974	39

[a] Sample contains 2138 ng/μl crude product comprising 17% thiocyanate which was not detected by GC–FT-IR (*cf.* Fig. 7, peak 5).

ly, for a mixture of isothiocyanates containing 50–70 ng of each compound (Table II). Fig. 3b and d show the corresponding responses for the isomeric thiocyanates at approximately 1900–2500 ng each. Comparison of Fig. 3b and d with Fig. 3a and c indicates that GC–FT-IR is appreciably more sensitive for the isothiocyanates than for the thiocyanates. Even when the thiocyanates are present in amounts 34–45 times greater than the corresponding isothiocyanates

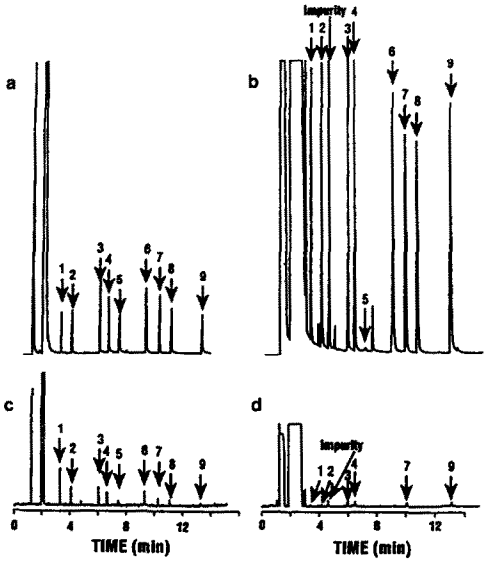

Fig. 3. GC–FID response of (a) isothiocyanates; (b) thiocyanates; and GC–FT-IR response of (c) isothiocyanates; (d) thiocyanates listed in Table II.

(Table II) their detection and subsequent identification by gas-phase FT-IR is not assured (Fig. 3d). Based on available information for liquid film spectra, these results were not expected.

In liquid film IR spectra, isothiocyanates display very strong, broad bands, or doublets, in the region 2200–2000 cm^{-1}, and thiocyanates are characterized by an intense, narrow band centred near 2160 cm^{-1} [11,17]. These features are exemplified by the liquid-film IR spectra of commercial allyl isothiocyanate (Fig. 4a), with the –NCS broad absorption band centred at *ca.* 2100 cm^{-1}, and allyl thiocyanate (Fig. 4b) with the –SCN absorption band at 2160 cm^{-1}. The liquid film spectrum of *n*-butyl thiocyanate [17] shows almost equal absorption intensities for the–SCN and alkyl groups. By comparing these liquid film spectra with the gas-phase spectra of *n*-butyl isothiocyanate (Fig. 4c), phenyl isothiocyanate (Fig. 4e) and the corresponding thiocyanates (Fig. 4d and f), it is obvious that the differences in detection sensitivity by GC–FT-IR is attributable to the relatively greater absorption intensity at *ca.* 2100 cm^{-1} of the–NCS chromophore in comparison to that of the much weaker–SCN chromophore. Examination of a number of alkyl and aryl isothiocyanates indicates that in the gas phase the–NCS chromophore is from 2–10 times more intense than the most intense C–H band. At the levels studied (50–90 ng), it is also possible to distinguish between alkyl and aromatic isothiocyanates by

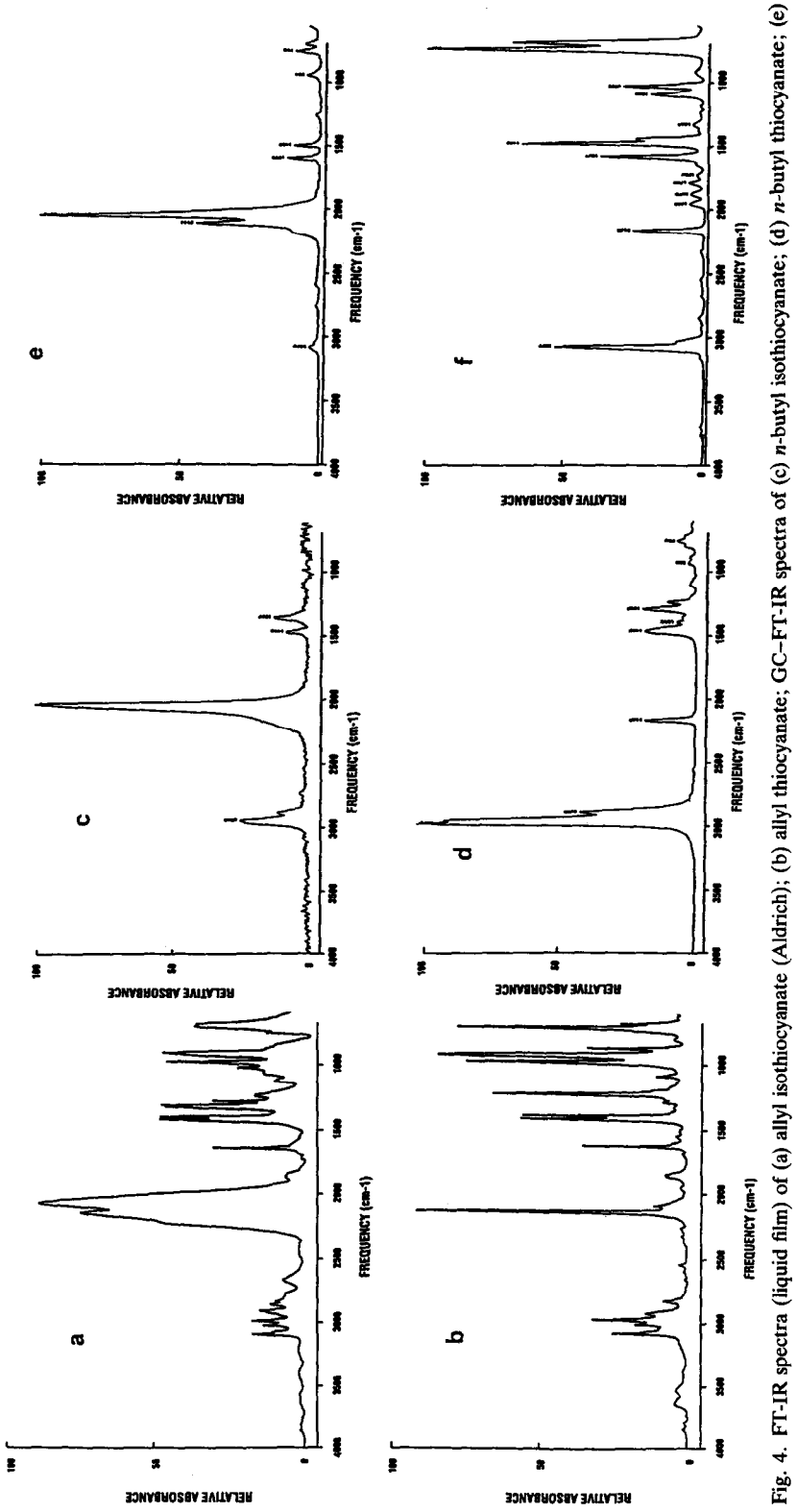

Fig. 4. FT-IR spectra (liquid film) of (a) allyl isothiocyanate (Aldrich); (b) allyl thiocyanate; GC–FT-IR spectra of (c) *n*-butyl isothiocyanate; (d) *n*-butyl thiocyanate; (e) phenyl isothiocyanate; (f) phenyl thiocyanate.

the bands in the region of 3000 cm^{-1} and 1600–1500 cm^{-1}, respectively (Fig. 4c and e).

In comparison to the isothiocyanates, gas-phase FT-IR detection of the thiocyanates is very poor relative to detection by FID (Fig. 3). The -SCN chromophore is only 0.1–0.3 times as intense as the most intense C–H band. Such findings were not expected based on available data (*cf.* Fig. 4b [10–12,17]).

The fact that aromatic compounds in general interact weakly with IR, coupled with the absence of an intense gas-phase thiocyanate absorption band, renders these molecules nearly transparent to the IR beam. Thus, neither the phenyl thiocyanate (Fig. 3b, peak 6) or benzyl thiocyanate (Fig. 3b, peak 8) in the amounts used (2500 ng, Table II), are detected by GC–FT-IR (Fig. 3d), even though they were present in concentrations greater than those of the detected alkyl thiocyanates (Table II). The GC–gas-phase IR spectra of *n*-butyl thiocyanate (Fig. 4d) and phenyl thiocyanate (Fig. 4f) are typical of the thiocyanates studied. However, allyl thiocyanate is a special case.

Analysis of allyl thiocyanate by GC–FT-IR is complicated by the tendency of this compound to isomerize, even at room temperature [3]. When an extract [16] of *Thlaspi arvense* (stinkweed, pennycress) is chromatographed with the light pipe at 100°C and transfer assembly at 125°C, two major peaks are observed (Fig. 5). The sharp peak (a) and the broad symmetrical peak (b) were previously identified [3] as allyl isothiocyanate and allyl thiocyanate, respectively. However, the gas-phase FT-IR spectra throughout the second peak are identical to the spectrum of allyl isothiocyanate (Fig. 6a) indicating complete racemization of the thiocyanate when the light pipe and transfer assembly are equal to, or greater than, the above temperatures.

When a partially racemized sample of allyl thiocyanate is chromatographed as above but with the light pipe at 70°C and transfer assembly at 80°C to reduce isomerization, the chromatogram in Fig. 6 (inset) is obtained. Allyl isothiocyanate exits the column first (7.67 min) followed by the thiocyanate peak beginning at about 8.10 min. Fig. 6b–f shows the variation of the IR spectra across the thiocyanate peak. The

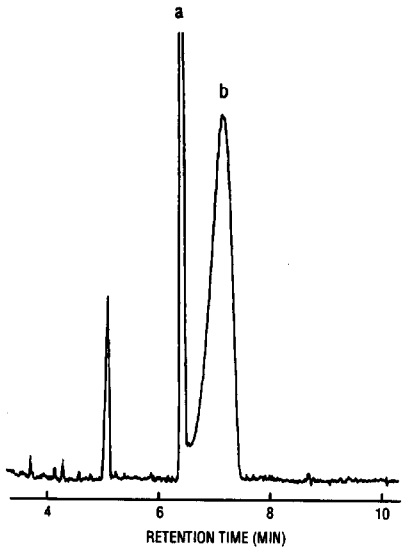

Fig. 5. GC–FT-IR chromatogram of *Thlaspi arvense* extract, cool-on-column (40°C) onto Supelcowax, light pipe at 100°C and transfer assembly at 125°C. See text.

spectrum at 9.04 min (Fig. 6b) indicates only allyl isothiocyanate (*cf.* Fig. 6a) whereas the spectrum taken at 11.80 min (Fig. 6f) suggests complete absence of this isomer. The ratio of the intensity of the band at *ca.* 2170 cm^{-1} to the most intense C–H band is similar to that found in GC–FT-IR spectra of aryl thiocyanates (*cf.* Fig. 4f). Thus, the spectrum in Fig. 6f appears to represent pure allyl thiocyanate (*cf.* Table III for IR data).The spectra in Fig. 6c–f are consistent with mixtures of this compound and progressively decreasing amounts of the isothiocyanate. Similar results are obtained with the light pipe at 60 or 80°C.

Searches of the gas-phase IR spectral libraries available from Nicolet/Aldrich, Hewlett-Packard/Aldrich and the US Environmental Protection Agency failed to correctly identify any of the thiocyanates examined in the present study. This is due to the scarcity of reliable data[a] for these compounds. Closest matches were for mercaptans, disulfides or halides.

[a] The Aldrich vapour library as supplied by Nicolet in 1985, contains only the spectra for *n*-octyl thiocyanate and benzyl thiocyanate. The latter appears to represent a mixture containing mostly benzyl isothiocyanate.

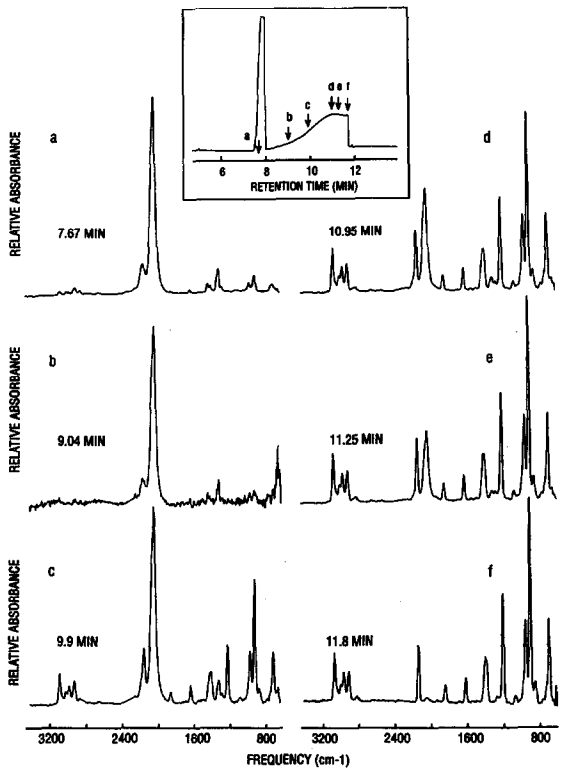

Fig. 6. GC–FT-IR chromatogram (insert) of partially racemized allyl thiocyanate, cool-on-column injection (40°C) onto Supelcowax, light pipe at 70°C, transfer line at 80°C. FT-IR spectra of (a) allyl isothiocyanate, (b–f) taken across the allyl thiocyanate peak.

The only essential difference between the GC–FT-IR system and that used for GC–MS analysis in the present, and previous work [3], is the light pipe. Since the previous work [3] showed that allyl thiocyanate injected at 75–100°C underwent mimimal isomerization, the present results indicate that isomerization during GC–FT-IR can occur in the light pipe, even at temperatures as low as 60°C, and may have been induced, in part, by the presence of the gold film and/or exposure to IR radiation.

CONCLUSIONS

Under normal GC–FT-IR conditions, allyl thiocyanate readily and completely isomerizes to the more stable allyl isothiocyanate. Allyl thiocyanate, in admixture with the isothiocyanate, can only be seen by GC–FT-IR if the light-pipe temperature is kept below 100°C. In general, isothiocyanates are readily detected and identified by GC–FT-IR. Thiocyanates are less easily detected and current gas-phase libraries do not give reliable identifications. Isothiocyanates give an intense–NCS band at *ca.* 2060 cm^{-1} which corresponds with their respective liquid film spectra. Conversely, the thiocyanates do not provide expected spectra by GC–FT-IR, only a weak band is observed at *ca.* 2160 cm^{-1}.

TABLE III

VAPOR-PHASE INFRARED SPECTRAL DATA FOR ALLYL THIOCYANATE WITH LIGHT PIPE AT 60°C

Peak No.	Wavelength (cm^{-1})	Intensity	Bandwidth (cm^{-1})
1	723.5	44	43
2	875.5	12	24
3	932.9	104	35
4	983.4	43	42
5	1234.9	57	38
6	1420.4	24	46
7	1434.6	25	22
8	1645.8	15	31
9	1869.6	11	49
10	2169.8	31	38
11	2846.4	6	46
12	2940.4	18	41
13	2996.9	18	26
14	3030.5	11	35
15	3101.7	27	31

The NH_3-CI mass spectra of alkyl thiocyanates contain only the base peak at m/z $(M + NH_4)^+$ and the comparatively abundant adduct ion $(M + NH_4 \cdot NH_3)^+$. This permits ready distinction of these compounds from the corresponding isothiocyanates whose NH_3-CI mass spectra are more complex and generally include M^+ and $(M + H)^+$ but essentially no adduct ions. The NH_3-CI mass spectra of linear alkyl isothiocyanates containing more than five carbons are further characterized by the presence of the ion at m/z 115 as the base peak. Although the allyl and aromatic thiocyanates fragment similarly to the corresponding isothiocyanates under NH_3-CI conditions, these isomers can also be distinguished easily by the presence of the ion

$(M + NH_4)^+$ as base peak and an abundant $(M + NH_4 \cdot NH_3)^+$ ion in the spectra of the thiocyanates.

Although GC–FT-IR does permit distinction between thiocyanates and isothiocyanates, the method, especially for thiocyanates, is not as sensitive as NH_3-CI-MS. In addition, the relative simplicity of the NH_3-CI spectra of thiocyanates allows ready distinction from the more complex fragmentation of the corresponding isothiocyanates.

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