Alkyl Cyanates

VII. Mass Spectra of Cyanates

KAI ARNE JENSEN, ARNE HOLM and CURT WENTRUP

Chemical Laboratory II (General and Organic Chemistry), University of Copenhagen, The H. C. Ørsted Institute, Copenhagen, Denmark

JØRGEN MØLLER

Physical Laboratory II, University of Copenhagen, The H. C. Ørsted Institute, Copenhagen, Denmark

The mass spectra of 10 alkyl cyanates, and phenyl cyanate, and, for comparison, the corresponding isocyanates, several thiocyanates, and isothiocyanates have been examined. With due precautions it is possible to obtain mass spectra which originate from the non-isomerised cyanates. The mass spectra of cyanates and isocyanates show small but significant differences. As a general rule fragments containing the functional group are more abundant in the spectra of isocyanates, whereas pure hydrocarbon fragments are more abundant in the spectra of cyanates. Fission of the functional group with elimination of CO has only been observed in a few cases. The difference between the spectra of thiocyanates and isothiocyanates are similar to those found for the cyanates and isocyanates but more pronounced. In the cyclization reactions, which take place with the higher alkyl derivatives, there are some remarkable differences between cyanates and thiocyanates; thus hexyl thiocyanate forms a cyclic ion by elimination of HCN, whereas hexyl cyanate forms a cyclic ion by elimination of ethylene.

With the exception of certain sterically hindered alkyl cyanates, such as neopentyl cyanate, alkyl cyanates isomerise easily to isocyanates and it was therefore, beforehand, considered doubtful whether it would be possible to obtain mass spectra characteristic of the alkyl cyanates. Since, however, the stabilities of alkyl cyanates increase with molecular weight, we considered it possible to determine their mass spectra and therefore initiated this investigation to see whether the chemical differences between cyanates and isocyanates were reflected in their mass spectra. With the following precautions it proved quite feasible to obtain mass spectra of cyanates:

a) The mass spectra obtained from alkyl cyanates may depend somewhat upon the previous history of the sample and very much upon the conditions of the experiment. It is therefore essential that gas-chromatographically pure cyanates are used for the experiment and that parallel runs are carried out each time with a cyanate and the corresponding isocyanate.

b) The temperature of the inlet system must be low (*ca.* 40°C), otherwise the cyanates will isomerise. If the temperature of the inlet line (the line from the leak to the ion source) is raised to 250°C the mass spectrum of a cyanate changes to that of the isocyanate; if the temperature is lowered, the cyanate spectrum appears again. Accordingly, any thermal isomerisation will take place before ionization. This seems reasonable, since ionization of a cyanate molecule after entering the ionization chamber will probably take place in less than the time needed for isomerisation, even at 170°C (the temperature of the ion source). When a cyanate has been kept in the reservoir of the mass spectrometer at 40°C and 10^{-2} mm Hg for some days, the mass spectrum will usually have changed to that of the isocyanate. These facts show clearly that it is actually possible to obtain mass spectra which originate from non-rearranged cyanates.

The nature of the ions — and especially the nature of the individual peaks in doublets — have been corroborated by addition of "cyanic acid" (*cf.* Ref. 1) or hexanol to samples of the alkyl cyanates. The mass spectra of branched chain cyanates and iso-cyanates show quite marked differences, as discussed below. The spectra of straight chain cyanates and isocyanates show much smaller differences; however, in both cases, the differences are mostly found in the intensities of the peaks and not in the appearance of different peaks. The most pronounced difference between straight chain alkyl cyanates and isocyanates is found for the ethyl compounds. With increasing chain length the spectra of isomeric cyanates and isocyanates differ less and less; the spectra of heptyl cyanate and heptyl isocyanate may in fact be considered identical. Since the stabilities of the cyanates increase with the chain length this fact cannot be due to isomerisation but simply means that the mass spectra of higher cyanates and isocyanates are practically identical.

The cracking patterns of cyanates and isocyanates have also been compared with those of the corresponding thiocyanates and isothiocyanates. For this comparison the spectra of isothiocyanates reported by Kjær, Djerassi *et al.*[2] could not be used directly because they were obtained with an inlet system temperature of 200°C and we found that the temperature of the inlet system may have a marked influence on the spectra also in the case of the sulfur compounds. The mass spectra of several thiocyanates and isothiocyanates corresponding to the cyanates and isocyanates investigated here have therefore been recorded at an inlet system temperature of 40°C.

EXPERIMENTAL

The mass spectra were obtained on an Atlas CH4 mass spectrometer. The inlet system was maintained at a temperature of 40°C and the temperature of the ion source was 170°C for the cyanates and isocyanates and 250°C for their thio analogues. An electron current of 35 μA and an ionizing potential of 70 eV were applied.

The data are presented in Tables 1—3. The mass spectra showing the most pronounced differences between cyanates and isocyanates have also been presented in the form of diagrams.

All compounds investigated were purified by gas-chromatography on a Perkin Elmer 116 gas chromatograph, with the exception of hexyl and heptyl cyanate which are not volatile enough to pass through the column without isomerisation. However, they were gas chromatographically pure in so far as the gas chromatogram showed only one peak, corresponding to the isocyanate. The purity of the compounds was in all cases monitored by infrared spectroscopy before they were used for mass spectrometry.

Cyanates. The cyanates were obtained as described earlier by decomposition of 5-alkoxy-1,2,3,4-thiatriazoles.[3] Pentyl, hexyl, and heptyl cyanates were prepared for the first time in connection with the present studies. The alkoxythiocarbonylhydrazines used have been described in another paper.[4] These yielded with nitrous acid the corresponding alkoxythiatriazoles (yields 90—99 % of crude products) which were recrystallised from ether by cooling in dry ice-acetone. Pentyloxythiatriazole and hexyloxythiatriazole decomposed as usual in ether solution at 20°C in the course of 24 h. The heptyl derivative decomposed incompletely in this way but readily on heating at 25—30°C without solvent. The crude product thus obtained contained about 10 % triheptylisocyanurate, but was otherwise pure cyanate according to the infrared spectrum. It could be distilled at 25—30°C and 0.1 mm Hg; the distillate was proved by its infrared spectrum to be heptyl cyanate. When the distillation was carried out at 60°C, the distillate consisted mainly of heptyl isocyanate.

Pentyl cyanate was distilled at 30°C and 0.4 mm Hg. Yield 0.85 g (26 %) from 5 g of the thiatriazole. The identity of the product was proved by its infrared and NMR spectra.

Hexyl cyanate prepared from 3 g of purified thiatriazole was distilled at 30°C and 0.1 mm Hg. When 1 g (50 %) had passed over the distillation was terminated; the residue was shown by analysis and infrared spectrum to be trihexylisocyanurate. The distillate was pure cyanate according to its infrared and NMR spectra.

Further, we have used the same method for preparing neopentyl cyanate since we did not succeed in obtaining it from neopentyl alcohol and cyanogen bromide according to Kauer and Henderson.[5] The thiatriazole was obtained in 99 % yield and yielded, on decomposition and distillation at 30°C and 0.1 mm Hg, 68 % of the cyanate. Neopentyl cyanate is only very slowly rearranged to the isocyanate (2—3 h at 145°C).

Phenyl cyanate was prepared according to Grigat and Pütter.[6]

Isocyanates. Pentyl isocyanate and *sec*-butyl isocyanate were prepared by the method of Boehmer,[7] the other alkyl isocyanates used were obtained by thermal rearrangement of the cyanates and purified by gas chromatography. Phenyl isocyanate was a commercial product, further purified by gas chromatography.

Thiocyanates and isothiocyanates. These were obtained commercially or synthesized by standard procedures.

DISCUSSION

Alkyl cyanates and isocyanates

Most of the peaks in the mass spectra of alkyl cyanates and isocyanates can be explained by a) cleavage of a C—C bond, especially the bond next to the functional group (α-cleavage), or b) elimination of the functional group (cleavage of the C—(NCO) or C—(OCN) bond, with or without transfer of hydrogen). Process a) is most pronounced for isocyanates and analogous with the corresponding process for amines, alcohols, *etc.* Process b) is most pronounced for cyanates. Two other types of fragmentation of a less general character have also been encountered: c) Fission of the functional group. This has only been observed in the case of phenyl cyanate and isocyanate and probably isobutyl isocyanate. d) Elimination of an alkene with the forma-

tion of a cyclic structure. This is a general reaction for higher alkyl cyanates and isocyanates.

However, the difference between the groups —OCN and —NCO is not great. Neither of these functional groups have a predominant influence on the fragmentation process in comparison with the hydrocarbon part of the molecule, as is evident from the fact that the positive charge may appear on one or the other of the two fragments without a clearcut difference in probability. When the chain length increases, the influence of the functional group becomes negligible in comparison with the influence of the alkyl group on simple cleavage. The main influence of the functional groups on the fragmentation of higher alkyl cyanates and isocyanates is that they may cause the formation of stable cyclic structures. However, in this respect there is no difference between the two types of compound.

Cleavage of a C—C bond. For primary isocyanates α-cleavage results in the formation of the resonance-stabilised ion CH_2NCO^+ with m/e 56. This peak also occurs to some extent in the spectra of cyanates and may be due to the same ion, since it seems possible that the ion CH_2OCN^+ is unable to stabilise a positive charge and rearranges into the more stable ion $CH_2=N^+=C=O$ (this may also arise directly from a rearranged molecular ion). By α-cleavage also the corresponding carbonium ions are formed, but in smaller amount.

As a general rule, fragments containing the functional group (molecular ions, M—1, M—alkyl) are more abundant in the spectra of isocyanates whereas pure hydrocarbon fragments are more abundant in the spectra of cyanates. This is in accordance with the greater electronegativity of O compared with N, which may also be inferred from NMR-spectroscopic and gas chromatographic data. It also indicates that the C—(OCN) bond is weaker than the C—(NCO) bond, which is born out by the fact that cyanates function as alkylating reagents in chemical reactions.[8] Accordingly it would be expected that fission of the bond to the functional group occurs to a higher degree in the cyanates and α-cleavage to a higher degree in the isocyanates.

The simplest straight chain alkyl cyanate, ethyl cyanate (methyl cyanate is too unstable to be investigated) shows the most pronounced differences from the isocyanate. Among the two simplest fragmentation processes, into $(C_2H_5)^+ + (OCN)$ or $(CH_3) + (CH_2OCN)^+$ (m/e 56) the former pair are favoured in the cyanate and, accordingly, the ethyl ion represents the base peak in the mass spectrum of ethyl cyanate whereas CH_2NCO^+ is the base peak in the spectrum of ethyl isocyanate.

For the higher aliphatic cyanates and isocyanates, the ion CH_2NCO^+ becomes less and less abundant and $C_4H_8^+$ constitutes an increasing part of the peak at m/e 56. In the mass spectra of butyl cyanate and butyl isocyanate about 50 % of the peak at m/e 56 is due to $C_4H_8^+$, formed by elimination of HOCN.

The higher cyanates also form $C_2H_5^+$ (m/e 29) and $C_3H_7^+$ (m/e 43) by β-, γ-, etc. cleavage, and alkenes by β-cleavage with hydrogen migration (m/e 42 from pentyl cyanate and m/e 56 from hexyl cyanate). A peak at m/e 41, which is probably due to the allyl ion, is also rather intense when the molecule contains at least three carbon atoms. It is always accompanied by an ion at m/e 39, which may be the cyclopropenylium ion, and a metastable

Table 1. Relative intensities of ions formed from straight chain alkyl cyanates and isocyanates expressed in per cent of $\sum_{25}$. 1: Alkyl cyanates, ROCN, 2: Alkyl isocyanates, RNCO.

R m/e	Ethyl 1	Ethyl 2	Propyl 1	Propyl 2	Butyl 1	Butyl 2	Pentyl 1	Pentyl 2	Hexyl 1	Hexyl 2	Heptyl 1	Heptyl 2
26	3.3	1.7	1.6	1.5	0.9	0.8	5.0	0.6	0.5	0.5	0.3	0.4
27	17.0	4.7	11.7	6.6	8.3	8.4	6.1	4.4	5.0	4.7	3.6	3.9
28	10.9	9.4	5.4	6.7	6.2	5.9	11.3	3.7	3.3	3.9	2.6	3.7
29	27.8	1.7	6.5	10.0	4.4	3.3	1.8	10.3	5.8	5.5	4.7	4.8
30	1.0		4.7	8.3	4.5	4.7	1.8	2.0	1.1	1.3	1.1	1.4
31			2.0	0.3	0.9							
38			0.8	0.4								
39		0.9	4.1	1.7	2.9	2.9	2.9	2.7	2.9	2.6	2.4	2.5
40	0.9	2.9	1.3	1.0	1.1	1.1	0.6	0.7	0.7	0.7	0.5	0.5
41	0.8	1.5	12.9	3.4	18.1	17.3	12.2	11.7	10.6	9.8	10.9	10.9
42a	1.2		0.7		1.0							
42b	1.2	3.4	6.8	8.1	3.0	4.4	12.7	12.1	5.5	4.4	4.8	4.6
43a	3.7	4.7	2.0	0.1	1.9	1.1	0.5	0.1	0.4			
43b			10.5	0.8	15.2	16.2	2.3	2.2	12.6	12.3	9.8	9.3
44	0.8	0.8			1.1	3.3	2.0	0.5	0.7	2.8	0.7	1.6
45							0.6					
53									0.5	0.5	0.5	0.5
54									0.6	0.5	0.8	0.8
55					2.3	2.8	7.8	6.6	7.6	6.5	7.6	7.0
56a	18.0	36.7	16.8	32.2	7.2	6.7	5.9	7.4	3.9	3.8	3.4	3.5
56b					8.1	8.4	1.4	1.5	8.0	8.0	3.8	3.3
57a			4.2	8.0	0.4	0.6	0.3	0.4				
57b					1.7	1.0	3.7	4.0	1.2	1.0	2.3	1.8
58					1.4	1.2	2.4	3.3	1.3	1.5	1.3	1.3
59							0.9	0.5			0.4	0.4
67									0.5	0.5	0.5	0.5
68							1.0	1.6	0.2	0.2	0.5	0.5
69							0.6	0.9	2.0	1.8	3.0	2.4
70	1.2	2.5	1.1	0.4	3.1	3.0	3.3	1.5	1.3	1.2	3.1	2.9
71	10.7	27.6			1.6	1.6	0.4	0.5	0.5	0.5	0.5	0.5
72	0.7	1.2										
81											0.6	0.6
82					0.4	0.4			0.6	1.1	0.3	0.3
83									0.3	0.4	0.5	0.5
84			4.9	9.9	0.2	0.2	1.8	2.8	2.9	2.8	2.8	3.1
85			2.1	4.0			2.3	3.6	3.5	3.9	4.1	4.3
86			0.1	0.3							0.3	0.3
91									0.5		1.5	0.1
93											0.5	
96											0.5	0.5
97											0.2	0.2
98					3.2	3.5	5.4	9.3	3.1	3.6	5.4	5.5
99					0.6	0.5	0.6	0.6	9.3	10.7	10.0	10.5
100									0.5	0.6	0.6	0.6
112							2.4	4.3	2.2	2.5	2.2	2.3
113							0.2	0.4			0.8	0.9
126									0.3	0.3	0.8	0.7
127									0.03	0.03		
128									0.007	0.005		
140											0.1	0.1
141											0.02	0.008
142											0.05	0.03

Doublets. *42* a: OCN; b: C_3H_6. *43* a: HOCN; b C_3H_7. *55* mainly C_4H_7. *56* a: CH_2NCO; b: C_4H_8. *57* a: C_2H_3NO; b: C_4H_9.
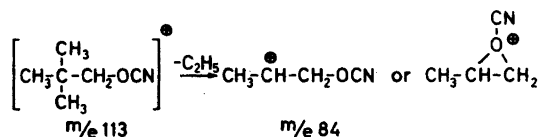
Because of incomplete resolution the error in ratio between the intensities of the components in a doublet may be as high as 25 %. Further the intensities of the peaks at m/e 28 and m/e 44 are rather uncertain because of possible contamination with N_2 and CO_2.

peak at m/e 37.2, corresponding to the process $41^+ = 39^+ + 2$ (calc. $m^* = 37.1$).

For branched cyanates and isocyanates, α-cleavage is favoured when the carbon chain has a substituent in α-position. Thus, $(M-Me)^+$ and $(M-Et)^+$ are base peaks for isopropyl and *sec*-butyl cyanate, respectively. In addition, the corresponding carbonium ions are formed by elimination of the radical OCN. This is especially the case with $C_4H_9^+$ (m/e 57) from *sec*-butyl cyanate.

When the site of the branching is the β-carbon atom, α-cleavage leads to the formation of a secondary or tertiary carbonium ion and a CH_2OCN or CH_2NCO radical. This occurs especially in isobutyl isocyanate (for which it is the base peak) and, to a much less extent, in isobutyl cyanate. Somewhat unexpectedly, the *tert*-butyl ion (m/e 57) is not much abundant in the spectrum of neopentyl cyanate and neopentyl isocyanate. Loss of methyl and ethyl occurs to some extent from the molecular ions. Neopentane also loses ethyl although it contains no ethyl group [9]) but the base peak is in both cases m/e 55, which may be the methylallyl ion or the methylcyclopropylium ion. The ion of mass 55 occurs together with an ion with mass number two units lower, corresponding to the methylcyclopropenylium ion, with a metastable peak at m/e 51.2 (calc. 51.2 from the process $55^+ = 53^+ + 2$), *cf.* the behaviour of the allyl ion. The ion m/e 55 is formed from another abundant ion, m/e 70, — corroborated by the occurrence of a metastable peak at $m^* = 43.2$ (calc. 43.2) — which in turn is formed from the molecular ion by elimination of HOCN (see below).
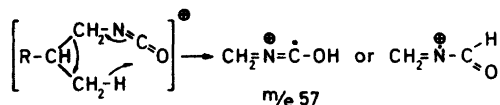
Neopentyl cyanate and neopentyl isocyanate both lose ethyl and form an ion of mass 84. This may have a cyclic structure so that the reaction for neopentyl cyanate may be written:

$$\left[\begin{array}{c} CH_3 \\ CH_3\text{-}\overset{\displaystyle|}{\underset{\displaystyle|}{C}}\text{-}CH_2\text{-}OCN \\ CH_3 \end{array}\right]^{\oplus} \xrightarrow{-C_2H_5} CH_3\text{-}\overset{\oplus}{C}H\text{-}CH_2\text{-}OCN \text{ or } CH_3\text{-}\overset{\oplus}{C}H\text{-}CH_2$$

$$m/e\ 113 \hspace{5cm} m/e\ 84$$

This would explain why the corresponding ion formed from neopentyl isocyanate is more abundant since the positive charge in this case would be stabilized by nitrogen.

Isobutyl cyanate also loses ethyl and forms an ion of mass 70. However, isobutyl isocyanate does not form the corresponding ion; it forms an ion of mass 71 which may be formed by loss of CO as in the case of phenyl isocyanate.

A peak corresponding to m/e 57 in the spectra of propyl, butyl, isobutyl, and pentyl cyanates and isocyanates is ascribed to the ions $(CH_2NCOH)^+$ and $(CH_2OCNH)^+$, respectively. It is analogous to the ion $(CH_2CNH)^+$, m/e 41, formed from nitriles, and may be formed *via* a 6- and 7-membered cyclic transition state, *e.g.*:

$$\left[R\text{-}CH \overset{\overset{CH_2\text{-}N}{\diagup}\diagdown}{\underset{CH_2\text{-}H}{\diagdown\diagup}} C \right]^{\oplus} \longrightarrow CH_2\overset{\oplus}{=}N\text{=}C\text{-}OH \text{ or } CH_2\overset{\oplus}{=}N\text{-}C\overset{H}{\diagdown}_O$$

$$m/e\ 57$$

These ions are more abundant in the spectra of isocyanates than in those of cyanates and only significant in the spectra of the propyl compounds. The homologue of mass 71 is not present in the spectra of the isopropyl and *sec*-butyl derivatives. The formation of these $(CH_2OCNH)^+$ or $(CH_2NCOH)^+$ ions from ethyl cyanate and ethyl isocyanate would require the elimination of CH_2, which is an unfavourable process, and, in accordance herewith, these ions are not observed in the spectra of the ethyl derivatives. For the higher cyanates and isocyanates this fragmentation is replaced by the formation of cyclic structures by elimination of alkenes, see later.

A characteristic difference between the branched and unbranched compound is the occurrence of $(M-1)^+$ peaks in the spectra of the latter (except ethyl cyanate). By this reaction the same ion is formed as by the α-cleavage of secondary alkyl cyanates and isocyanates. Like the loss of alkyl it is most pronounced for the isocyanates.

The ions $(M-1)^+$ are normally (exceptions: ethyl cyanate and isocyanate) much more abundant than M^+, but both $(M-1)^+$ and M^+ diminish much in intensity with increasing chain length so that it may be difficult to identify the molecular weight. The molecular ions are generally more abundant for the isocyanates (exception: neopentyl isocyanate, for which the peak due to the molecular ion is almost imperceptible).

The higher cyanates and isocyanates (hexyl and heptyl) form pressure dependent $(M + 1)^+$ ions. This is also the case with hexyl thiocyanate but not with hexyl isothiocyanate.

Formation of cyclic structures. A peak at m/e 99 is comparatively intense in the spectra of heptyl and hexyl isocyanate and is probably due to an ion analogous to the m/e 115 ion formed by hexyl and heptyl isothiocyanate: [2]
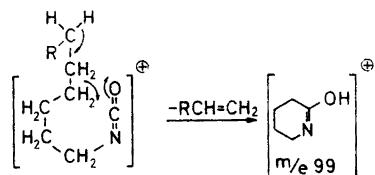
The mass spectra of hexyl and heptyl cyanate show the same peak, m/e 99, of almost the same intensity as the isocyanates, and this is probably due to the same (and not an isomeric pyranoid) ion formed by the rearrangement:
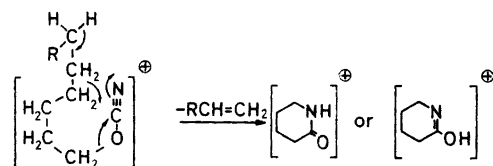
or from a rearranged molecular ion.

In this respect, they differ from the corresponding thiocyanates which lose HCN instead of the alkene. The reason for this difference between the
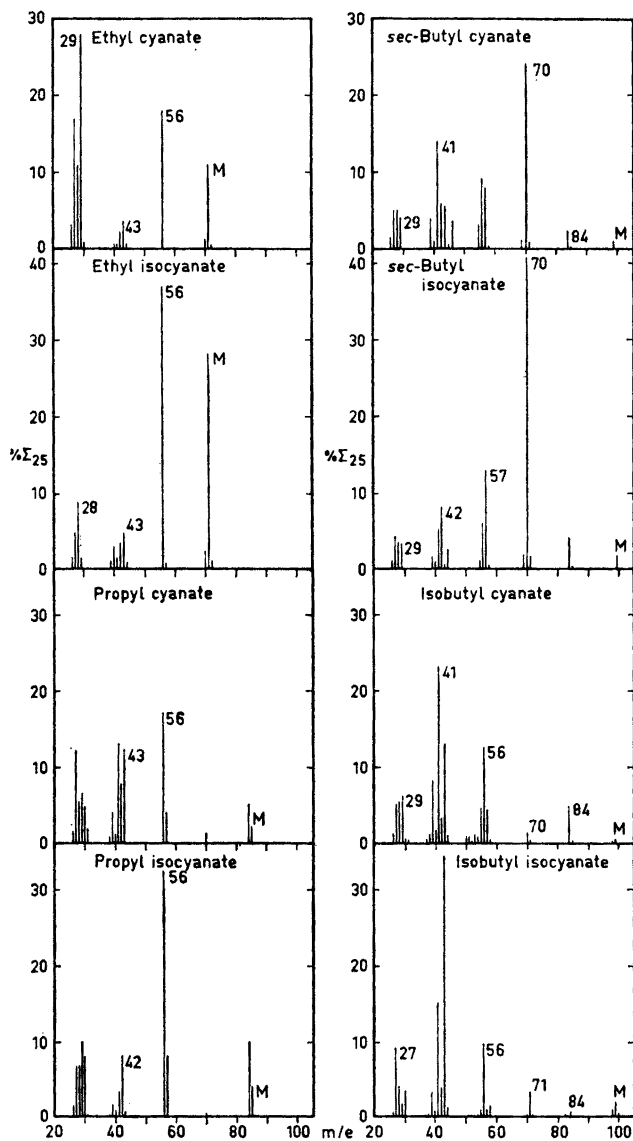
Fig. 1.

cyanates and thiocyanates may be that a sulfur atom stabilizes a positive charge on the molecule more easily than does oxygen. For the same reason an oxygen-containing ion at m/e 71, corresponding to the sulfur ion at m/e 87, formed by hexyl thiocyanate, is not formed by hexyl and heptyl cyanate.
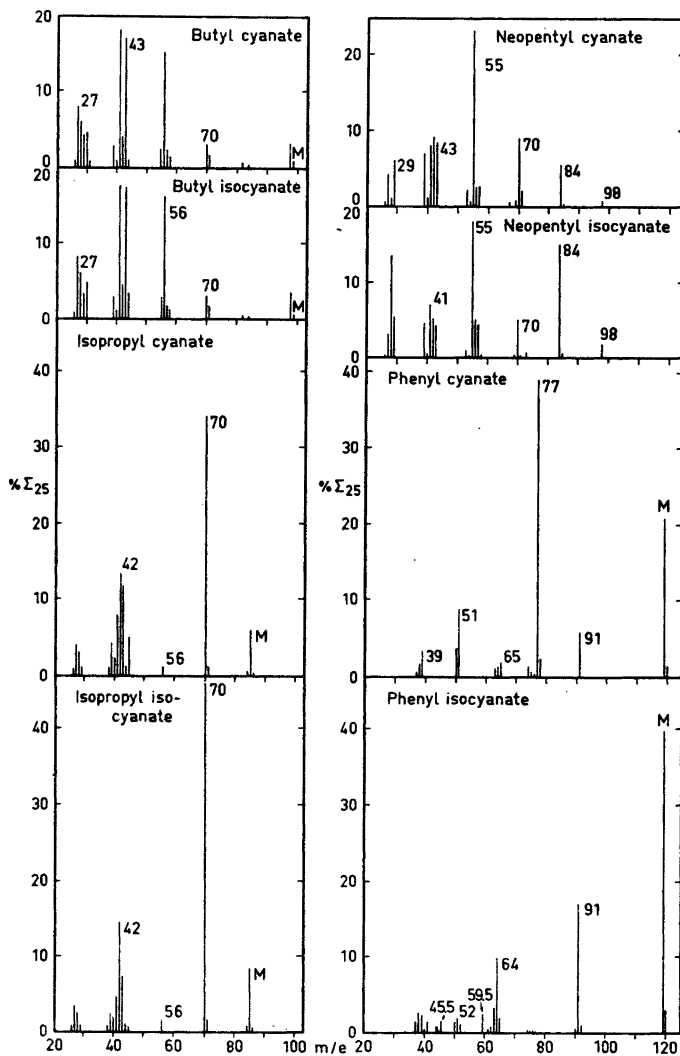
Fig. 2.

The spectra of pentyl cyanate and pentyl isocyanate show a peak at *m/e* 85, corresponding to the loss of ethylene, and this may similarly be due to ring closure to 2-pyrrolidone. The peaks occurring one mass unit lower than the one corresponding to loss of ethylene may be due both to loss of ethyl from the molecular ion and the loss of one hydrogen atom from the pyrrolidone ion.

Elimination of the functional group. Cleavage of the C—(OCN) or C—(NCO) bond with transfer of one hydrogen atom leads to an *m/e* 43 ion (HNCO$^+$ or HOCN$^+$) or a hydrocarbon ion; the HNCO$^+$ component of the *m/e* 43

doublet is always more abundant in the mass spectra of cyanates than in those of the corresponding isocyanates, (except for ethyl) but the alkene ions formed by elimination of HNCO are formed in approximately the same amounts from cyanates and isocyanates. This process is most important for the lowest straight chain compounds and branched compounds (especially the neopentyl derivatives) and becomes less and less important with increasing molecular weight of straight chain compounds.

The spectra of branched alkyl cyanates and of straight chain cyanates up to butyl cyanate also show a peak at m/e 42, which is a doublet consisting of OCN^+ and $C_3H_6^+$. With one exception (neopentyl isocyanate) OCN^+ ions are never formed from isocyanates. The formation of OCN^+ is a special type of C—(OCN) cleavage. Since this ion is not formed from isocyanates (except neopentyl isocyanate), although these form $HOCN^+$, it cannot be formed from $HOCN^+$, and the ion $HOCN^+$ cannot in these experiments arise from preformed cyanic acid as this forms $HOCN^+$ (m/e 43) as well as OCN^+ (m/e 42). It seems very improbable that the difference should be due to the formation of $HNCO^+$ from the cyanates and $HOCN^+$ from the isocyanates, since these ions are present in activated states which may be theoretically indistinguishable and which would, at any rate, not be expected to differ so fundamentally that only one of them would be able to split off a hydrogen atom. The remaining possibility that the cyanates R—OCN may be split directly into R radicals and OCN^+ ions — as well as into R^+ ions and OCN radicals — is in accordance with the fact implied from chemical reactions of the cyanates that the R—(OCN) bond is weaker than the R—(NCO) bond. The abundance of the OCN^+ ions is much smaller than that of the R^+ ions; thus, as expected, the positive charge remains preferentially with the hydrocarbon moiety in this fragmentation process.

The molecular ion of neopentyl cyanate forms an ion of mass 70 by elimination of HOCN. As discussed above, the ion m/e 70 may probably further be transformed into a cyclopropylium ion (m/e 55) or a cyclopropenylium ion (m/e 53). The following scheme can accordingly be written for this fragmentation of neopentyl cyanate:
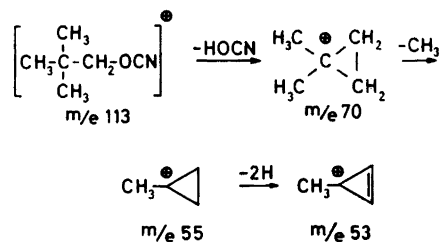
These carbonium ions are most abundant in the spectra of the cyanate but the ratio between their abundances is almost exactly the same for the cyanate and the isocyanate, as expected if they are formed from the same ion, m/e 70.

Isobutyl cyanate similarly eliminates HOCN and forms $C_4H_8^+$. This may, of course, be the isobutene ion and not a cyclic ion. It forms m/e 55 and m/e 41

by loss of H and CH_3 respectively as shown by the occurrence of metastable peaks corresponding to these reactions. Isobutyl isocyanate forms $C_4H_8^+$ in much smaller amount.

Phenyl cyanate and isocyanate

As usual for aromatic compounds, the peaks due to the molecular ions are large. Further, a doubly charged ion $M^{2+} = 59.5$ is formed, in greatest abundance from the isocyanate (*i.e.* the isocyanate is most "aromatic").

When one compares our results with those of Kjær *et al.*,[2] it is seen that the spectrum of phenyl cyanate is analogous to the spectrum of phenyl isothiocyanate. The peak of greatest intensity (m/e 77) is due to the phenyl ion. Most of the ions with smaller mass numbers are fragments of the benzene ring.

A characteristic feature of the spectrum of phenyl isocyanate is the absence of a peak at m/e 77 and, accordingly, it is not analogous to the spectrum of phenyl isothiocyanate. The presence of an intense peak at m/e 91 shows that another cleavage is preferred in the case of phenyl isocyanate. This peak can only be due to $C_6H_5N^+$ formed by elimination of CO from the molecular ion:
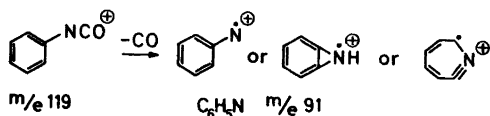
Evidence for this fragmentation is also found in the occurrence of a metastable peak $m^* = 70$, corresponding to the process $119^+ = 91^+ + 28$.

This peak also occurs in the mass spectrum of phenyl cyanate, although with smaller intensity. It may be formed *via* rearrangement of an ion $C_6H_5-O-CN^+$; an ion with m/e 93 ($C_6H_5O^+$) is not formed. The ion of mass 91 also occurs as the doubly charged ion m/e 45.5, which supports the assumption of its aromaticity. The ratio of the intensities of the peaks m/e 91 and m/e 45.5 is almost the same for the cyanate and the isocyanate, which confirms that we are dealing with the same ion.

The mass spectra of both phenyl cyanate and phenyl isocyanate show a metastable peak, $m^* = 45.1$ (calc. 45.05) corresponding to the process $91^+ = 64^+ + 27$, or:
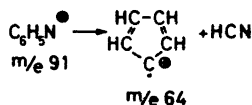
Thiocyanates and isothiocyanates

The mass spectra of thiocyanates and isothiocyanates are more different than those of the cyanates and isocyanates in accordance with the greater difference in electronegativity between N and S than between N and O.

The difference between our spectra of isothiocyanates and those of Kjær *et al.*[2] is mainly confined to a lower intensity of the m/e 28 and 41—43 peaks.

Table 2. Relative intensities of ions formed from phenyl and branched chain alkyl cyanates and isocyanates expressed in per cent of $\sum_{25}$. 1: Alkyl cyanates, ROCN, 2: Alkyl isocyanates, RNCO.

m/e	Isopropyl 1	Isopropyl 2	Isobutyl 1	Isobutyl 2	sec-Butyl 1	sec-Butyl 2	Neopentyl 1	Neopentyl 2	Phenyl 1	Phenyl 2
26	0.9	0.9	1.2	0.7	1.5	1.0	0.6	0.4		
27	4.0	3.4	5.1	9.4	5.0	4.0	4.2	3.3		
28	3.2	2.5	5.4	4.1	5.0	3.5	1.2	13.6		
29	1.1	0.9	6.4	1.7	4.2	4.8	6.2	5.5		
3.0			0.5	3.5						
37			0.5	0.3					0.9	1.6
38	1.1	0.7	1.0	0.5					1.9	2.7
39	4.4	2.5	7.6	3.2	4.1	1.5	6.6	4.7	3.6	2.5
40	2.4	2.0	1.7	0.8	1.1	1.0	1.1	0.7		0.5
41	7.6	4.7	23.2	15.4	13.7	5.1	8.2	7.1		1.6
42a	1.4		1.7		1.3		2.1	0.9		
42b	12.2	14.3	1.5	4.0	4.6	7.7	7.0	4.4		
43a	8.9	5.8	9.0		5.6		5.8	3.0		
43b	2.7	1.6	3.9	33.7	0.4	0.5	2.4	1.4		
44	1.2	1.0	1.0	1.2	0.7	2.6				0.9
45	5.0	0.6			3.6					0.3
50			1.0	0.1					4.0	1.6
51			0.8	0.2					8.8	2.0
52			0.3	0.2						1.2
53			1.1	0.2			2.3	1.2		
54			0.8	0.4			0.7	0.3		
55			4.5	1.0	3.2	1.1	26.5	17.9		
56a	1.2	1.7	1.4	5.9	4.0		0.6	1.3		
56b			10.5	3.8	5.2	6.1	2.0	3.9		
57a			0.3	0.8						
57b			4.0	0.3	7.9	12.4	2.7	4.6		
58			0.3	1.8	0.3	0.4		0.6		
61										0.6
62										1.0
63									1.3	3.5
64									1.5	10.1
65									2.1	1.9
67							0.6	0.2		
69					1.1	1.9	0.9	0.6		
70	34.4	46.1	1.3	0.2	23.7	40.7	9.4	5.6		
71	1.3	1.7	0.3	3.2	0.9	1.6	2.1	0.5		
73								0.8		
74									1.5	0.5
75									0.8	0.3
76									0.6	0.3
77									38.6	0.2
78									2.6	
84	0.6	0.8	4.6	0.6	2.2	3.9	5.5	14.9		
85	6.1	8.4	0.2		0.1	0.2	0.4	0.7		
86	0.3	0.5								
90										0.7
91									6.3	16.9
92										1.2
98			0.1	0.7			0.8	1.9		
99			0.3	1.8	0.9	1.6				
100				0.1						
119									21.5	40.1
120									1.8	3.3

Doublets (a and b): See footnote to Table 1.

When the temperature of the inlet system was raised from 40°C to 150°C, the spectra became almost identical with those reported by Kjær *et al.*[2]

The differences between the spectra of thiocyanates and isothiocyanates are similar to those found for the cyanates and isocyanates, but much more pronounced. Thus, alkyl fragments, formed by α-fission, predominate in the spectra of the lower straight chain thiocyanates; not only $C_2H_5^+$ for ethyl thiocyanate, but also $C_3H_7^+$ for propyl thiocyanate and $C_4H_9^+$ for butyl thiocyanate; m/e 41, found in the spectra of propyl and butyl thiocyanate is probably the allyl ion, $C_3H_5^+$. The NCS-containing fragments, on the other hand predominate in the spectra of isothiocyanates, especially CH_2NCS^+, whereas CH_2SCN^+ is practically absent in the spectra of thiocyanates. $HSCN^+$ or $HNCS^+$ is formed both from thiocyanates and isothiocyanates (except the ethyl compounds) in almost equal amounts.
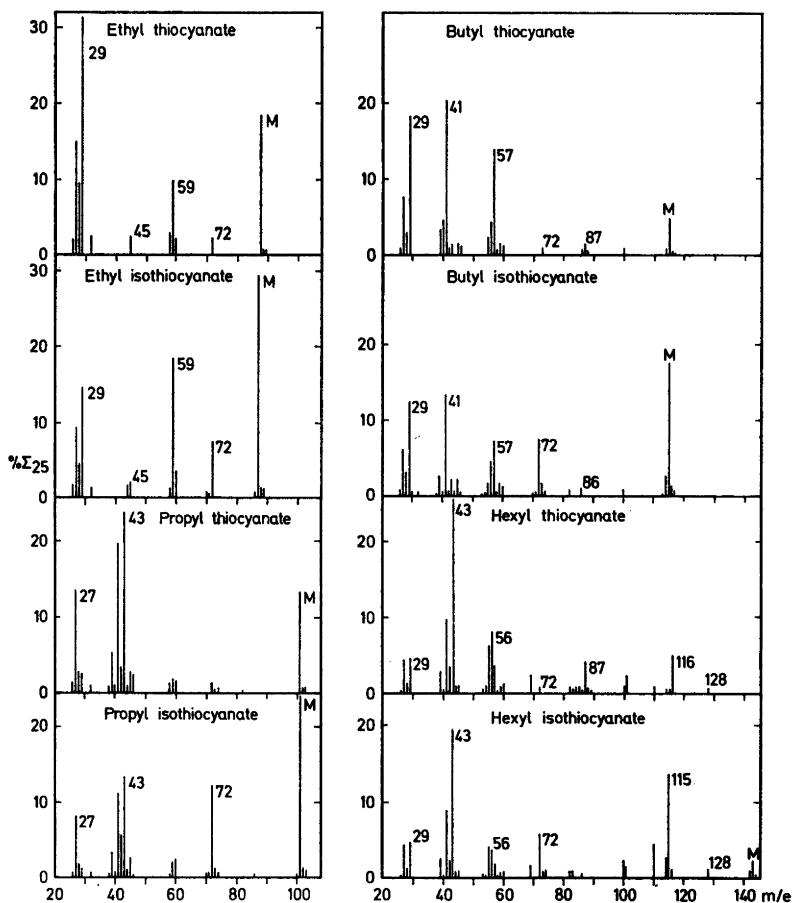

Fig. 3.

Table 3. Relative intensities of ions formed from thiocyanates and isothiocyanates expressed in per cent of $\sum_{25}$. 1: Alkyl thiocyanates, RSCN, 2: Alkyl isothiocyanates, RNCS.

R m/e	Ethyl 1	Ethyl 2	Propyl 1	Propyl 2	Butyl 1	Butyl 2	Hexyl 1	Hexyl 2
26	2.1	1.8	1.2	0.8	1.1	0.8	0.4	0.4
27	14.8	9.3	13.3	8.1	7.6	6.1	4.5	4.4
28	9.4	4.5	2.6	1.8	3.0	3.1	1.4	1.3
29	31.0	14.4	2.3	1.3	18.1	12.3	4.6	4.7
30						0.6		
32	2.5	1.4	0.9	0.9		0.6		
38			0.9	0.7		0.3		
39			5.1	3.4	3.5	2.7	2.9	2.6
40			0.9	1.0	4.8	0.6	0.5	0.5
41			19.4	11.0	20.2	13.2	9.8	8.9
42			3.3	5.7	1.0	0.7	3.5	2.3
43			23.6	13.3	1.6	2.2	25.6	19.5
44		1.8	0.8	1.2		0.6	0.9	0.9
45	2.5	2.1	2.6	2.7	1.7	2.2	1.0	1.0
46			2.2	0.5	1.3	0.5		
53						0.3	0.6	0.5
54						0.5	1.0	0.4
55					2.4	1.7	6.3	4.2
56					4.4	4.6	8.0	3.8
57					13.8	7.2	3.6	1.9
58	3.0	1.4	1.2	0.6	0.9	0.6	0.3	0.4
59	9.7	18.3	1.6	2.3	1.7	1.8	0.9	0.8
60	2.2	3.6	1.5	2.5	1.4	1.2	1.3	1.0
69							2.4	1.7
70		0.9		0.6		0.3		
71		0.7		0.7		0.5		
72	2.2	7.5	1.2	12.1	1.0	7.4	0.8	5.8
73			0.3	1.2		1.7		
74			0.5	0.6		0.7		
82			0.2			0.8	0.8	1.0
83							0.6	1.0
84							0.9	
85							0.9	
86		0.8		0.5	0.7	1.0	0.4	0.7
87	18.4	29.0			1.6		4.1	
88	0.8	1.4			0.6		0.6	
89	0.8	1.3					0.4	
100				0.5	0.9	1.0	1.0	2.3
101			12.9	23.8			2.2	1.6
102			0.7	1.4				
103			0.6	1.1				
110							1.0	4.6
113						0.2		
114					0.8	2.7	0.6	2.7
115					5.0	17.4	0.5	13.8
116					0.4	1.3	5.0	1.1
117					0.2	0.8		
128							0.6	1.3
142							0.1	0.9
143								1.8
144							0.2	0.4

For the lower weight isothiocyanates, the base peaks are due to the molecular ions whereas for the isomeric thiocyanates the propyl or allyl ions at m/e 43 and 41, respectively, form the base peaks. The molecular ions are always much more abundant in the spectra of isothiocyanates than in the spectra of thiocyanates for which they become almost imperceptible compared with the $(M-1)^+$ ions. For hexyl thiocyanate no M^+ peak could be ascertained but the molecular weight is apparent from the presence of both a $(M-1)^+$ peak and a pressure dependent $(M+1)^+$ peak which must originate from the second order process:

$$C_6H_{13}SCN + C_6H_{13}SCN^+ \longrightarrow C_6H_{13}SCNH^+ + C_6H_{12}SCN$$
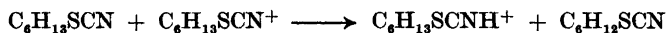
In the spectra of higher isothiocyanates cyclic fragments play a role, as discussed by Kjær et al.[2] Thus, hexyl isothiocyanate can form a cyclic ion of mass 115 by elimination of ethylene, cf. the corresponding ion formed from hexyl isocyanate, discussed above. This peak is very weak in the spectrum of hexyl thiocyanate, which has instead a peak at m/e 116, corresponding to a fragment formed by elimination of HCN. Further, m/e 87 is formed only by hexyl thiocyanate and not by hexyl isothiocyanate. Since there is a metastable peak, $m^* = 65.3$, corresponding to the process $116^+ = 87^+ + 29$, it is reasonable to assume that m/e 116 and 87 are formed according to the following scheme:
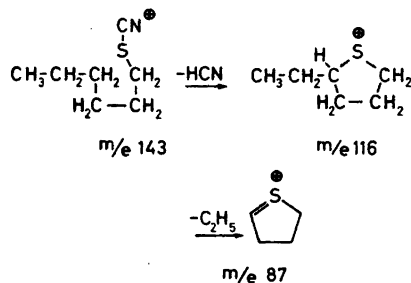
Butyl thiocyanate also forms peaks corresponding to $(M-HCN)$ and m/e 87, although with slight intensity; actually, butyl thiocyanate is the first alkyl thiocyanate which should be able to be cleaved according to this scheme.

The ion at m/e 110, formed by elimination of SH from the molecular ion, is more abundant for hexyl isothiocyanate than for hexyl thiocyanate. Contrary to the statement of Kjær et al., it is also formed by the butyl homologues. The following mechanism [10] appears plausible:
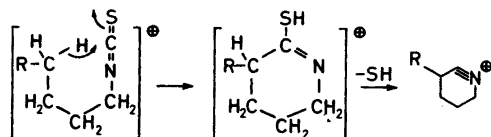
However, apart from the ring-closure reactions and the occurrence of the ion m/e 72 (CH_2NCS^+) in greater abundance in the spectra of isothiocyanates, the spectra of straight chain thiocyanates and isothiocyanates become more and more alike with increasing chain length as was the case for the cyanates and isocyanates.

REFERENCES

1. Groving, N. and Holm, A. *Acta Chem. Scand.* **19** (1965) 1768.
2. Kjær, A., Ohashi, M., Wilson, J. M. and Djerassi, C. *Acta Chem. Scand.* **17** (1963) 2143.
3. Jensen, K. A., Due, M. and Holm, A. *Acta Chem. Scand.* **19** (1965) 438.
4. Jensen, K. A., Anthoni, U. and Holm, A. *Acta Chem. Scand. To be published.*
5. Kauer, J. C. and Henderson, W. W. *J. Am. Chem. Soc.* **86** (1964) 4732.
6. Grigat, E. and Pütter, R. *Chem. Ber.* **97** (1964) 3012.
7. Boehmer, J. W. *Rec. Trav. Chim.* **55** (1936) 380.
8. Jensen, K. A., Due, M., Holm, A. and Wentrup, C. *Acta Chem. Scand.* **20** (1966) 2091.
9. Biemann, K. *Mass Spectrometry: Organic Chemical Applications*, McGraw, New York 1962, p. 49.
10. Budzikiewics, H., Djerassi, C. and Williams, D. H. *Interpretation of Mass Spectra of Organic Compounds*, Holden-Day, San Francisco 1964, p. 120.