SOME STUDIES ON MASS SPECTROMETRY
OF ORGANIC COMPOUNDS

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by

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To my wife Safi

SUMMARY

The present thesis contains five chapters:

1. The historical development of mass spectrometry and the theory of various designs of instrumentation are discussed.

2. This chapter records the synthesis of a series of alcohols, acids, and iodides (C_5-C_7) enriched with ^{13}C at C-1. The mass spectra of these nine compounds have been obtained and compared for the more abundant ions with those of the normal mass spectra obtained from the unenriched molecules. The characteristic fragmentation pathways of these compounds were clarified. The importance of β-cleavages to the other bonds are emphasised. No evidence was obtained to support the rupture of a ^{13}C-^{12}C bond prior to β-cleavage, although this bond is weaker than the ^{12}C-^{12}C bond.

3. Chapter three reports the synthesis and interpretation of the mass spectra of some heterocyclic compounds with special emphasis on rearrangement processes. Some comments upon the McLafferty rearrangement are reported. Attempts were made, without success, to replace sulphur firstly by selenium and then by tellurium in the synthesis of thioamides.

4. The fourth chapter discusses a computer matching technique for the identification of organic compounds. Programmes have been developed to compare the unknown spectrum with the library file without using the molecular weight of the compound. A successful result was obtained after each search.

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5. In this chapter the analysis of unknown mixtures by mass spectrometry is described. The use of high resolution mass spectrometry clarified the occurrence of certain synthetic reactions in the source of mass spectrometer. In this investigation the composition of fifteen extra compounds and also ten protonated ions, induced by electron impact of a four component mixture, are reported. From the results obtained it is concluded that the analysis of mixtures by mass spectrometry may not always be an efficient technique, particularly when the mixture contains sulphur compounds.

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CHAPTER (I)

INTRODUCTION

In 1886 Goldstien (I) was the first to report the discovery of positive rays in a low pressure discharge tube. Subsequently W. Wien (2) showed the deflexion of positive ions using electrical and magnetic fields. In the meantime, J. J. Thomson (3) demonstrated the existence of two stable isotopes of neon with atomic weights of 20 and 22. This was the first demonstration of isotopes, the second being the contribution of Aston (4). His fairly elaborate instrument found favour with investigators of isotopes for precise mass measurement. In 1918 Dempster (5) produced a somewhat less elaborate instrument for the measurement of relative abundances of isotopes. Dempster's instrument could not be used for precise mass measurement; it was better suited for measuring the relative abundance of the ionic species present and studying electron impact processes in gases. It should be emphasized that these early instruments did not have the benefit of modern high-vacuum technology and thus were operated at higher pressures than those used today.

Rapid development in electronics and vacuum technology led eventually to an increasing interest in the field of mass spectrometry. In 1922 Aston (6) had anticipated the use of a mass spectrograph for the separation of isotopes. After a number of attempts by several workers, two groups succeeded in making isotope separations about the same time. The group of Smythe et al. (7) obtained one mg. of ^{39}K in a seven-hour run.

Oliphant *et al*. (8) separated and collected as much as 10^{-8}g. of a pure lithium isotope. Nier and co-workers (9) isolated ^{235}U and ^{238}U.

Thomson (3) had anticipated the application of mass spectrometry even in the area of chemical analysis, he not only suggested using mass spectrometry for determining atomic and molecular weights, but claimed that information thus obtained was superior to emission spectrography. He recognized the advantages of the small size and even showed the possible use of mass spectrometer for the identification of the components of air. The first report of actual chemical application appears to have been the work of Conrad (10), who studied organic compounds. Mass spectrometry has grown into a very large field since these early beginnings.

INSTRUMENTATION

Because of the widespread application of mass spectrometry, a basic knowledge of the instrumentation is useful for interpretation of mass spectroscopic data. The occurrence of entire phenomena and the behaviour of organic materials in a mass spectrometer should be recognized. The common feature of all mass spectrometers is the production of ions, the separation of ions by masses and their collection and recording of the intensities of the ions. The method of production, separation and collection of ions varies. However, the most common technique will be discussed as follows:

A-ION SOURCES

Production of ions in mass spectrometry is usually by the following methods of ionization.

1. Electron impact or bombardment
2. Chemical ionization
3. Field ionization
4. Photoionization
5. Vacuum spark
6. Surface emission

In addition there are a few special sources available of some particular interest.

1. THE ELECTRON IMPACT SOURCE

The electrons are produced from a heated wire filament (a) and travel through the slit (b) across the evacuated space toward an anode or trap (t). Vapour atoms or molecules (M^o) are introduced normal to the electron beam through an entrance slit (c). The particles suffer collisions with the electrons at the point (x) (Fig.1). The ions are formed when the energy of the electron beam is sufficiently great in accordance with the general equation

$$M^o + \bar{e} \longrightarrow M^+ + 2e^-$$

Interaction between the electron beam and the organic molecules results in an energy exchange of around 10 to 20 eV which is sufficient to cause ionization of the molecule and in many cases, decomposition to smaller fragment ions. The assembly of molecular and fragment ions in the ion chamber is accelerated through the ion slits into the mass spectrometer analyser by a positive potential on the ion repellers. The total amount of positive ion current (10^{-10}-10^{-15}A) and the nature of the fragmentation pattern depends upon the energy of the bombarding electron beam.

Several factors contribute to this process: stability, ease of operation, precise beam intensity control, relatively high efficiency of ionization, convenient control of temperature, and narrow kinetic energy spread in the ions formed. These are amongst the advantages of electron impact source. The details of this subject can be found in the excellent text of Beynon (11).

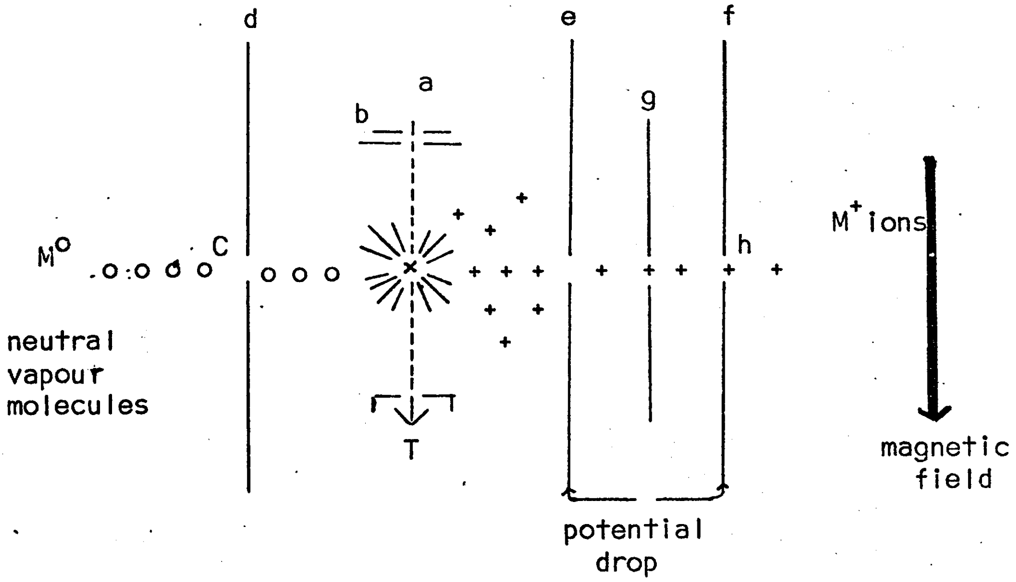

Fig. 1 - Schematic of an Electron Impact Ion Source

2. CHEMICAL IONIZATION

Munson and Field (12) were the first to describe a chemical ionization source which has recently emerged as an important new technique to obtain additional information not provided by electron impact methods (13-21). One of the problems of conventional electron impact data is that many types of compounds give a very weak signal for the molecular ion, even when the molecular ion is as high as one or two per cent relative abundance; this often means two orders of magnitude higher sample requirement if the molecular weight is an important piece of evidence (and it always is).

The extensive fragmentation observed in the electron impact spectra of many compounds results from the fact that during the initial electron/molecule interaction, many molecules receive considerable energy above the ionization voltage. On the other hand, the chemical ionization process occurs with a much lower transfer of energy, and as a natural consequence, the fragmentation process is modified and greatly reduced.

Chemical ionization mass spectra result from the ion -molecule reaction that occurs between a low-pressure sample gas and the primary ions of a high pressure reactant gas. A typical ion chamber pressure will be 4×10^{-7} to 4×10^{-6} Newtons/sq. metre (0.3-3Torr) for the reactant gas and 1.3×10^{-12} Newtons/sq. metre or lower for the sample. Both gases are introduced into the ion chamber where they are bombarded by an electron beam, but because of the very low abundance of the sample, virtually all primary ionization due to electron bombardment occurs in the reactant gas.

A variety of reactant gases have been proposed for chemical ionization, but most common to date are the simple hydrocarbons, e.g. methane and isobutane. If methane is used, the ions produced initially are CH^{+}_{4}, CH^{+}_{3}, CH^{+}_{2}, CH^{+}, C^{+}, H^{+}_{2}. Secondary reactions occur to produce new ions:

$$CH^{+}_{4} + CH^{\cdot}_{4} \longrightarrow CH^{\cdot}_{3} + CH^{+}_{5}$$

The increased relative abundance of the quasi-molecular ion has proven to be of great value in many studies, particularly with relatively complex biological molecules (16-20).

In a chemical ionization mass spectrometer, it is essential that the vacuum system is optimized to pump a large volume of gas. Typically, 2-5 cm^{3} atm/min of reactant gas passes into the ion chamber corresponding to a quantity Q equal to $2.5 - 6.3 \times 10^{-2}$ litre Torr/sec.

Conjunction of chemical ionization processes with conventional electron impact analysis is very effective, Arsenault (20) designed a dual ionization source that provides both chemical ionization and electron impact; the system can be used with each source operating by itself or with both sources simultaneously.

3. FIELD IONIZATION

The field ionization source is another technique that provides sample ionization at relatively low energy with resultant reduced fragmentation and increased relative abundance of the parent ion. The ions are formed as the result of an intense electrostatic field set up at the end of a metal tip.

Inghram and Gomer (22a,b) first used such a source to produce ions and a mass spectrum. The spectra produced were much simpler than electron impact spectra. Parent-molecule ions dominated the spectra almost exclusively.

In 1968 developments in field ionization were discussed by Beckey and Beckey et al. (23,24) and also at Mass Spectrometry Conference (No.4 Berlin, Institute of Fuel; Ed. E. Kendrick) by many other workers (25-29). Weiss and Hutchison (30) reported on the field ionization mass spectra of some hydrocarbon and monochloro-substituted derivatives, while Mead (31) extended consideration of this type of spectrometry to waxes. The structure determination and quantitative analysis by field ionization mass spectrometry was further extended by Beckey (32).

4. PHOTOIONIZATION

In this process (33) the ionization occurs by using electromagnetic radiation in the ultraviolet range. Hurzeler et al. were the first who employed ultraviolet radiation, variable in energy but essentially monochromatic. They used a monochromator design similar to that of Seya and Namioka. Ion currents of about 10^{-15}A were detected. In addition, investigation of the fine structure of ionic species was made possible.

5. VACUUM- SPARK SOURCES

In 1935, Dempster (34a,b) developed the vacuum spark as a source of positive ions for studies of the isotopic constitution of the elements. In this technique the spark is formed between two electrodes by application of a high voltage of the order of 50KV. Obviously, under these conditions, the electrodes would melt, this is avoided by the use of pulsed electronic oscillators. The filament of the usual ion source is replaced by a primary electrode of the material or of a tube containing the material to be analysed. Monoisotopic metals such as gold or aluminium are usually employed for these tubes. A portion of the vapour yields the ions and these are then accelerated and collimated into a beam.

B - SEPARATION OF IONS

The ion of mass (m) and charge (e) that has been accelerated by a voltage (V) follows a path of radius (r) in a magnetic field of strength (H), where

$$\frac{m}{e} = \frac{r^2 H^2}{2V}$$

The ions of different mass-to-charge ratios can be separated by varying R, H or V. The separation of ion beams can be improved by focusing which at the same time increases the intensity of these ions, therefore, the measurement of the position of the ion beam is made more precise, and the sensitivity of the instrument increased. Among the different types of focusing are velocity focusing, direction focusing, double focusing, and "time" focusing.

SINGLE FOCUSING

The most common type of mass spectrometer is a single focusing magnetic deflexion instrument, the principle first used by Dempster (35a, b, c).

The mechanism of a typical magnetic-sector analyser is illustrated in Fig.(2). Ions formed in the source are accelerated through a source slit (s_1) toward a homogeneous magnetic field. For ions with an electronic charge (e) and mass (m) the kinetic energy will be related to the accelerating voltage (V) by the equation

$$eV = \tfrac{1}{2}mv^2$$

where v = ion velocity

The electrical signal is then amplified in one of various ways, generally with an electrometer-tube d-c amplifier or electron multiplier.

As the ions enter the magnetic field (H), they experience a force orthogonal to the field which results in a curvature of the ion path. This accelerating force (Hev) is balanced by the centripetal force, so that

$$Hev = \frac{mv^2}{\underline{r}}$$

where r is the radius of curvature.

Elimination of the velocity term gives the equation

$$m/e = \frac{H^2\underline{r}^2}{2V}$$

Thus, at a fixed radius $\underline{r}$ and for a singly charged ion the mass focused at (S_2) and collected by the detector is proportional to the square of the magnetic field and inversely proportional to the accelerating voltage. By varying either of these two parameters, ions of different mass-to-charge ratio can be deflected to the collector and in this fashion the mass spectrum is scanned.

For most applications it is preferable to vary the magnetic field and maintain a constant accelerating voltage. When the voltage is varied over the course of a mass scan the efficiency of transmitting ions of low mass is much greater than that for ions of high mass. A typical single focusing instrument is the AEI MS12 with a 90° magnetic sector and an ion path radius of 0.3 metre. The ion source region has four inlet ports which are directly in line with the ionization region and can be used for connecting up a variety of inlet systems including a direct sample insertion lock, reservoir inlet system and chromatographic inlets such as flow splitters or Biemann separators.

The ion source can be completely isolated from the rest of the vacuum system for venting to atmosphere. The ion source and analyser are differentially pumped and the instrument can, therefore, be operated with relatively high sample pressures, (of the order of 1.3×10^{-10} Newtons/sq. metre).

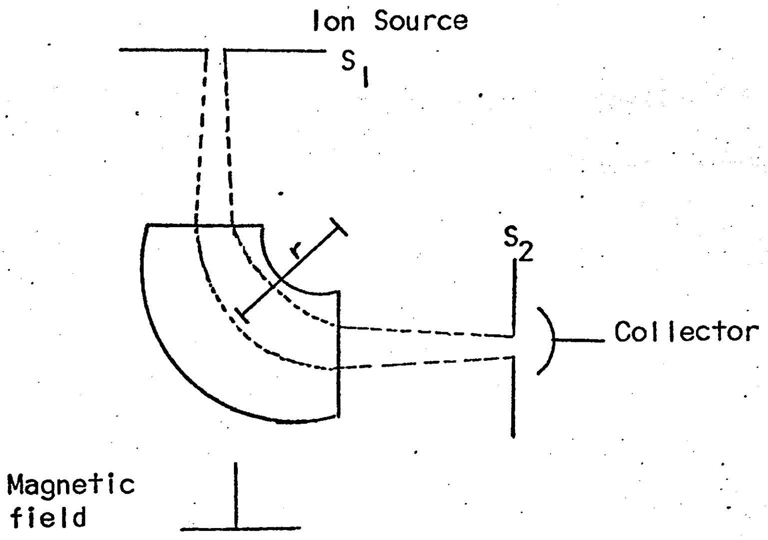

Fig. 2 Schematic diagram of 90° magnetic sector showing direction focusing of divergent ion beam.

DOUBLE FOCUSING

A combination of a magnetic sector with one or more electrostatic field sectors can be arranged to give first order velocity focusing and angular focusing simultaneously; such arrangements are said to be "first order double focusing".

Dempster, Bainbridge and Nier have described designs of instrument in which the first order double focusing conditions are met for one radius of curvature in the magnetic field. Johnson and Nier extended the parameters considered to include second order angular focusing, giving rise to a design, using asymmetrical sectors, which allows the use of a relatively large angle of divergence in the initial beam.

MATTAUCH - HERZOG GEOMETRY

The design of Mattauch and Herzog is one of the earliest for double focusing instruments and has been widely employed in commercial instruments. This type of instrument separates and focuses all the ions on a focal plane such that they all fulfil the double focusing condition simultaneously. A photographic plate held at this focal plane records all the ions all the time, and thus avoids the restrictions imposed by scanning. An electron amplifier positioned at one end of the photoplate assembly is used for "tuning" the instrument, or for electrical recording if a scan of the mass spectrum is desired. One advantage of the photographic plate is that the entire spectrum is recorded simultaneously, thus averaging out any small instrumental deviations that could, for example, minimize or exaggerate a peak or two during an electrical surge. It is also useful for recording the spectrum in a short period of time.

NIER - JOHNSON GEOMETRY

In the design of Johnson and Nier, a (90^o) electrostatic analyser is followed by a (90^o) magnetic sector to bring the ions to a focal point under double focusing conditions. An electron multiplier is placed at this focal point where only the ions of one mass-to-charge value meet the double focusing condition at any given time. The entire high resolution mass spectrum is usually obtained by scanning the magnetic field strength.

DOUBLE BEAM MASS SPECTROMETER

The double beam instrument is actually two mass spectrometers in one. This commercial development incorporates two independent but adjacent ion sources and two electron multipliers. The ion sources and detectors are arranged so that both mass spectrometers utilize the same radial electric field and sector magnet for simultaneous double focusing (Nier-Johnson) of the two beams. Either of the ion sources may be used independently; however, the principal advantage of the design is achieved when an unknown compound introduced into one ion source while a calibration compound is admitted to the other. In this manner, the spectra of unknown and calibration compound are obtained separately but simultaneously under strictly identical conditions; the spectra in this instrument are not superimposed but recorded with opposite peak deflexions on the same record.

C- DETECTION OF IONS

The ion intensities for a given set of mass-to-charge ratio can be recorded by various methods (36a,b). An unsuitable recording system can reduce the resolving power, sensitivity, accuracy of intensity measurement, and the speed of analysis. Improvements in detectors and recording systems have extended the applications of mass spectrometry in recent years; whilst the availability of high speed computers and the advances made in data processing, ensures that the information contained in a spectrum is rapidly made available. However, some of the common methods will be discussed as follows:

THE ELECTRON MULTIPLIER

The electron multiplier is now universally used in qualitative organic mass spectrometry. In this method the electron multiplier collects energetic ions on the metal surface of electrode (called the cathode in this apparatus). Secondary electrons are emitted and accelerated to another electrode where additional electrons are emitted. These in turn are accelerated to another dynode, and the process is repeated. After about ten to twelve stages, all of the electrons are collected on an anode which has grid protecting it to prevent secondary emissions. A large electron current can be obtained for each positive ion collected on the cathode, resulting in about a 10^5 or 10^6 multiplication of the signal.

Most multipliers in common use contain 10-20 dynodes electrically connected through a resistive network. The measurement of the ions is not as satisfactory as may be desired, the difficulty arises from the vacuum system which may not be reproducible. Some other factors such as surface reaction of ions and magnetic field may have serious effects upon amplification.

THE ELECTROMETER AMPLIFIER

This method is being employed in most precision quantitative mass spectrometry and also used for current/voltage conversion of the electron multiplier output.

Electrometer vacuum tubes are designed to have a high ground impedence and low ground capacity, thus permitting an input resistance at least as high as 10^{11} ohms.

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CHAPTER (2)

STUDIES IN ISOTOPICALLY LABELLED MOLECULES

INTRODUCTION

In 1932 Urey (37) and his colleagues discovered the deuterium isotope; later on, the earliest work was done by Harvey and Hofer (38).

The study of intermediary metabolism of lipids on various organisms with deuterium was pioneered by Schoenheimer and Rittenberg (39a). Deuterated oleic acid was prepared from animals (by isolation) which had been given the labelled stearic acid (39b). The study of various "amino acids" was made possible by the availability of ^{15}N (40).

Urey (41a) and his co-workers succeeded in fractionating carbon -13. In the same year (1939), Nier (41b) and Gulbransen investigated the natural abundance of ^{13}C in different sources and found small variations. Within the next year, the first biological experiment with isotopes was carried out by Rittenberg and Waelsch (42a). The isotope dilution method with stable isotope for quantitative determination of amino and fatty acids was developed by Rittenberg et al. (42b).

In 1937 Huffman (43a) and Urey obtained some enrichment of ^{18}O by fractional distillation of water.

AVAILABILITY OF STABLE ISOTOPES

1. Deuterium is being produced in the United States in the form of 99.8% D_2O. The Atomic Energy Commission supplies about 180 tons of deuterated water each year from the Savannah River Complex. Deuterium is also available in the form of completely and partially deuterated organic compounds.

2. Carbon-13 is being produced in the United States at the rate of several grams per day of high concentration of carbon-13 by Mound National Laboratory. This is also being produced in England at the rate of approximately 1.4g per day of sixty per cent carbon-13. Fractional distillation of carbon monoxide or isotopic exchange reaction are procedures for preparation of this heavy stable isotope which has been used in tracer studies (43b).

3. Nitrogen-15 is produced by one of the largest commercial producers (44) in the United States, which supplies several hundred grams per year, in the form of ninety-five per cent enriched material.

4. Oxygen-17 is currently being produced at Oak Ridge National Laboratory, Los Alamos Scientific Laboratory in the United States and at the Yeda Research Development Company in Rehovoth, Israel. Oxygen-18 is also being produced by the same company. This isotope is available in the form of $D_2{}^{18}O$ and $H_2{}^{18}O$ up to approximately 97% enrichment and as ${}^{18}O_2$ with ninety-nine per cent enrichment of the higher isotope.

PREPARATION OF LABELLED COMPOUNDS

Many organic compounds have been synthesised with stable isotopes for biochemical purposes. Biosynthesis by living cells is one of the general methods which can be applied to a trace pathway mechanism in the human body. It has the advantages of being capable of producing certain compounds which cannot be synthesised in the laboratory. Detailed reviews of this subject can be found in other works (45-48).

General methods of synthesis are similar to isotope labelling except in the substitution of isotopically labelled reagents. On the other hand, because of the cost of isotopic compounds, it is important to design a scheme in such a manner that the isotope is introduced in one of the final steps of a multistep reaction, to prevent the loss of valuable isotope compounds. The following outline is one of the most common procedures in labelling methods.

(a) Deuterium Labelling

A very common reaction for deuterium labelling is hydrogen exchange i.e. usually replacing the active hydrogen of a molecule in a deuterated solvent or gas. The disadvantages of this method arise from the presence of two or more active hydrogen in the molecule, because of its reactivity. Hydrogen atoms attached to oxygen, sulphur, nitrogen and halogens, exchange with deuterium in deuterated water which has been commonly used for biological synthesis.

The exchange reaction can occur also in the inlet system of a mass spectrometer by introducing a small amount of some amino acids, fatty acids, ethanol, sulphydryl groups etc., accompanied by deuterated water.

Enolizable hydrogen atoms, specially those adjacent to activating groups, e.g. -CO, -CHO, -COOH, $-SO_3$, $-NO_2$ and -CN groups, will react with deuterated water in the presence of a base catalyst to give the deuterated compound. Deuteropalmitic acid was prepared using deuteriosulphuric acid (49).

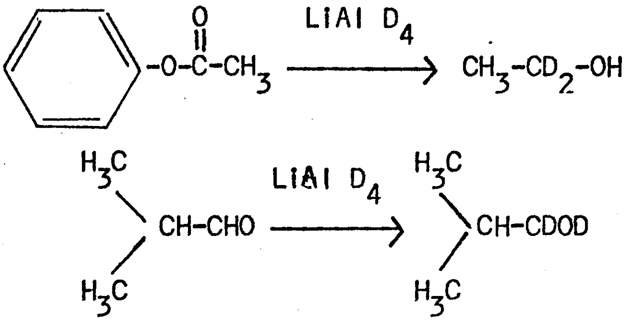
$$CH_3\text{-}(CH_2)_{13}\text{-}CH_2\text{-}COOH \xrightarrow{D_2\ SO_4} CH_3\text{-}(CH_2)_{13}\text{-}CD_2\text{-}COOH$$

Exchange of hydrogen in non-activated CH bonds of organic molecules is more difficult.

Reduction of certain organic compounds in the presence of a suitable catalyst is another method of deuterium labelling. Alanine was prepared by reduction of pyruvic acid; palladium was used as the catalyst in this reaction (50).

$$CH_3\text{-}CO\text{-}COOH \xrightarrow[NH_3,\ C_2H_5\,OH]{D_2,Pd} CD_3\text{-}CD\text{-}NH_2\text{-}COOH$$

Lithium aluminium deuteride (51a) has also been used for deuteration of organic compounds. Aldehydes, esters, epoxides, amides, halides, sulphonic esters and p-toluenesulphonyl hydrazones can be deuterated or reduced by this reagent.



Deuterium has also been incorporated in the multiple bond of unsaturated compounds. Deuterohydrazine (N_2D_4) was used for reducing the double bond in methyl oleate and some of its isomers.(51b)

(b) Labelling with Carbon-13

The reaction between carbon dioxide and an organomagnesium halide is one of the simplest methods of incorporating carbon-13 into an organic molecule (43,52); the general formula is:

$$R\,Mg\,X + \overset{*}{C}O_2 \longrightarrow R\,\overset{*}{C}OOMgX \xrightarrow{H^+} R\,\overset{*}{C}OOH$$

This reaction may be used as an intermediate stage in other syntheses. Preparation of alcohols has been carried out in this manner. Lithium aluminium hydride or deuteride was used as reductant for the reaction.

$$R\overset{*}{C}OOH \xrightarrow{LiAl\,H_4} R\,\overset{*}{C}H_2OH$$

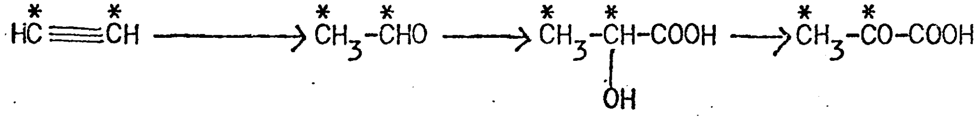
$$R\overset{*}{C}H_2OH \xrightarrow[H_2SO_4]{HBr} R\,\overset{*}{C}H_2Br$$

Succinic acid was synthesised by the use of labelled cyanide.

$$K\,\overset{*}{C}N+RX \longrightarrow R\,\overset{*}{C}N \longrightarrow R\,\overset{*}{C}OOH$$

Doubly labelled molecules, such as acetic and pyruvic acid, can be obtained by using acetylene under certain conditions (a and b)

a) $$H\overset{*}{C}\equiv\overset{*}{C}H \xrightarrow[(2)\ H^{+}]{(1)\ KOH} \overset{*}{C}H_3-\overset{*}{C}OOH$$

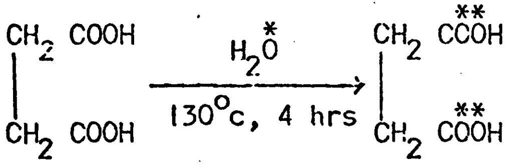
b) 

$$H\overset{*}{C}\equiv\overset{*}{C}H \longrightarrow \overset{*}{C}H_3-\overset{*}{C}HO \longrightarrow \overset{*}{C}H_3-\underset{OH}{\overset{*}{C}H}-COOH \longrightarrow \overset{*}{C}H_3-\overset{*}{C}O-COOH$$

Fermentation of glucose (53) by "Clostridium thermoaceticum" in the presence of labelled carbonate gives doubly labelled acetates. Biosynthetic reactions of microorganisms may be used for preparation of aliphatic acids in specific positions (44).

c) <u>Oxygen-18 Labelling</u>

Exchange reactions provide one of the most useful methods for the preparation of labelled molecule with oxygen-18. A simple example is heating succinic acid (54) with $H_2{}^{18}O$ for about four hours at 130°c; all four oxygen atoms easily undergo replacement.



Maleic acid will also completely exchange when treated at 100°c for 45 hours (55). Acid chlorides and anhydrides, exchange with $H_2\overset{*}{O}$ at room temperature. Amides, such as acetamide and benzamide do not exchange in $H_2\overset{*}{O}$ or acid solution but show a slow exchange in basic solution (56). Many of the organic aldehydes such as acetaldehyde and benzaldehyde readily exchange in water with oxygen-18. Alcohols exchange only under certain conditions in acid solution. Glycerol, methanol, diphenylmethanol and amyl alcohol do not exchange in neutral or basic solution (57).

Hydrolysis of alkyl halides, sulphates or phosphates can be used for the preparation of related alcohols. Methanol has been synthesised in this manner (58).

$$(CH_3O)_3\ PO \xrightarrow[\text{Limited reaction}]{H_2\overset{*}{O}} (CH_3O)_2\ POOH + CH_3\ \overset{*}{O}H$$

Methanol may also be prepared by oxidation of methyl magnesium bromide (59)

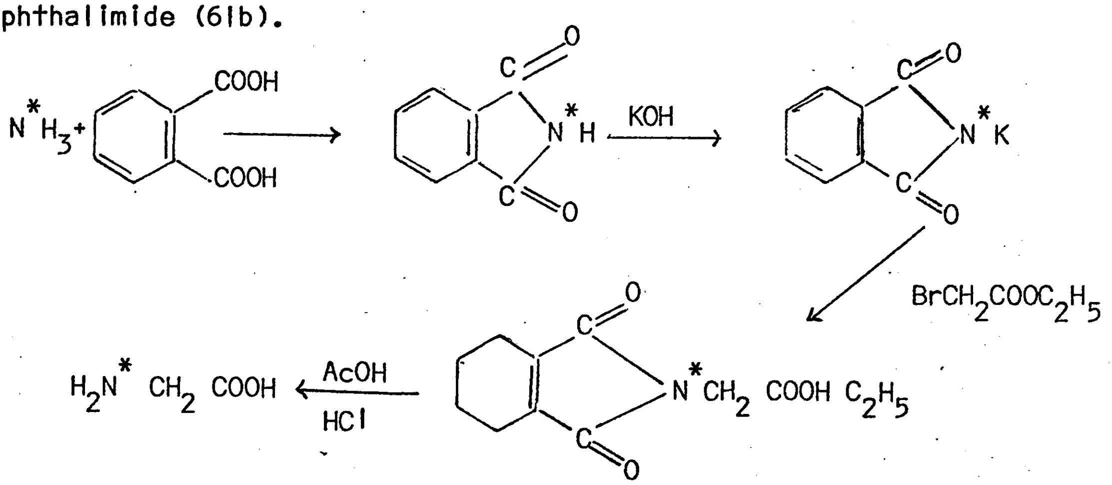
$$CH_3\ Mg\ Br \xrightarrow[(2)\ H_2O,\ H^+]{(1)\ \overset{*}{O}_2} CH_3\overset{*}{O}H$$

Direct oxidation (60) with $^{18}O_2$ can be used for the preparation of some ^{18}O- labelled compounds, e.g. sulphur dioxide, carbon dioxide and carbon monoxide may be labelled in this manner.

(d) Labelling with nitrogen-15

The use of phthalimide-^{15}N in the coupling of esters of 2-bromo carboxylic acid with potassium phthalimide is a general method for introduction of nitrogen-15 into the $\underline{\alpha}$ amino group of an amino acid (61a). The labelled reagent can be prepared by treating phthalic acid with $^{15}NH_3$ and then with potassium hydroxide.

Glycine-^{15}N was prepared from ethyl bromoacetate and the labelled phthalimide (61b).



Other amino acids and nitrogen - containing compounds, may be also labelled by this method.

OTHER STABLE ISOTOPES

Sulphur and halogens possess isotopes which have been used in some trace analyses; the isotopic abundance of sulphur-34 can be determined by measuring the intensities of the ions at m/e = 64 and 66 (62).

Conversion of organosulphur compounds into sulphur dioxide by burning the sample in a stream of pure oxygen and separation of sulphur dioxide from the other product, can be used as a procedure for trace analysis (63).

Chlorine and bromine are the only halogens that have heavy stable isotopes. They can be determined in the gases produced by burning organic halogen compounds at high temperatures in a stream of oxygen in the presence of platinum (64).

APPLICATION OF STABLE ISOTOPES

The low cost and reactivity of deuterium makes this isotope the most popular of stable isotopes. A second reason for this is the facile deuteration of organic compounds. However, in some particular cases (e.g. amino acids) nitrogen-15 will give a better result. Further advantages are safe handling and infinite lifetime (65).

Stable isotopes have been used in the investigation of biochemical phenomena and chemical reaction mechanism. The structural elucidation of organic compounds rests largely on an interpretation of the mass spectra of various transformation products in which the isotope was introduced in one or more of the labelled positions.

The detail of this subject can be found in other works (66-69).

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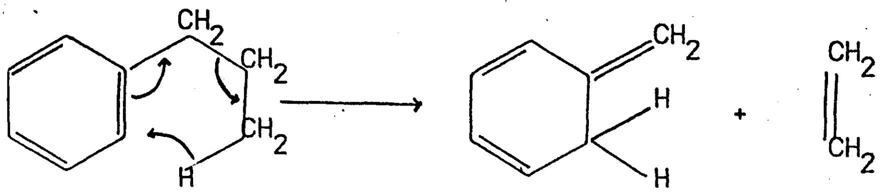
SURVEY OF THE ELUCIDATION OF MOLECULAR STRUCTURE BY MASS SPECTROMETRY

Correlation studies of organic mass spectra have been mainly of interest to mass spectroscopists, for the elucidation of mechanism of the behaviour of organic compounds upon electron impact. In certain cases, the use of isotope labelling has clearly shown the type of rearrangement and has revealed particular fragmentations which cannot be recognized from the general spectrum. It is necessary to decide in which part of the molecule the tracers should be incorporated.

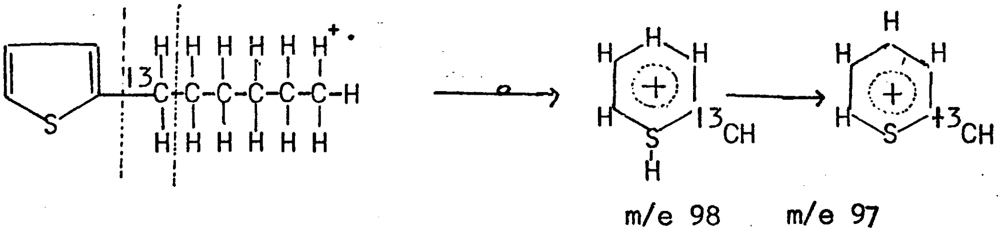
Burr (70) has given a comprehensive list of tracer applications (using both radioactive and stable isotopes) for the study of organic reactions. A similar use of tracers to biology and medicine has been reviewed by Arnstein and Bentley (71).

References are cited to some of the early work on structure elucidation by mass spectrometry (72-88), and a selection of recent investigations will be discussed to clarify how these tracers have been used (by a number of scientists) to elucidate the nature of organic molecules by mass spectrometry.

McCollum and Meyerson (89) studied the deuterated propylbenzenes and demonstrated a rearrangement from their mass spectra.



Benz and Biemann (90) studied a series of alcohols (n-butyl through n-heptyl) labelled with deuterium to examine the elimination process of water from alcohols. The mass spectra of three specifically deuterated ethyl butyrates (91) proved the position of migrated hydrogen in a McLafferty rearrangement. Gerrard and Djerassi (92) employed deuterium and carbon-13 labelling in a series of isomeric 1-phenylheptenes. They obtained evidence for extensive hydrogen and phenyl rearrangement. Meyerson and Field (93) studied the labelled 2- and 3- phenylthiophenes and confirmed the occurrence of reorganization of the molecular ion and ring breakdown. The mass spectra of carbon-13 labelled 2-hexylthiophene was reported by Foster et al. (94). A ring expansion after initial β cleavage of the neutral olefine was observed.



β rearrangement

Carboxylic acid labelling with carbon-13 in the case of n-butyric acid confirms the occurrence of a rearrangement process. Roberts and Urey (96) studied the mechanism of esterification of benzoic acid with oxygen-18 labelled methanol, and suggested the following reaction:

$$C_6H_5COOH + CH_3{}^{18}OH \longrightarrow C_6H_5CO^{18}OCH_3 + H_2O$$

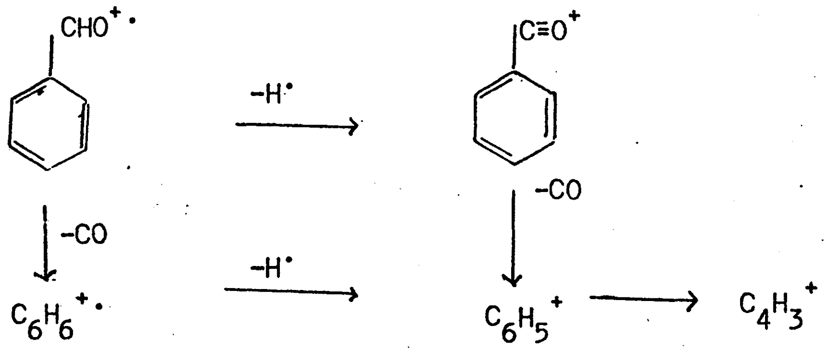
Deuterated propenes in three different positions were synthesised (97)

$CD_3CH = CH_2$, $CH_3\ CD = CH_2$, $CH_3\ CH = CD_2$

and their mass spectra obtained. Evidence suggested that the formation of $(C_3H_5)^+$ ion is induced by loss of a hydrogen atom with equal probability from the two terminal positions. The above argument for the central carbon can also be assumed. Deuterated alcohols in the range; ethanol,(98) propanols(99), butanols(100), have been studied. It was concluded that the characteristic $(M-1)^+$ ion, always results from the expulsion of the hydrogen atom attached to the carbinol atom.

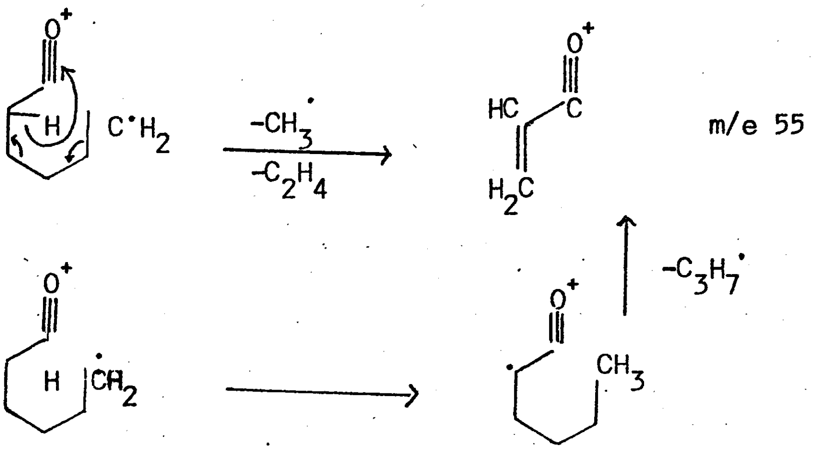
Studies of keto steroids labelled with deuterium have indicated that the rearrangement proceeds only if the interatomic distance between the $\underline{\gamma}$ hydrogen and the receptor oxygen, is less than 1.8A° (101-104).

The behaviour of benzyl alcohol upon electron impact has been investigated by deuterium labelling (105,106). Loss of one hydrogen atom from molecular ion was pronounced. In the case of benzaldehyde (107), loss of the aldehyde hydrogen gives the fragment of $(M-1)^+$, which is as abundant as the intense molecular ion. The investigation was carried out with a deuterated molecule and the following mechanism was proposed:

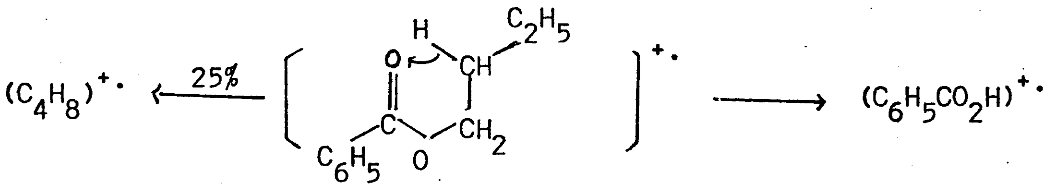


The mass spectra of cyclohexanone has been studied by deuterium labelling (108) in order to trace the mechanism of its decomposition.

It was shown that the base peak at m/e = 55 corresponded to $(C_3H_3O)^+$ ion and the following pathway was suggested.



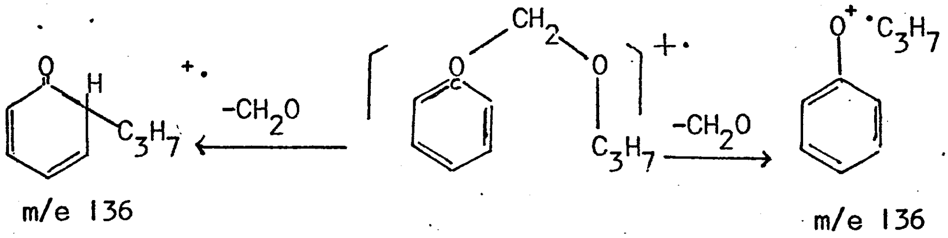
Djerassi et al. (109) investigated the source of migrated hydrogen in the mass spectra of butyl benzoate. Deuterium labelling was used in this study. The observed phenomenon was shown as follows:



An interesting study was carried out by Beak et al. (110a) to determine the mechanism of formation of $(M-CO)^+$ and $C_3H_3^+$ ions which are abundant in the mass spectra of 4- pyrone. Deuterium and oxygen-18 were used for double labelling. They reported slightly different result from that of 2- pyrone (110b). The mass spectra of deuterated benzoic acid (111,112) established that the loss of a hydroxyl radical does not consist solely of the original hydroxy group. In the spectrum of O-d_1-benzoic acid, a metastable peak was evidence for elimination of hydroxyl and deuteroxyl from molecular ion.

$$(C_6H_5COOH)^{+\cdot} \xrightarrow{-OH^{\cdot}} \underset{m/e\ 105}{C_6H_5C\equiv C^+} \xrightarrow{-CO} \underset{m/e\ 77}{C_6H_5^{\ +}}$$

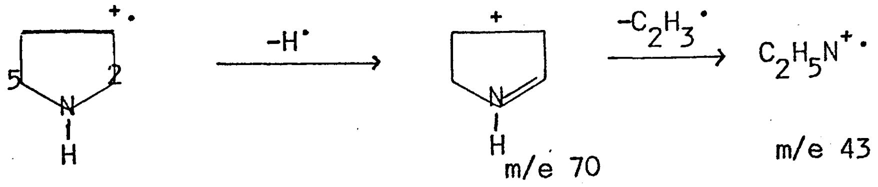
Ejection of formaldehyde from the molecular ion of mixed alkyl aryl formaldehyde acetals such as n-propoxyphenoxy methane, was demonstrated by deuterium labelling (113). The possible reaction shows that the formaldehyde molecule stems from the aldehyde portion of the acetal as follows:



The mass spectra of thiophenol and its deuterated analogue (114,115) were compared; in contrast to phenol loss of a hydrogen atom from the molecular ion was emphasized. It was shown that half of the ejected hydrogen, stems from the-SH group and the rest therefore must originate from the nucleus

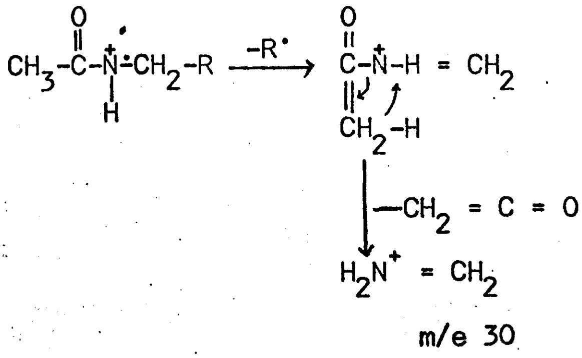
Pelah et al. (116), interpreted the mass spectra of n-ethylcyclopentylamine. The correlation was carried out with deuterated analogues. They indicated the $(M-C_2H_5)^+$ ion as a base peak and the simple α cleavage produces the $(M-CH_3)^+$.

Decomposition of pyrrolidine upon electron impact was studied and different pathways were suggested (117-119). However, deuterium labelling (120,121) of the -NH group as well as of the C-2 and C-5 (carbon) positions determined the peak shifts and the formation of $(M-1)^+$, the nitrogenous portion of m/e = 43 containing all four d-hydrogens.

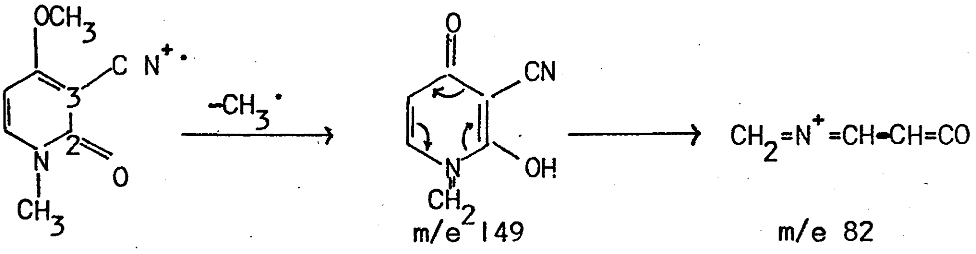


The fragmentation process of piperidine was clarified by exact mass measurements (120), as well as by deuterium labelling (121). The mass spectra of isomeric nitroanilines were studied by many groups (122-124). In the case of *p* and *m* nitroanilines, loss of an oxygen atom was exhibited, while the *O*-isomer showed an $(M-OH)^+$ fragment. Deuterium labelling (124) suggested the path for the loss of an hydroxyl group.

The phenomenon of the hydrogen rearrangement and the double α- and C-N$<$ bonds cleavage process was investigated by a comparison of the mass spectra of *n*-butylacetamide (116) and *n*-butyl-d_3-acetamide; the breakdown was suggested to occur as follows:



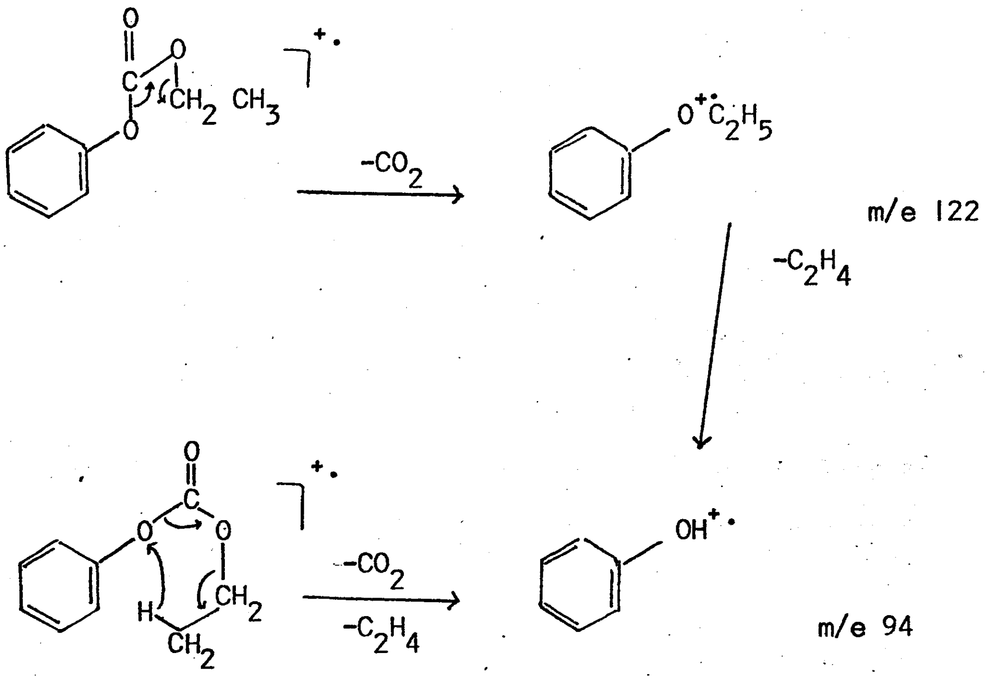
The peak at m/e 30 shifts to m/e 31 in the deuterated spectra. The fragmentation of ricinine (125) has been traced by carbon-13 and nitrogen-15 labelling. The results obtained suggest the following mechanism:



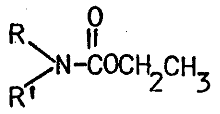
Exact mass measurements and deuterium labelling have shown all principal bond fissions which occur in di-n-propyl ketone semicarbazone (126). It is much more complicated in the case of the mass spectra of isohexyl cyanide (127); the mechanisms of main fragmentations were elucidated. McFadden and Lounsbury (128) studied some deuterated aliphatic halides; elimination of hydrogen halides generally occurs. They reported that the involvement of hydrogen from carbon -1 in the case of 1, 1-d_2 butyl bromide is not significant.

An examination of deuterated n-amyl-1,2- and n-hexyl-3-acetates (129), demonstrated that the acetates behave differently upon electron impact. In fact, 1,3-elimination induces 45% and 1,2 produces the remainder of the acetic acid in the mass spectra.

The behaviour of alkyl aryl carbonates has been studied. A typical example is the mass spectra of ethyl phenyl carbonate, in which the peak occurs at m/e=94; corresponding to ionized phenol. This was confirmed by deuterium labelling. The following process was suggested:

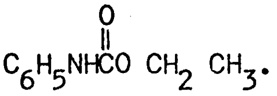


Lewis has studied the mass spectra of a number of *n*- substituted ethyl carbamates (132,133) of general formula



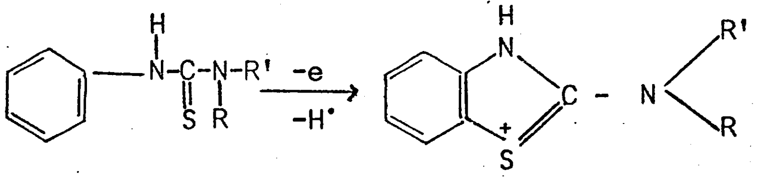
$$\begin{matrix} R \\ R' \end{matrix} \!\!>\! N\!-\!\overset{O}{\overset{\|}{C}}OCH_2CH_3$$

A very abundant peak arises at m/e=29 corresponding to $C_2H_5^+$ ion and the neutral ethylene eliminates from the ethoxy group. However, the mechanism was established for deuterated ethyl *n*-phenylcarbamate (132)

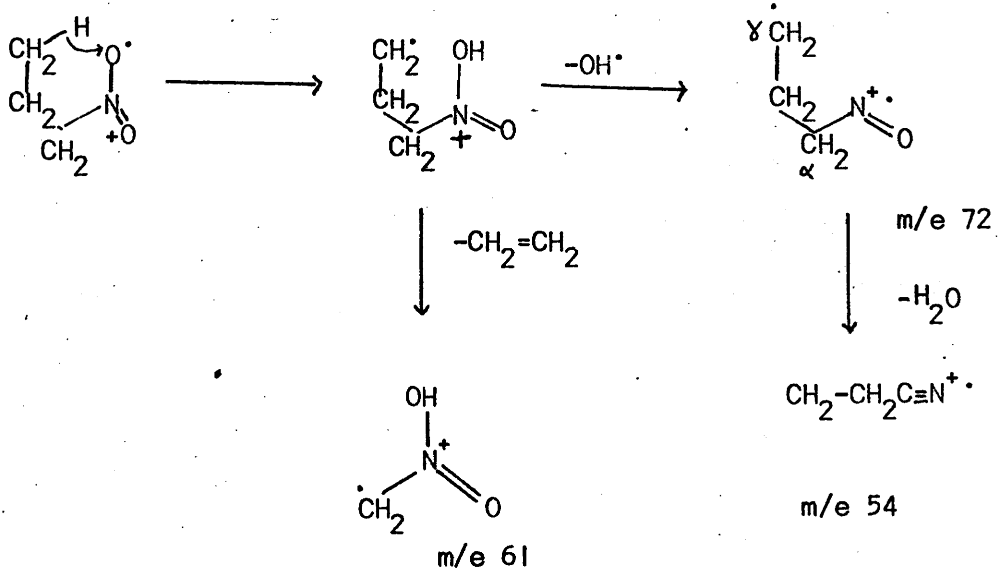


$C_6H_5NHCOCH_2CH_3$.

A moderately abundant $(M-1)^+$ is a common feature of the spectra of phenyl thioureas (134); an interesting result was obtained by deuterium labelling, which suggests that the loss of hydrogen by fission of an N-H bond is not involved, but the formation of a cyclic ion is much more pronounced.



The mass spectra of nitropropane and the specifically deuterated analogues were studied and the following fragmentation suggested (135).



o-Nitrotoluene labelled in the methyl group with carbon -13 gives a similar fragment at m/e=92 or its analogue (136). This experiment indicates that the carbon atom of the nitro group becomes a nitrite.

Isomerization in the portion of molecular ion is unlikely; it seems to be a hydroxyl elimination.

The mass spectra of some simple pyrimidines (137) have been studied and several useful techniques, such as deuterium labelling and high resolution mass spectrometry, were utilized. The loss of hydrogen cyanide was pronounced as a first step in its decomposition. Shapiro et al. (138) reported the mass spectra of ethyl benzoate, and some information on the loss of hydroxyl and deuteroxyl radical from $(M-C_2H_4)^+$ ion was obtained. Toluenes (139) were deuterated in different positions; their mass spectra showed that the loss of H$^\bullet$ atom was effected by isotope labelling.

Corval and Masclet (140) studied the decomposition of deuterated methanol. Behaviour of the label in various positions was shown by comparative kinetic studies.

Deuterated pyrazoles (141) were studied, and the loss of H$^\bullet$(D$^\bullet$) and HCN (DCH) from their molecular ion reported. McFadden et al. (142) obtained the mass spectra of three deuterated bromobutanes; the cracking pattern was compared with unlabelled analogues. The expulsion of hydrogen bromide to form $C_4H_8^+$ from 2-bromobutane has shown that the hydrogen on carbon-4 is involved in this fission.

The mass spectra of deuterated butanols (143) were compared with those of unlabelled compounds and parallel features of fragmentation were observed. Venema et al. (144) investigated the structure of the $(C_8H_9)^+$-ion from l-phenylethylbromide and the $(C_8H_8)^+$ ion from styrene by use of carbon-13 labelling. They explained that the complete randomization occurs by assuming an eight-membered ring structure for the $(C_8H_9)^+$ and $(C_8H_8)^+$ ions.

The use of deuterium, carbon-13 and nitrogen-15 labelling established the mechanism of hydrogen cyanide expulsion from benzylcyanide and of o-, m-, and p-cyanobenzylcyanides (145).

The Mass Spectra of Some Carbon-13 Labelled Compounds

INTRODUCTION

The previous discussion presented encouraging results that have been obtained during the past thirty years. The utility of stable isotopes in the progress of knowledge of chemistry induced by electron impact in the mass spectrometer was established. Most such labelling has been done with deuterium but considerable experience has been gained with other isotopes, notably Carbon-13, as well.

The purpose of the present investigation is to study the mechanism of the bond rupture and a probable carbon atom rearrangement in a homologous series of acids, alcohols and iodides from C_5 - C_7 by incorporating Carbon-13 isotope in the 1-position of these molecules. Therefore the work necessitate the synthesis of isotopically labelled materials and subsequently the interpretation of their mass spectra.

The synthesis:

The selection of the tracer element, where any choice exists, is made on the basis of factors such as stability of labelling, ease of synthesis and concentration of isotope available.

Ideally, an isotopic synthesis should be simple and should combine a high recovery of isotope with low dilution by unlabelled material. A high yield is sought for reasons of economy and the isotope is therefore introduced at as late a stage in the synthesis as is possible. Yields are improved by careful selection of reaction conditions, and by systematic refinements in experimental technique.

In any particular synthesis, the loss involved if low yields are obtained must be set against the extra effort required to secure higher yields.

Purity of Labelled Compounds:

The usual criteria of purity of organic compounds may also be applied to labelled compounds but are often inadequate. Sensitive determination of chemical impurities is sometimes valuable, but most satisfactory tests of purity are those designed to demonstrate the extent to which the isotope is associated with the compound being studied. Thus an isotopic compound must be purified not only to meet criteria such as constant melting point, boiling point, or refractive index, but also to constant isotopic composition, and reliance should not be placed on one method of purification alone.

Many of the conventional methods of purification (e.g. precise fractional distillation) are quite unsuitable on the relatively small scale of most isotopic synthesis. Losses are involved in all purification procedures and it is therefore desirable to devise synthetic methods which give very pure products or products containing unexceptionable or easily removable impurities. Paper chromatography is applicable on the small preparative scale and has been very widely used in the separation and purification of labelled substances.

EXPERIMENTAL

The synthetic method with isotope was developed and the following procedures (146 - 148) were modified to prepare some labelled compounds on a very small scale for our study. The first stage of the synthesis was carried out with unenriched molecule in order to establish a satisfactory yield, and then was repeated with labelled species.

ACIDS

The appartus consisted of a high-vacuum manifold equipped with attachments to a reaction flask, carbon dioxide generator, mercury manometer and a nitrogen inlet and outlet, (Fig. A). The cone-shaped, three-necked reaction flask was used with an overhead induction stirrer. The generator consisted of a round-bottomed flask, containing barium carbonate - ^{13}C, and fitted with a pressure-equalizing addition funnel containing concentrated sulphuric acid and attached to a drying tube.

The Grignard reagent was prepared under dry nitrogen in an all-glass apparatus, and an aliquot of the etheral solution was assayed by titration. The system was evacuated to 0.1 mm Hg and filled with dry nitrogen. The carbonation flask was charged quickly with a 10% excess of the Grignard reagent. The side arm stopper was replaced, the solution was frozen with liquid nitrogen, and the system was evacuated to 0.1 mm Hg. The mixture was thawed with a Dry Ice/acetone bath at - 20°C and refrozen with liquid nitrogen; then the system was evacuated to remove entrapped nitrogen. The stirred Grignard reagent was then carbonated at - 20°C by dropping sulphuric acid slowly on to the barium carbonate while the pressure was kept below 50 cm. The last of the gas was evolved by warming the generator gently to dissolve the salts. Absorption was complete when the manometer reading was constant, 10 - 15 minutes being

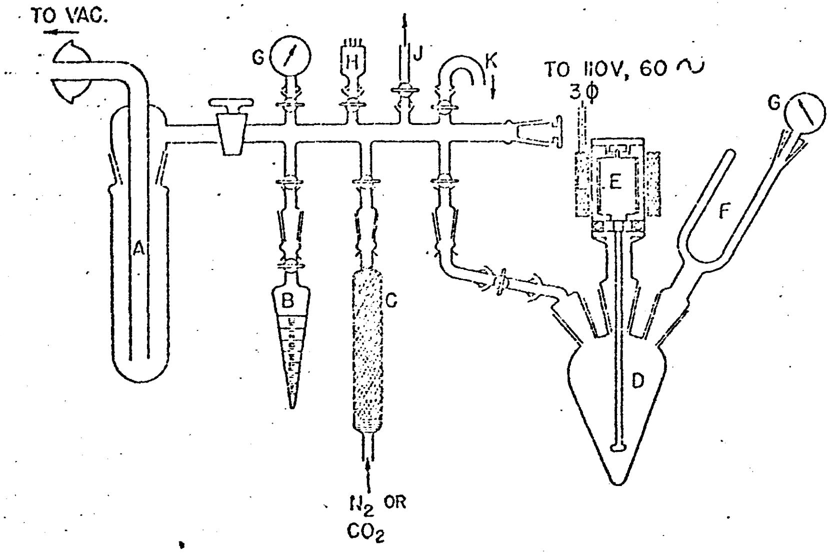


FIG. A. Grignard preparation and carbonation unit. A, large liquid air trap; B, alkyl iodide storage vessel; C, drying tube; D, Grignard flask; E, induction stirrer; F, dry ice-acetone reflux condenser; G, Bourdon type vacuum gages; H, thermocouple type vacuum gage; J, to CO_2 storage bulb; K, mercury manometer; L, Selsyn generator stator.

required for the process. The mixture was frozen with liquid nitrogen to draw any remaining Carbon-13 dioxide into the reaction flask, the stopcock to the generator was closed, and the mixture was stirred fifteen minutes at - 20°C to ensure complete absorption. The system was filled with nitrogen and vented to the atmosphere; then the complex was decomposed with dilute sulphuric acid. The acid mixture was extracted with ether, and the product was removed from the ether solution with dilute sodium hydroxide. The alkaline solution was acidified, and the product was collected by filtration. A further quantity was obtained by ether extraction of the filtrate, then the whole was purified by distillation.

YIELD AND REACTIONS

In the case of valeric acid, a Grignard solution was prepared from 1.0 g of magnesium turnings and 4.5 g of n-butyliodide in absolute ether.

$$CH_3 \cdot (CH_2)_3\ I + Mg \longrightarrow CH_3\ (CH_2)_3\ Mg\ I$$

Butylmagnesium iodide was carbonated with the Carbon-13 dioxide liberated from 2.5 g of barium Carbonate - ^{13}C.

$$C_4H_9MgI + {*CO_2} \longrightarrow C_4H_9\ {*COOMg}\ I$$

Following hydrolysis, the ethereal solution was extracted exhaustively with dilute sodium hydroxide; then the alkaline solution was washed, acidified and extracted with ether, which in turn was extracted with a small volume of sodium hydroxide solution. The hot aqueous solution was acidified and cooled to precipitate the product; yield 1.2 g.

$$C_4H_9\ {*COOMg}\ I \xrightarrow{H^+} C_4H_9\ {*COOH}$$

The same procedure was used to prepare n-caproic and n-oenanthic acids. Some of the acids so obtained were reduced to corresponding alcohols.

$$C_4H_9\ {}^{*}COOH \xrightarrow{LiAlH_4} C_4H_9\ {}^{*}CH_2OH$$

REDUCTION

A solution of 0.8 g of valeric I - ^{13}c acid in 50 ml. of absolute ether was added dropwise to a stirred suspension of 20 m.moles of lithium aluminium hydride in 50 ml. of ether. After fifteen minutes of additional stirring, the mixture was decomposed with ice water and 10% sulphuric acid. The aqueous phase was saturated with sodium chloride, separated and extracted with ether. The ether extract was washed with 4% sodium hydroxide solution, dried over sodium sulphate and concentrated; then the product was distilled; yield 0.6 g.,

HALOGENATION

A solution of 0.1 g. of purified red phosphorus in 0.4 ml. of enriched n-amyl alcohol was placed in a flask and 0.5 g. of iodine in the special apparatus (Fig. B), then it was heated up gently. The alcohol vapour gradually passed into (B) through the wide-bore side tube C and eventually the hot alcohol dissolved the iodine. The formation of n-amyl iodide was practically complete and little iodine vapour was visible. The product was tranferred to a microdistillation flask and purified in the usual manner; yield 0.3 ml.

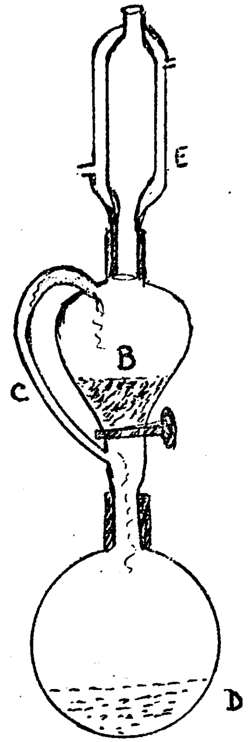


FIG. B

Collection of Spectra

In all cases the appropriate acid, alcohol or iodide, were carefully purified by distillation and checked by gas chromatography (tables 1, 2).

These compounds which were uniformly labelled in the 1-position with Carbon-13 were then examined, together with purified samples of the enriched compounds upon an AEI-GEC MS902S; having an ion accelerating voltage of 8.0 kV and trap current of 100μA. The results are illustrated in (tables No. 3-5).

The instrument was tuned in the manner recommended by the manufacturer except that particular attention was paid to peak shape. Considering that peakheight was to be used as the measure of ion abundance in all cases, it was essential to obtain peaks which were flat topped (or trapezoidal) i.e. gaussian shapes were to be avoided.

TABLE No. 1

Compound	Mass	
	Observed	Calculated
^{13}C-1-*n*-amyl iodide	199.089437	199.089426
^{13}C-1-*n*-hexyl iodide	213.105073	213.105075
^{13}C-1-*n*-heptyl iodide	227.120756	227.120725
^{13}C-1-*n*-amyl alcohol	89.092255	89.092165
^{13}C-1-*n*-hexyl alcohol	103.107817	103.107814
^{13}C-1-*n*-heptyl alcohol	117.123463	117.123464
^{13}C-1-*n*-valeric acid	103.071420	103.071430
^{13}C-1-*n*-caproic acid	117.087157	117.087079
^{13}C-1-*n*-oenanthic acid	131.102771	131.102728

TABLE No. 2

BOILING POINTS

Radical	Iodide	Alcohol	Carboxylic Acid	% Enrichment of Acid
n-Amyl	163-165	137.4	185.1	62.8
n-Hexyl	178-180	158.0	205	62.8
n-Heptyl	198-201	176.0	223	62.8

Table No. 3

m/e	n-Pentanol		n-Hexanol		n-Heptanol	
	normal	enriched	normal	enriched	normal	enriched
27	30.35	41.30	28.45	29.75	26.40	45.55
28	6.42	37.75	13.50	34.25	31.67	54.15
29	46.73	60.20	28.95	65.93	32.83	55.25
30		7.85		38.17		6.60
31	48.25	19.50	29.70	15.22	27.67	22.85
32	1.54	38.10	3.10	21.42	7.43	23.25
39	21.10	23.71	20.90	19.90	20.10	30.50
40	5.55	87.62	5.50	6.15	6.05	8.75
41	67.80	72.16	54.55	54.10	7.50	65.34
42	100.00	100.00	42.90	42.35	46.26	46.63
43	23.39	51.54	73.40	72.92	64.18	70.75
44	7.75	13.40	6.65	7.05	8.00	20.35
45	6.70	11.80	9.65	4.50	6.15	10.86
46						3.25
55	74.30	50.80	58.80	38.50	65.00	65.75
56	17.60	58.20	100.00	100.00	90.20	93.15
57	19.77	27.50	9.90	27.43	26.80	56.50
69	7.57	8.12	17.45	15.85	54.20	47.85
70	60.83	29.20	13.40	17.46	100.00	100.00
71	5.25	52.00	9.90	2.55	7.85	45.68
84			23.35	4.25	1.36	12.35
85			4.35	15.85		9.43
97					2.50	6.15
98					18.90	6.75
99					1.75	13.66

Table No. 4

m/e	*n*-Valeric Acid		*n*-Caproic Acid		*n*-Oenanthic Acid	
	normal	enriched	normal	enriched	normal	enriched
27	22.85	42.85	18.90	68.50	29.10	46.50
28	14.40	24.60	25.00	23.40	45.80	38.35
29	20.65	34.00	15.00	40.45	22.90	42.85
31	3.50	4.70	2.60	3.20	2.8	4.6
39	12.90	22.35	11.40	46.20	21.00	36.25
41	23.40	34.60	27.10	74.00	42.50	76.65
42	15.00	8.70	13.65	21.20	14.50	28.56
43	16.10	10.20	21.10	27.00	37.30	85.30
45	15.05	10.10	13.65	12.10	12.50	13.25
46		13.50		14.90		9.75
55	18.40	15.10	16.15	23.20	29.25	35.36
56	8.20	20.45	17.20	25.35	8.20	43.75
60	100.00	43.30	100.00	56.40	100.00	63.80
61	9.25	100.00	14.80	100.00	14.20	100.00
73	43.70	15.80	42.20	23.40	46.20	13.25
74	5.80	38.50	7.20	42.50	6.25	37.65
87	3.80	1.80	14.50	8.28	25.00	18.35
88		2.60	1.90	14.85		32.50
102	2.45	0.90				
103	0.75	2.35				
116			1.20	0.85		
117			0.65	2.25		
130					3.70	5.25
131					0.50	12.35

Table No. 5

m/e	n-Amyl Iodide		n-Hexyl Iodide		n-Heptyl Iodide	
	normal	enriched	normal	enriched	normal	enriched
27	32.87	44.50	31.40	13.80	17.20	47.20
28	18.73	20.85	91.85	37.60	24.50	28.85
29	36.20	42.30	28.80	14.85	23.35	55.40
30		11.35		3.50		4.65
39	29.83	28.75	23.40	19.15	12.64	24.45
41	54.70	51.55	60.50	52.25	44.25	65.30
42	40.75	39.40	16.85	15.45	18.95	23.35
43	100.00	100.00	100.00	100.00	41.28	65.80
44	19.20	54.55	8.20	43.05	2.85	10.27
55	42.30	14.90	42.60	12.85	14.60	20.25
56	7.75	13.20	28.46	16.65	5.85	13.50
57	11.75	6.80	30.75	18.60	100.00	100.00
70	26.90	3.85	4.70	8.20	2.95	7.15
71	69.75	26.65	11.74	6.75	3.50	14.80
72		38.45				
83			10.90			
84			6.85			
85			41.50	27.50	8.30	24.20
86				43.58		2.25
98					1.05	1.95
99					5.45	3.25
100					0.80	5.35
127	8.62	10.50	5.60	7.25	2.95	8.37
128	4.25	4.35	8.20	3.70	3.35	4.24
198	15.90	7.25				
199	0.50	12.45				
212			15.45	8.05		

Cont. Table No.5

m/e	n-Amyl Iodide		n-Hexyl Iodide		n-Heptyl Iodide	
	normal	enriched	normal	enriched	normal	enriched
213	-	-	-	14.35		
226	-	-	-	-	12.20	6.30
227	-	-	-	-	1.20	11.50

Discussion of the Mass Spectra

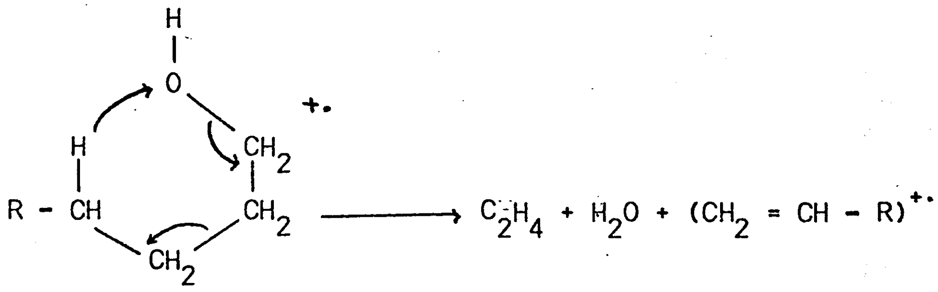
ALCOHOLS

An examination of the C_5 - C_7 straight chain alcohols and the corresponding labelled compounds show prominent peaks in their mass spectra related to losses of water and ethylene from the parent ion. The general feature of this pattern is as follows:

$$(\text{Alcohol})^{+\cdot} \longrightarrow (P - 18)^{+\cdot} \xrightarrow{-C_2H_4} \text{base peak}$$

$$\begin{tikzcd}
(C_5H_{12}O - 18) \arrow[dr] & & \\
& 70 - 28 \arrow[dr] & \\
(C_6H_{14}O - 18) \arrow[r] & 84 - 28 \arrow[r] & \text{base peak} \\
& 98 - 28 \arrow[ur] & \\
(C_7H_{16}O - 18) \arrow[ur] & &
\end{tikzcd}$$

The base peaks are formed by the expulsion of ethylene and water following the formation of a six-membered transition state:



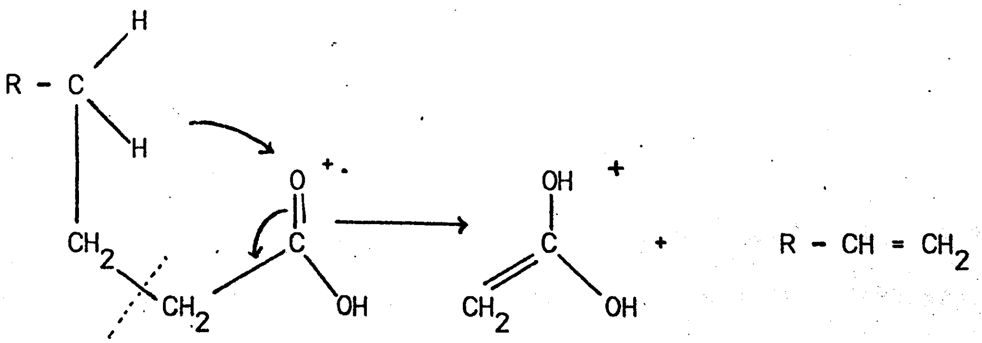
where; R = CH_3, C_2H_5 or C_3H_7

The heaviest ions in these spectra are of masses 70, 84 and 98 appearing in the labelled homologous at 71, 85 and 99. The group of peaks immediately below these differ by 13, 14 and 15 units respectively. This suggests that the group is not formed by fragmentation of the ions at masses 70, 84 and 98 but by fragmentation of a heavier ion, and thus indicates that all the peaks observed may be fragmentation products. The other major fragments are 29, 31, 41, 43 and 55. Masses 31 and 43 represent cleavage of the β bond, the charge remaining respectively on the oxygenated or on the hydrogen fragment. The composition of mass 31 is $(CH_2OH)^+$ which is abundant in their mass spectra (149 a) and has been reflected at mass 32 in the labelled molecules.

The ion of mass 46, which is prominent in the longer chain alcohols (e.g. heptanol), represents $(C_2H_{60})^+$. The formation of $C_4H_8^+$ is particularly noticeable.

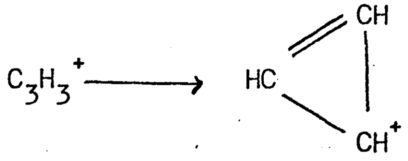
CARBOXYLIC ACIDS

The most abundant ion in these spectra is the fragment of mass 60 which is the result of a β cleavage and a rearrangement process, accompanied by migration of a γ hydrogen to the carbonyl group (149 b). High resolution measurement in both normal and enriched molecules show the $(C_2H_4O_2)^+$ ion, and confirms the occurence of a McLafferty rearrangement.



m/e 60

The peak at mass 45 due to $(COOH)^+$ is invariably larger than the peak at mass 31. Many of the other ions arise by simple fission in the carbon chain as evidenced by ions at m/e = 29, 43, 57 etc., corresponding to $C_2H_5^+$, $C_3H_7^+$, $C_4H_9^+$ etc., or by the formation of unsaturated ions e.g. m/e = 27, 41 with possibly cyclic ion m/e = 39



IODIDES

The iodides n-amyl, n-hexyl and n-heptyl were examined and the following conclusions were drawn. Fragmentation in these normal iodides tends to afford ions in the series m/e = 29, 43, 57 etc., or m/e = C_nH_{2n+1}.

Cleavage of the carbon-iodine bond with the positive charge remaining on the halogen fragment is noticable. Loss of the halogen atom is accompanied by a hydrogen transfer leading to the ions at m/e = (70, 71), (84, 85) and (98, 99) due to $(P - HI)^+$ and $(P - I)^+$ respectively. The following mechanism canbe assumed:

$$R - CH_2 - CH_2 - I^{+\cdot} \longrightarrow R\ CH_2\ CH_2^+ + I^{\cdot}$$
$$\searrow R\ CH = CH_2^+ + HI$$

However, the neutral fragment of HI is less abundant, and the separation of iodine is more emphsized. The peaks at m/e = 71 and 85 are evidence for a facile cleavage of the amyl and hexyl groups.

In the isotopically enriched species the results are similar although the comparable masses are increased by one.

CONCLUSION

Comparison of the series of spectra reveals that the behaviour of the enriched molecules upon electron impact is similar to those of normal species, it was also clarified that the carbon rearrangement does not occur and the label was completely retained in its position. No evidence was obtained to support the rupture of ^{13}C - ^{12}C bond prior to β cleavage, although the noted bond is weaker than ^{12}C - ^{12}C bond and it was reported (150) for propane 1 - ^{13}C.

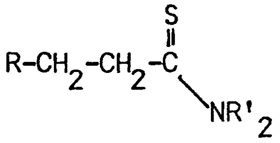
CHAPTER (3)

STUDY OF McLAFFERTY REARRANGEMENT

INTRODUCTION

The study of the behaviour of organic molecules upon electron impact has been one of the basic topics of mass spectrometry, in order to elucidate the structure of the organic compounds.

The present investigation involves the study of a typical thioamide, assuming the McLafferty rearrangement will occur. A synthetic route is suggested by the following structure:



$R{-}CH_2{-}CH_2{-}C({=}S){-}NR'_2$

Where $R{=}CH_3$ or C_2H_5

NR'_2 = Secondary amine-H (Morpholine-H)

Very many reports on rearrangement processes have been published recently in a series of papers, of carboxyl group, corresponding acids, ketones, amides etc. This chapter is in four parts, (1) rearrangement process, (2) McLafferty Rearrangement, (3) synthesis of thioamides, (4) discussion and interpretation of mass spectra.

PART ONE - REARRANGEMENT PROCESSES

Electron impact of organic molecules induces fragmentation and rearrangement which is very important for the identification and determination of the structure of organic compounds. Many various classifications of rearrangement have been recommended and recognized by mass spectroscopists. McLafferty (151) has discussed in detail all probabilities of this classification and recognized that four important conditions may be distinguished.

I - Odd-electron ion ⟶ odd-electron ion + even electron molecule (single rearrangement)

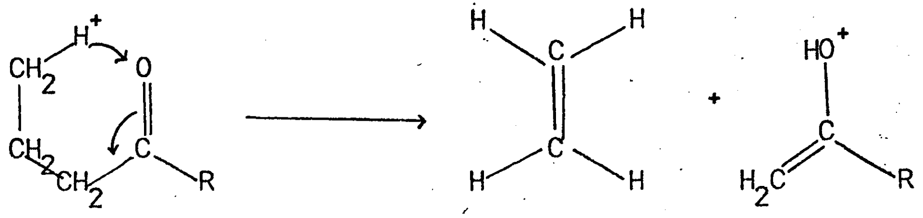
II - Odd-electron ion ⟶ even-electron ion + odd-electron radical (double rearrangement)

III - Cyclic odd-electron ion ⟶ even-electron ion + odd-electron radical (single rearrangement)

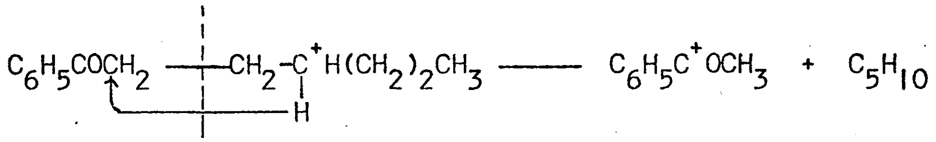
IV - Even-electron ion ⟶ even-electron ion + even-electron molecule (single rearrangement)

I ODD-ELECTRON ION (SINGLE REARRANGEMENT)

A simple example of this group concerns ketones: fragmentation of a $\underline{\beta}$ bond accompanied by $\underline{\gamma}$ hydrogen migration occurs. The mechanism for this type of fragmentation has been devised by McLafferty (152) for a methyl ketone. The cyclic transition state of this is as follows:

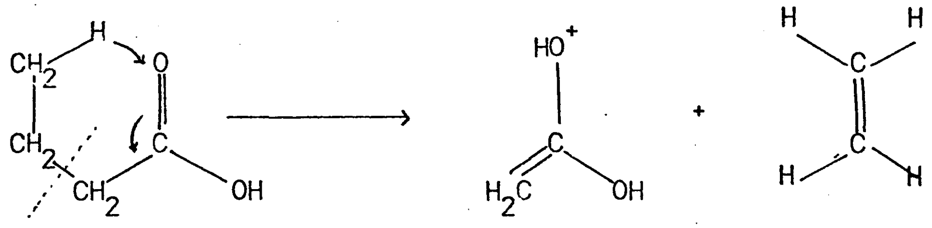


A similar rearrangement has been postulated for n-hexyl-ketone ion and a metastable ion (153) at m/e 75.8 is evidence for the entity of neutral fragment separation.



$$C_6H_5COCH_2 - CH_2-\overset{+}{C}H(CH_2)_2CH_3 \longrightarrow C_6H_5\overset{+}{C}OCH_3 + C_5H_{10}$$

Fragmentation of carboxylic acids by electron impact exhibits the same behaviour as the other carboxyl group e.g. the presence of a γ hydrogen in n-butyric acid induces the rearrangement by electron impact which does not occur in propionic acid.



The thermodynamic argument (154) to derive this reaction suggests the ability to form a stable olefine molecule. However, all evidence which has appeared in the literature, requires that the cleavage involves a β bond fission and migration of a γ hydrogen to the carbonyl group. The use of isotopically labels for some aryl substituted alcohols has been reported.

The migration of hydrogen occurs, but from the hydroxyl group.

$$C_6H_5-CH_2 \mid CH_2OH \longrightarrow C_7H_8^+ + CH_2O$$

(2) ODD-ELECTRON ION (DOUBLE REARRANGEMENT)

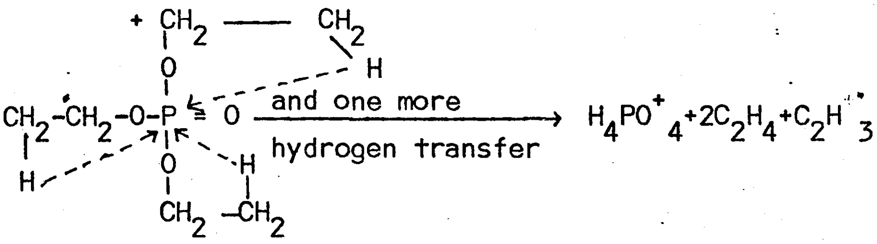
The phenomenon of double rearrangement has been observed from the spectra of some esters and carbonates. The fragmentations involve at least migration of two hydrogen in the molecule. McLafferty (155) pointed out that the second hydrogen need not be taken from the same carbon atom as the first. McLafferty and Peard (156) studied the fragmentation of alkoxy alcohols and glycols.

$$HOC^{+}H_2\text{-}CH_2OH \longrightarrow CH_3\text{-}O^{+}H_2 \quad + \quad HCO$$

$$CH_3O^{+}\text{-}CH_2\text{-}CH_2OH \longrightarrow (CH_3)_2{}^{+}OH \quad + \quad HCO$$

Beynon (157), Lester and Williams reported the same phenomenon in the decomposition of aniline; hydrogen cyanide is the prominent fragment ion in this cleavage.

Quayle (158) and co-workers studied the phosphate esters. The product shows a protonated orthophosphoric acid, two molecules of ethylene and an ethyl radical which involves three carbon bond fissions and four migrations



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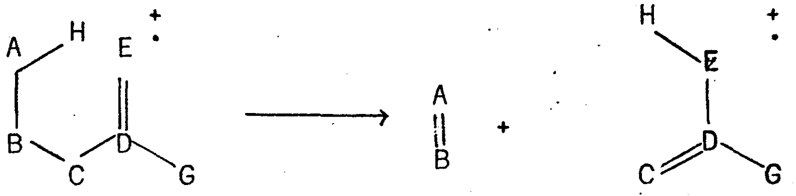
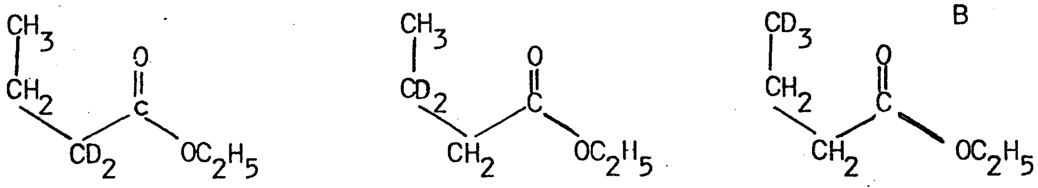
PART TWO - McLAFFERTY REARRANGEMENT

Migration of a γ hydrogen to the carbonyl group involving a six-membered cyclic transition state to form an olefine was proposed by McLafferty (151). A general scheme (A) shows the basic structure of the molecule.



A

There must be a double bond between D and E, a γ hydrogen atom must also be available to migrate to the D-E multiple bond. A very careful investigation has been carried out to establish this type of fragmentation. The study of specifically deuterated ethyl butyrates (B) has clearly proved the mechanism of this rearrangement (159).

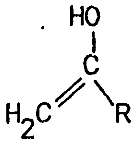


B

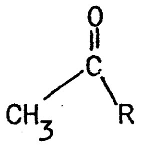
1 2 3

Elimination of an olefine molecule and retaining both alpha hydrogens, in fragmentation of the labelled compound shows that the proposed mechanism is probably correct.

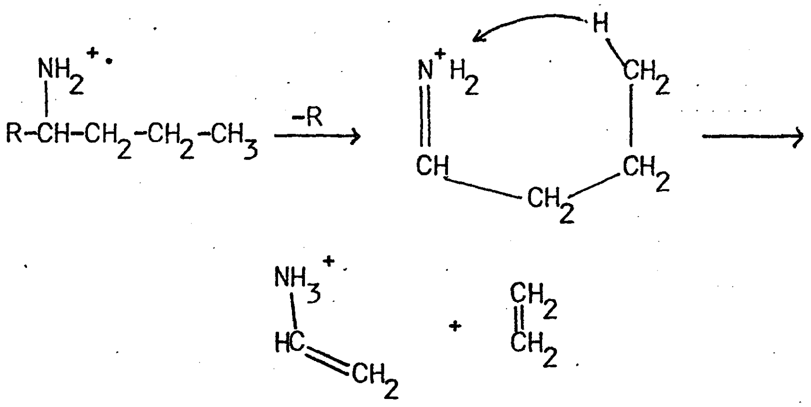
The positively charged enolic form of ion indicated by appearance potential measurement, was evidence to support the above mechanism and the site of migrated γ hydrogen in the molecule (160) which is:



not



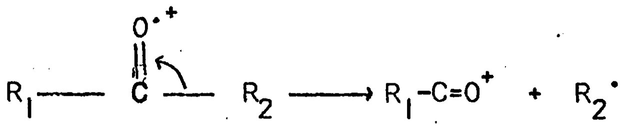
It is notable that the McLafferty rearrangement may occur even though the D-E double bond is not present in the original molecule. A double bond can be generated by "oxonium" ion formation from the simple cleavage. The following example shows the process in an amine in which R is large (161):



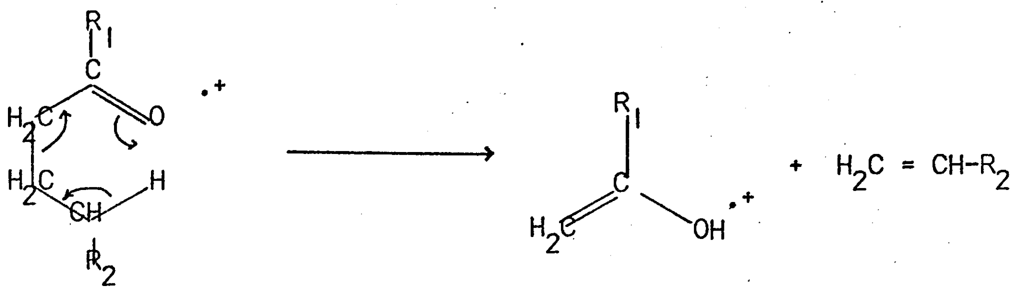
The widespread occurrence of McLafferty rearrangement has been investigated by many workers; detail of this survey is as follows:

1. KETONES

The rearrangement occurring in the aliphatic ketones possessing a chain of three or more carbon atoms attached to the carbonyl group was studied by McLafferty (162). The cleavage of bonds alpha to the carbonyl group has been observed in their spectra.



He proposed that a six-membered cyclic transition state is formed.

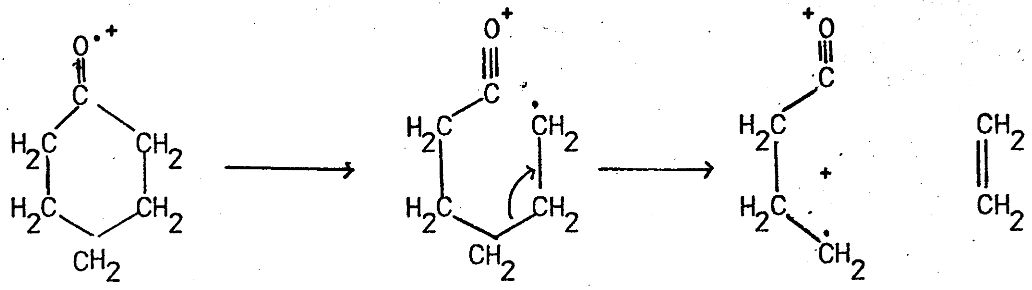


Carpenter et al. (163) obtained the mass spectra of 1,1,1,7,7,7, hexafluoroheptane-4-one, and demonstrated that the corresponding transfer of an fluorine atom does not occur. They also examined some isotopically labelled aliphatic ketones at low voltage (10 eV) and showed that deuterium scrambling occurs among the carbon atoms of aliphatic chains.

Kulkarni et al. (164) observed the McLafferty rearrangement in some polyalkylcyclohexanones. They substantiated the fragmentation pattern by deuterium labelling, exact mass measurement and the study of metastable ions.

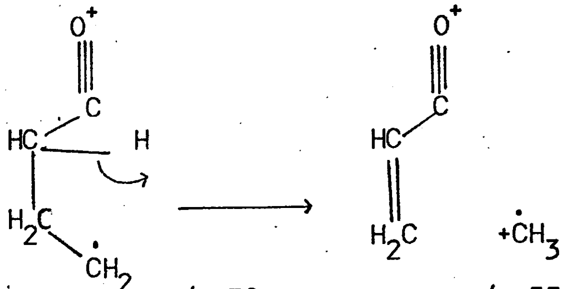
In 1970 Bursey et al. (165) compared photochemical reactivity with McLafferty rearrangement which occurs in butyrophenone, 1-phenyl-2-pentanone, 1-phenyl-3-hexanone, 4-phenyl-4-methyl-2-pentanone, 2-butyro-naphthone and 2-butyryl-anthracene.

Williams et al. (166) investigated the rearrangement process for some monocyclic ketones. The following stages obtained for cyclopentanone.



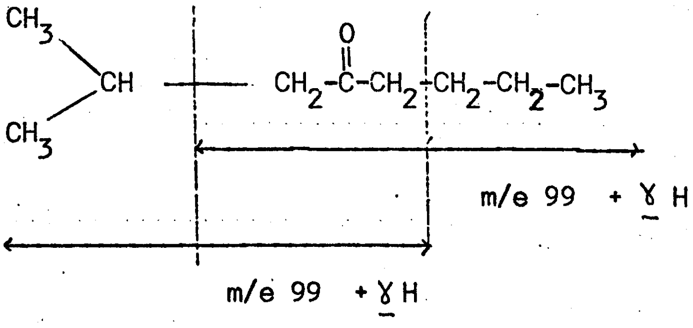
m/e 70

and then by loss of $^{\bullet}CH_3$

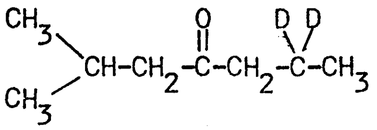


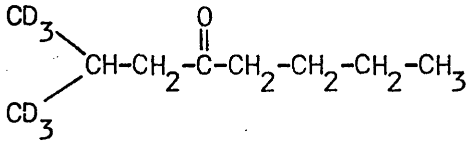
m/e 70 m/e 55

J. K. McLeod and C. Djerassi (167) studied the competition between functional groups in the same molecule, by electron impact, and indicated that the rearrangement takes place preferentially to the carbonyl moiety in the phenylalkylmethyl ketones and the keto esters, but that the dominant fragmentation process in some of the compounds is a 1,6 elimination. The occurrence of a McLafferty rearrangement in n-butyl iso-butyl ketone induced a positive ion at m/e 100 - scheme (a)



In this case, deuterium labelling on the γ hydrogen positions (primary and secondary) showed the preference of a secondary hydrogen to a primary one, although two secondary hydrogens are available versus six primary hydrogens, scheme (b) and (c)


(b)


(c)

Deuterium labelling (168) studies of keto steroids have indicated that the rearrangement proceeds only if the interatomic distance between the $\underline{\gamma}$ hydrogen and the receptor oxygen is less than 1.8 A^{o}.

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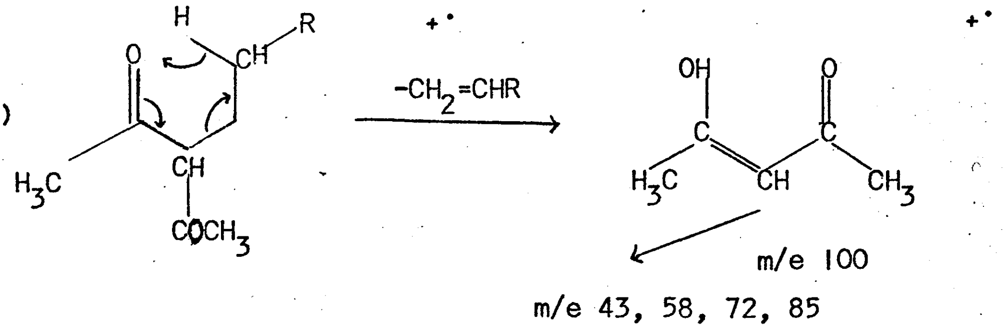
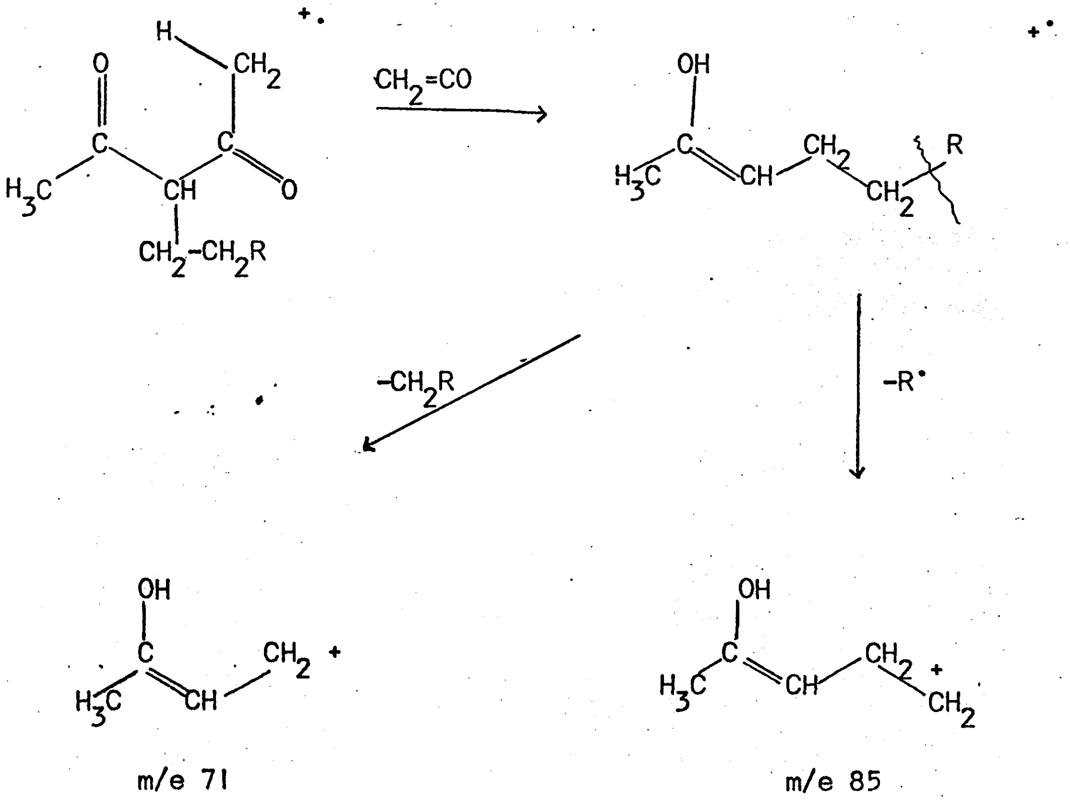
2. DIKETONES

The mass spectra of some diktones have been reported by J. H. Bowie *et al.* 169. The observed results are similar to that of mono ketones. The γ fission process for (c-alkyl-acetylacetones and 3-acetyl-heptan-2-one) is as follows:

a)

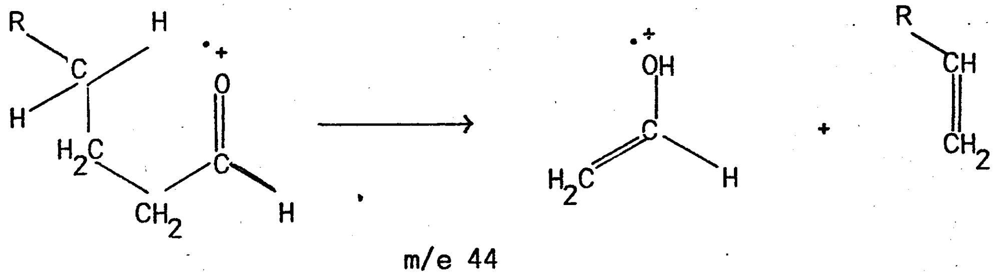


b)



3. ALDEHYDES

J. A. Gilpin and F. W. McLafferty (170) reported the mass spectra of twenty aliphatic straight chain and branched aldehydes. They used oxygen-18 to show the fragmentation pathway. The β bond cleavage accompanied by a γ hydrogen transfer was reported for butanal and higher aldehydes unbranched on the α carbon atom.



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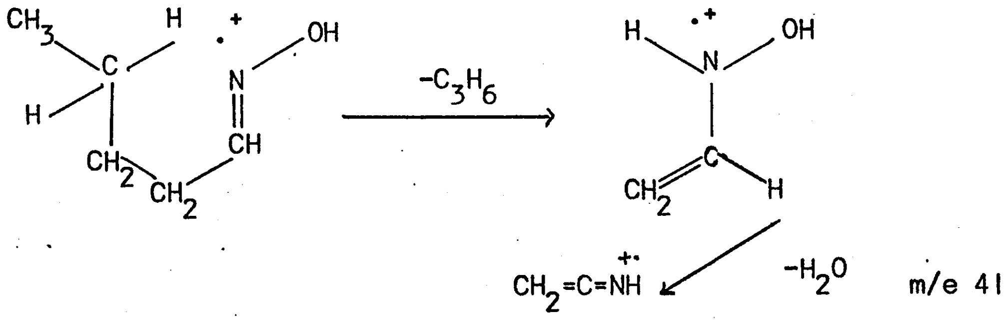
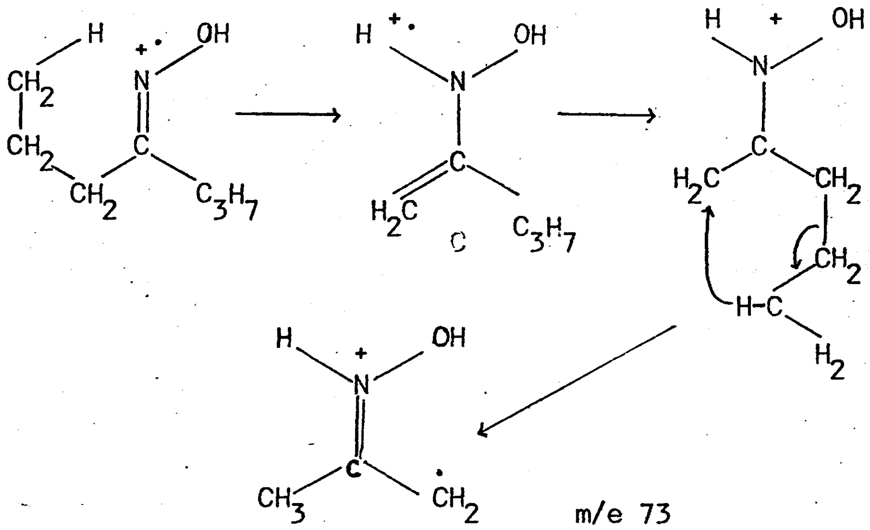
4. ALIPHATIC ALDOXIMES AND KETOXIMES

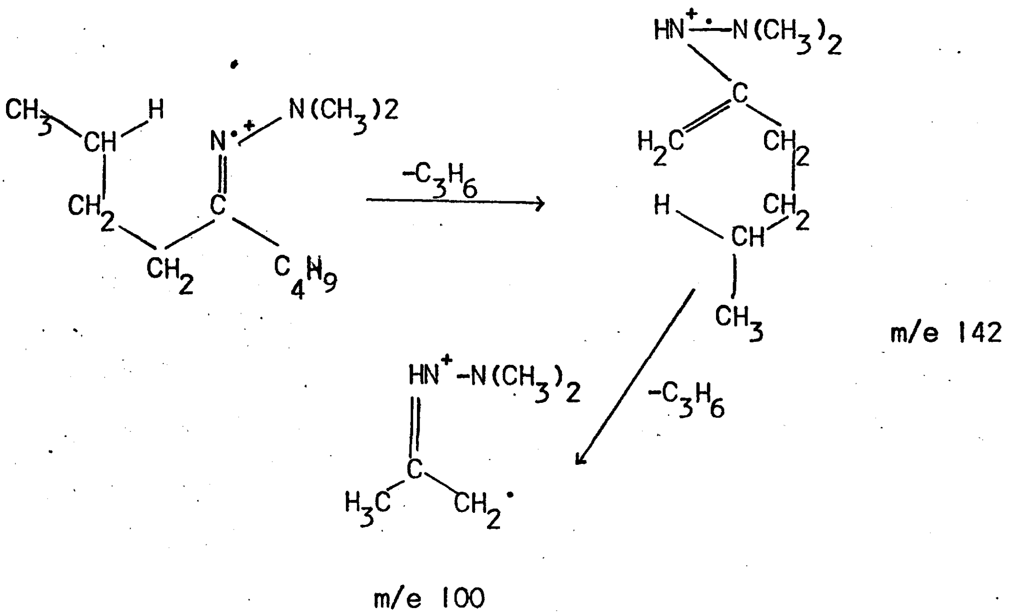
The mass spectra of butyraldehyde and valeraldehyde oximes show the base peak at m/e=59 which is due to a McLafferty rearrangement.



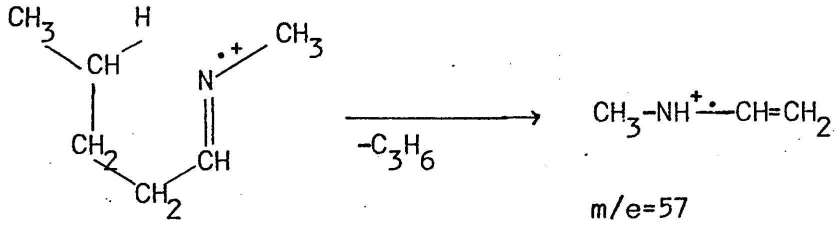
Accurate mass measurement confirmed that the ion at m/e=41 arises from the product of McLafferty rearrangement by loss of water. It involves a double rearrangement and should not be confused with the hydrocarbon ion ($C_3H_5^+$) (171). The main characteristics of single and double McLafferty rearrangements in oximes have been proved by deuterium labelling in the case of di-n-propylketoxime. The mechanism is as follows:



Another compound (172) in the same class is n-dibutyl ketone n,n-dimethylhydrazone; the mass spectrum shows both single and double McLafferty rearrangements.



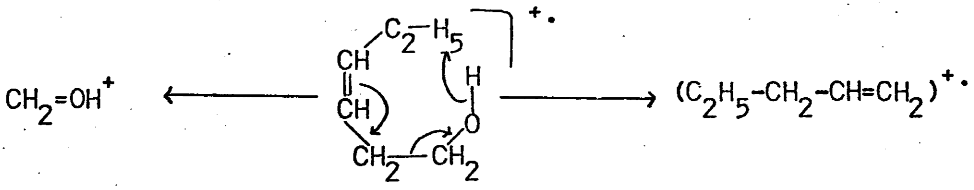
The mass spectrum of valeraldehyde oxime shows the occurrence of a McLafferty rearrangement. The preferential migration of a secondary hydrogen atom as compared with a primary one was demonstrated.



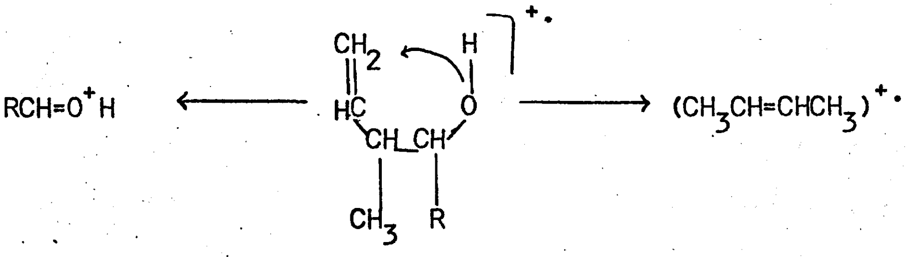
5. <u>ALCOHOLS</u>

Unsaturated aliphatic alcohols (173) (a.b) and their branched analogues show only two important abundant peaks, one due to $\underline{\alpha}$ cleavage and the other concerns McLafferty rearrangement.

(a)

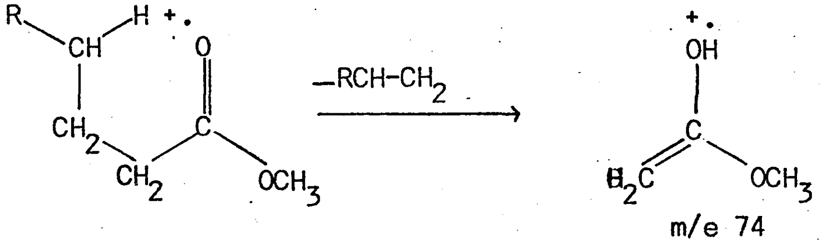


(b)

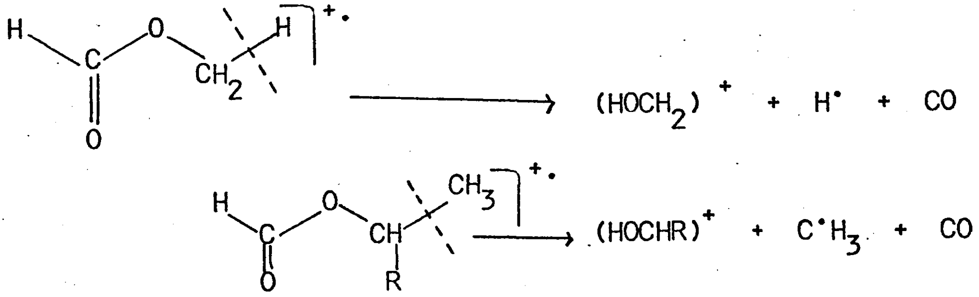


6. ESTERS

The fragmentation of the straight chains of methyl esters (174) in the C_6-C_{26} range give an abundant peak which arises from β - cleavage accompanied by a γ hydrogen atom transfer. It confirms the occurrence of the McLafferty rearrangement in the mass spectra of this type of esters.



The spectra of methyl and ethyl formate show the following fragments and characteristics

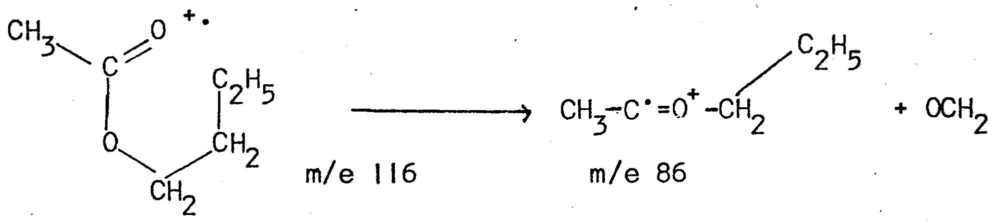


where: R=H in ethyl formate

The mass spectrum of butyl acetate shows an abundant peak at mass 61, corresponding to $(RCOO+2H)^+$, which confirms the molecular weight in conjunction with the $(R'-H)^{+\cdot}$ ion. The rearrangement of two hydrogen atoms of this type frequently occurs in the spectra of esters.

Djerassi and (Mrs.) Fenselau (175) studied the spectra of n-butyl propionate and its deuterated analogues. They noted that the source of hydrogen atoms in these rearrangement processes is not always the same; it could originate from every possible carbon atom, but those attached to the *β* and *γ* carbons provided the largest supply.

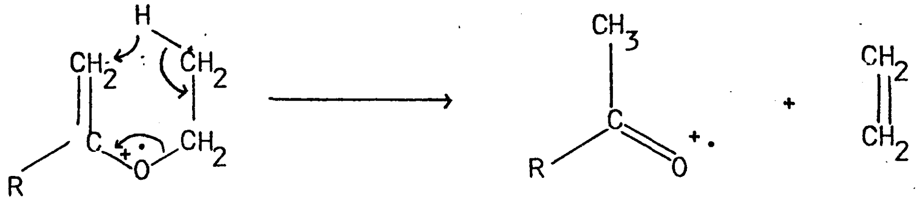
Black and his co-workers (176) reported the loss of CH_2O from *n*-butylacetate is another type of fragmentation process.



McFadden and his co-workers (177) studied the spectra of butylacetates, propanoates and hexanoates. They showed the specific rearrangement by using deuterated compounds.

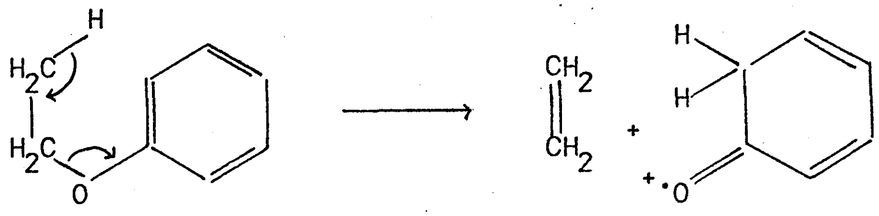
7. ETHERS

The mass spectra of vinyl derivatives was studied by McLafferty (178). A *β* fission process accompanied by a *γ* hydrogen transfer occurred. The following degradation process is postulated.

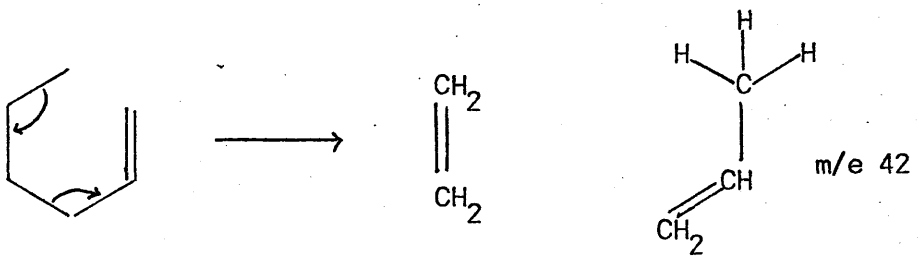


where R represents a hydrogen atom or an alkyl group. When R=H, the ion $(O\text{-}CH{=}CH_2)^+$, formed by simple cleavage generally produces a peak larger than that of the above rearrangement ion.

He also observed the rearrangement in the spectra of some aromatic ethers.

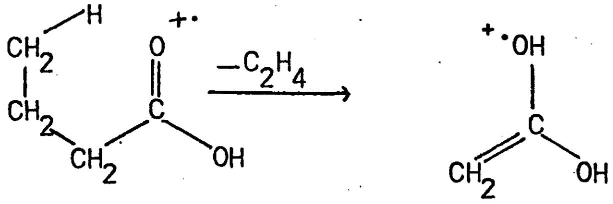


The same mechanism was suggested for vinyl compounds, containing carbon and hydrogen. I-Pentene gives a peak which rises at m/e=42.

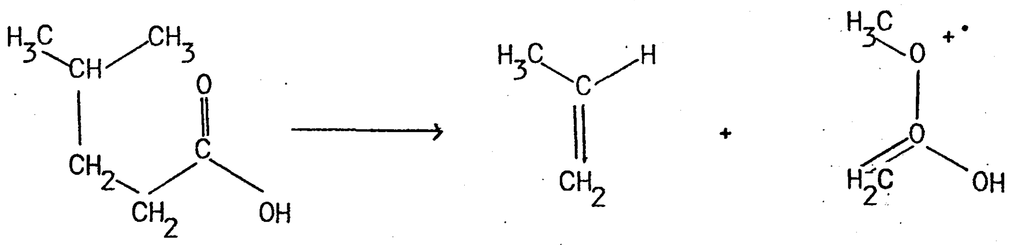


8. ACIDS

Happ and Stewart (179) studied the mass spectra of the lower aliphatic acids (formic to valeric). The base peak at m/e=60 occurs only for butyric and valeric acids in which a hydrogen atom is available for transfer. A McLafferty rearrangement is thought to occur as follows:



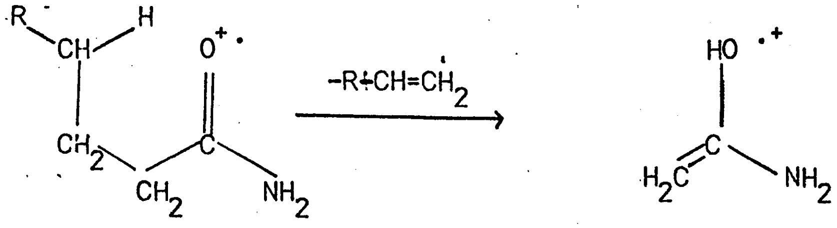
N. C. Rol (180) observed the rearrangement process in the mass spectra of carboxylic acids. He suggested that McLafferty rearrangement should be extended or modified to include the possibility of γ methyl group migration to the functional group with simultaneous cleavage of the beta C-C bond in 4-methylpentanoic acid.



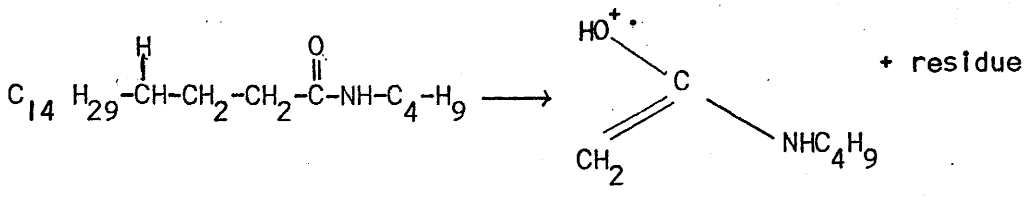
He also found evidence for transfer of a δ hydrogen (instead of γ atom) to the β position along with a cleavage of the γ C-C bond.

9. AMIDES

The mass spectra of thirty five aliphatic primary, secondary and tertiary amides have been reported by Gilpin (181). In *n*-butyramide the β cleavage process accompanied by a γ hydrogen transfer to the carbonyl group was observed.



He also obtained the rearrangement process in only one secondary amide with a γ hydrogen atom available in the alky! chain attached to the carbonyl group. The spectra of n-butyloctadecaneamide showed the McLafferty rearrangement as reported for primary amides.

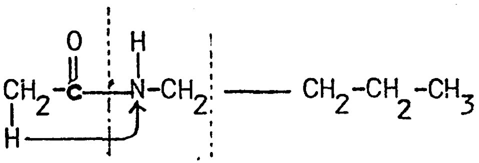


m/e 115

An interesting comparison between normal butyric acid and normal butyramide shows a typical rearrangement which is common in many compounds containing a carbonyl group.

Pelah and his colleagues (182), studied the mass spectra of a number of secondary and tertiary amides. They employed some deuterated compounds to establish the route of formation of mass thirty in n-butyramide.

In fact they proved the pathway of the rearrangement. They obtained a mass of thirty one in n-butyl-d_3 acetamide spectrum, and the following route was postulated.

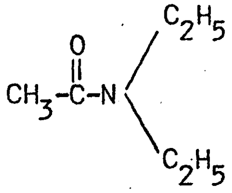


$CH_2{=}C{=}O + NH^+_2 = CH_2 + {}^{\bullet}C_3H_7$

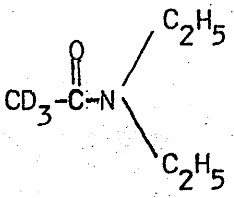
Ketene m/e 30 propyl

In the case of tertiary amides they reported the mass spectrum of n,n-diethylacetamide, and deuterated analogues as indicated.

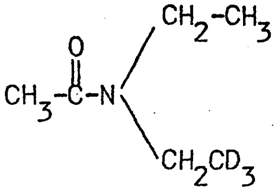
a)



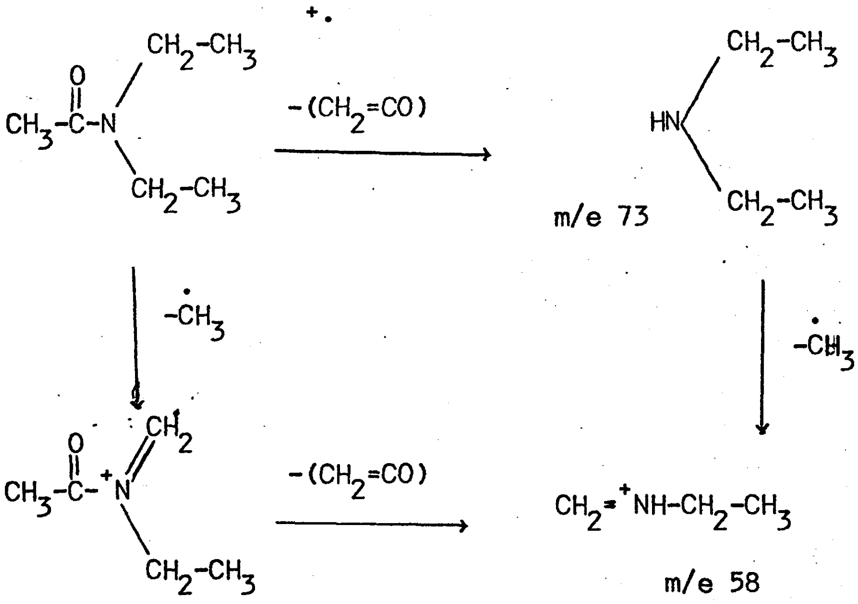
b)



c)



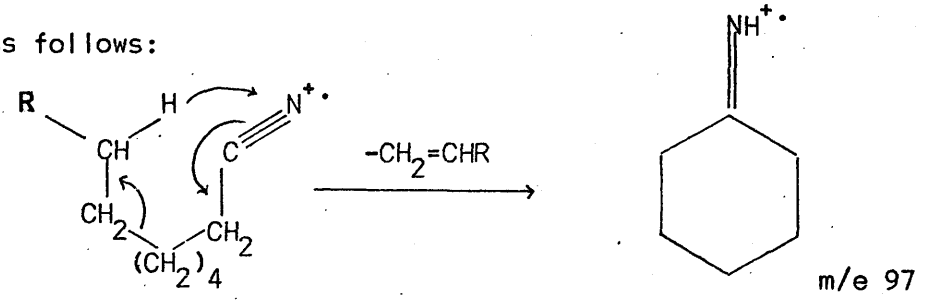
In compound (b) they obtained a base peak at mass (59) instead of (58) in the undeuterated molecule, confirming that the pathway of decomposition is similar to that in the secondary amides. The mechanism involves the loss of $\dot{C}H_3$ from one of the ethyl groups and the loss of a ketene molecule as follows:



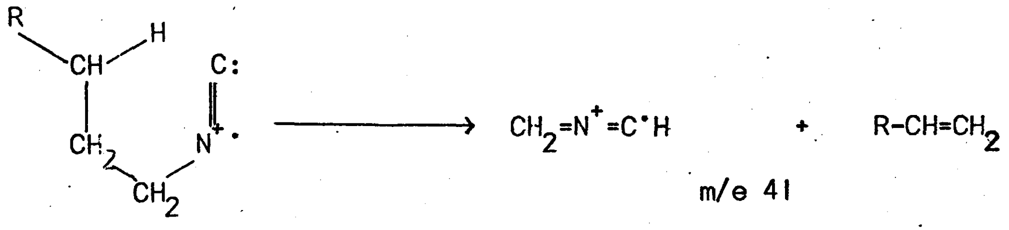
Both routes to the formation of the mass 58 have been confirmed by the presence of a metastable ion.

10. NITRILES

McLafferty (183) studied the mass spectra of eighteen aliphatic nitriles. The cleavage mechanism, in the case of octyl cyanide is as follows:



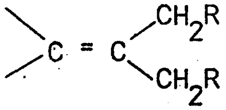
The peak at m/e=97 indicated a six-membered intermediate transition state which is half as intense as the base peak. In one respect the behaviour of isocyanides and cyanides is similar mainly in the formation of m/e=41 ions in the mass spectra of both groups. A β Cleavage accompanied by a γ hydrogen transfer in a six-membered ring transition state seems reasonable.



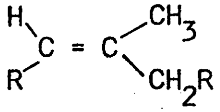
11. OLEFINES

Kraft and Spiteller (184) have discussed the McLafferty rearrangement for some olefines with an alkyl group substituted at the double bond and claimed the occurrence of McLafferty rearrangement for the following compounds (except 7).

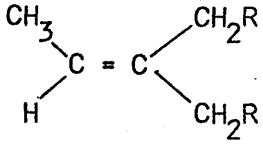
(1)



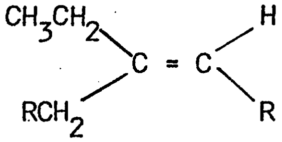
(2)



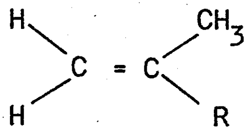
(3)



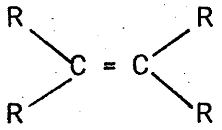
(4)



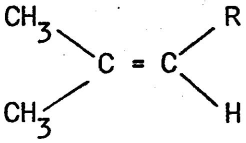
(5)



(6)



(7)



- - o - -

12. ALKYL SULPHITES

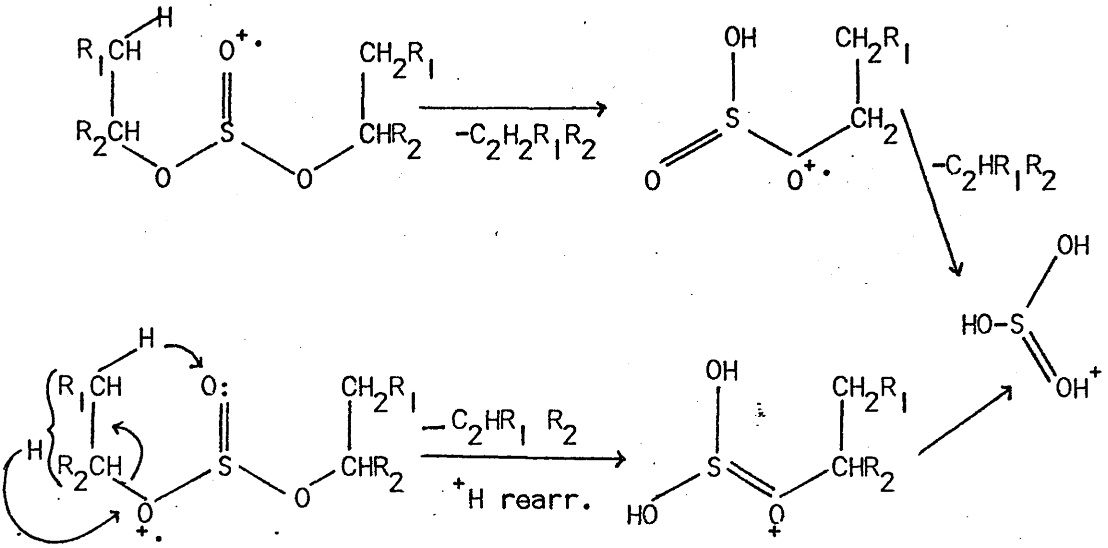
Gamble *et al.* studied a series of dialkyl sulphites and observed three main fragmentation pathways:

(a) the loss of alkyl radical,

(b) S-O bond cleavage to lose an alkoxy group and

(c) a McLafferty rearrangement.

The mechanism of the third one has been shown as follows:

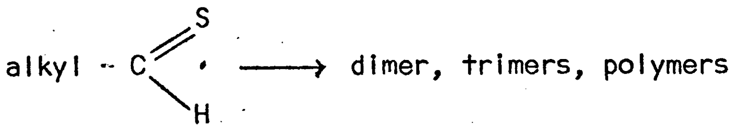


The indicated paths were established by employing labelled molecules.

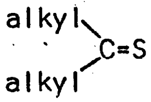
PART THREE - THIOAMIDE COMPOUNDS

Synthesis:

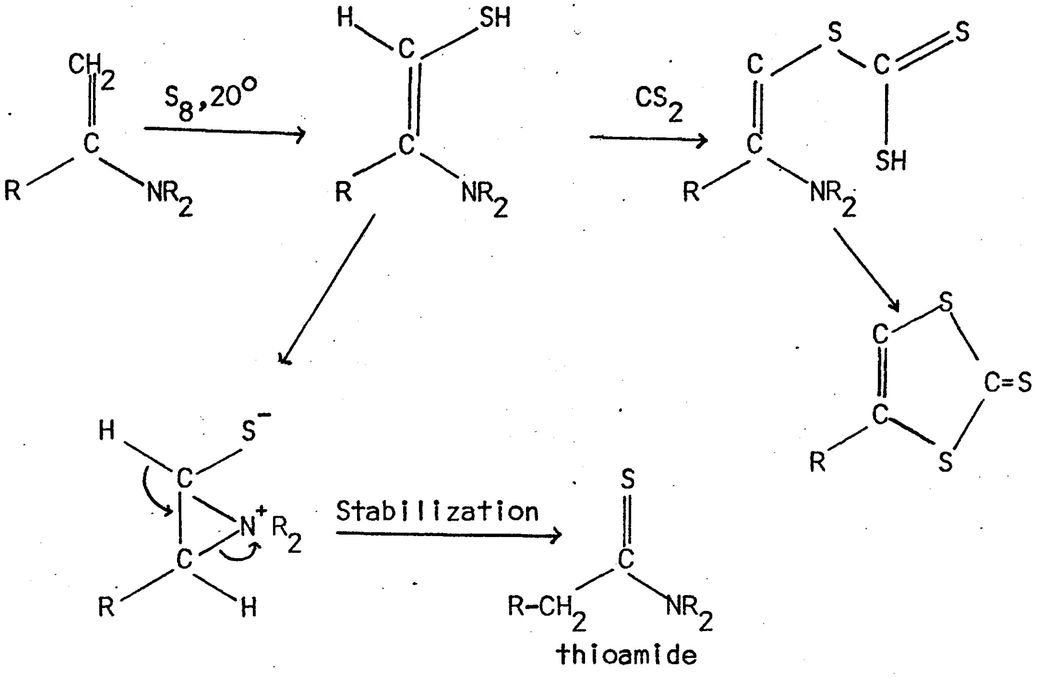
Thiolation of carbonyl compounds has been investigated by R. Mayer and his co-workers (186,187). They reported that the aliphatic compounds are unstable in monomeric form because of their molecular structure.



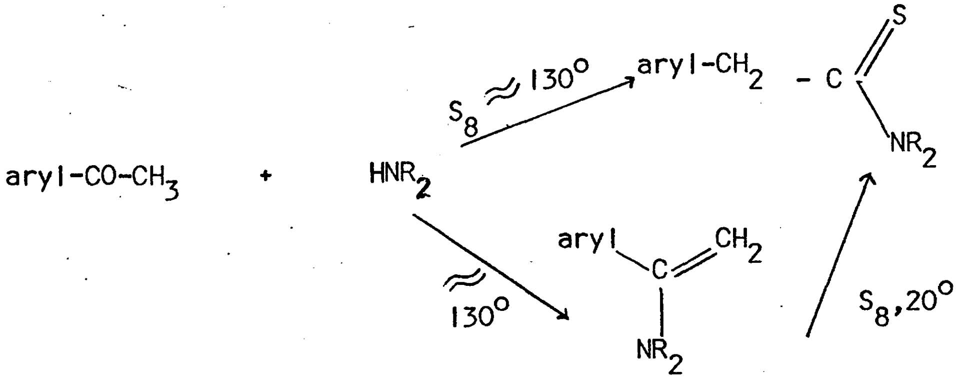
Thioaldehyde: mono unknown



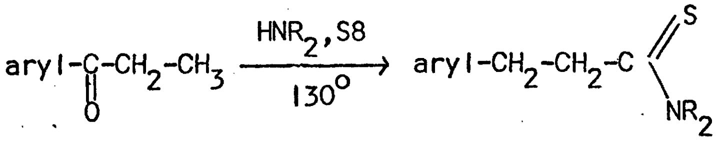
(thio ketones) are relatively stable in the monomeric form. Mayer (188) reported that, the formation of thioamide takes place while sulphur reacts with enamine in the following way:



Furthermore, the conversion of aryl ketone with a secondary amine is effected by the Willgerodt - Kindler reaction.



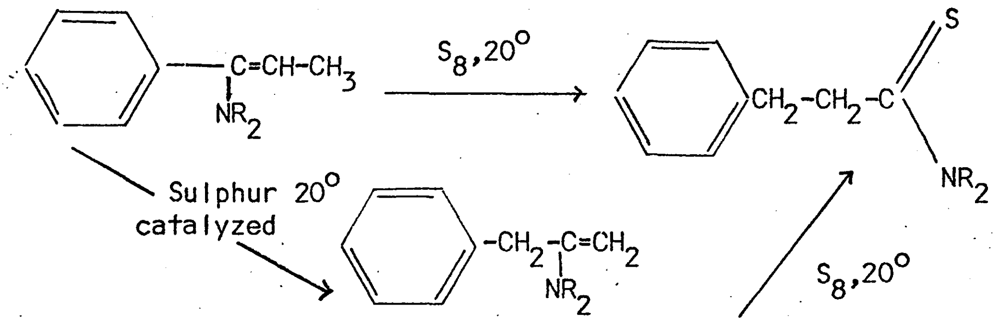
Aryl ketones with longer aliphatic chains in Willgerodt-Kindler reaction can also be converted to a thioamide.



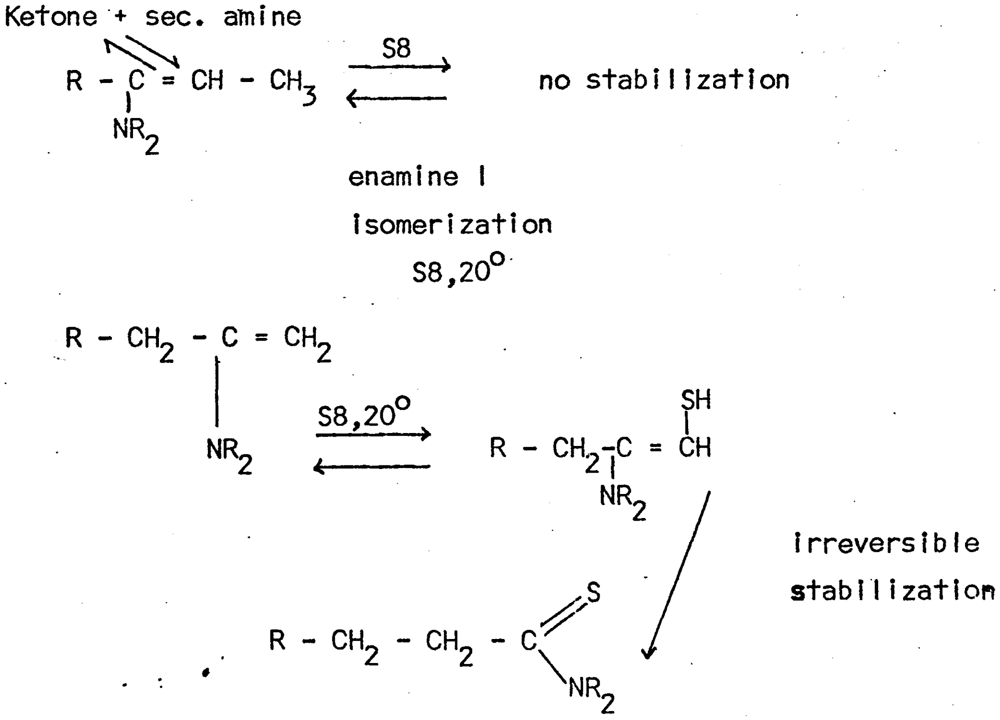
$$\text{aryl-}\underset{\underset{\text{O}}{\|}}{\text{C}}\text{-CH}_2\text{-CH}_3 \xrightarrow[130^{\circ}]{\text{HNR}_2,\text{S8}} \text{aryl-CH}_2\text{-CH}_2\text{-C}(=\text{S})\text{NR}_2$$

The mechanism of this equation has been investigated by many teams (189-196), specially F. Asinger (197,198) and his co-workers.

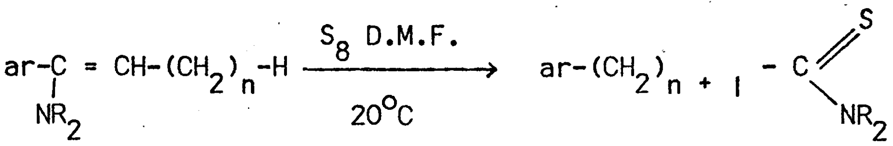
The final is that the enamine reacts with sulphur and gives thioamide.



The main steps of the Willgerodt reaction is as follows:



Asinger and co-workers have established the fact that the enamine is formed first from the ketone and secondary amine, the temperature for this formation is above 100°C. They found that, the enamines formed in the reaction of methyl ketones and secondary amine, react with sulphur to form thioamide. The enamine with longer chain gives much lower yields and enamines of iso-butyrophenone and iso-valerophenone do not give thioamides at room temperature. The enamine of the following type give thioamides by reaction with sulphur at room temperature.



$$\mathrm{ar{-}\underset{\displaystyle NR_2}{C}=CH{-}(CH_2)_n{-}H \xrightarrow[20^{o}C]{S_8\ D.M.F.} ar{-}(CH_2)_{n+1}{-}C{\overset{\displaystyle S}{\diagup\!\!\diagup}}\!\!\diagdown NR_2}$$

n = 1 or 2

The migration of the carbonyl group of aryl ketones to the end of the chain in the Willgerodt - Kindler reaction as an isomerization has been interpreted by R. Mayer (187)

- - o - -

PREPARATION OF COMPOUNDS

(1) Preparation of amides

The morpholino-1-butyro amide was prepared from the corresponding ketone and secondary amine (morpholine) by the standard method (199).

(2) Preparation of thioamide:

The procedure is a modification of the methods of R. Mayer (200) et al. and Ludwig Maier (201). A 250ml round bottom flask was fitted with a cold finger reflux condenser with attached drying tube containing anhydrous potassium carbonate. The reaction was carried out by refluxing a solution of 10.8g methyl ethyl keton, 4.8g of sulphur in

26.1g of morpholine for 96 hours. (Addition of 0.5g p-toluensulphonic acid as a catalyst gives a higher yield.) The crude product was distilled and the fraction of 165°-175°C (a mobile yellow brown liquid) was collected and mixed with 25ml of methanol. The crystalline form was obtained by cooling the product in a mixture of dry ice and acetone; recrystallization gave an analytical sample; removal of the methanol was carried out under reduced pressure. The purity of all compounds was checked by gas chromatography and elemental analysis.

The mass spectra of the four compounds were obtained upon an A.E.I. MS 902S double focusing mass spectrometer at 70 eV and a trap current of 500 μ A through a direct inlet system (probe) at 120°C.

Attempts were made to replace sulphur by firstly selenium and by tellurium; both these attempts however, proved unsuccessful.

The empirical formula was identified and the molecular weights of these compounds were accurately mass-measured and the following result was obtained. (Table I)

TABLE No. I

Compound	Molecular Formula	accurate masses
A Morpholino-I-butyroamide	$C_8H_{15}O_2N$	obs. 157·11013 calc. 157·110272
B Morpholino-I-butyrothioamide	$C_8H_{15}NOS$	obs. 173·087428 calc. 173·087438

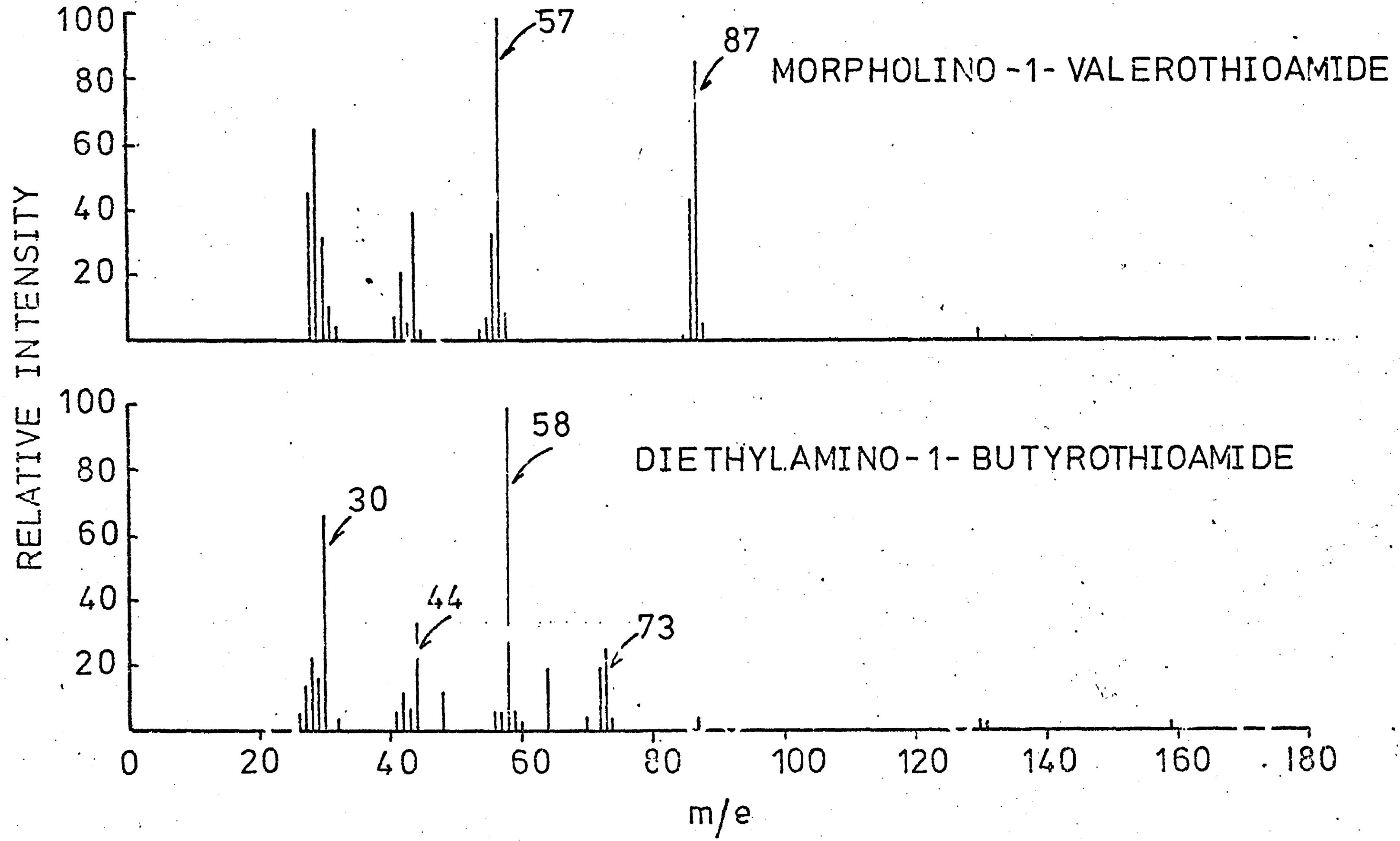
TABLE No. 1(cont)

Compound	Molecular formula	accurate masses
C Morpholino-1-valerothioamide	$C_9H_{17}NOS$	obs. 187·10298 calc. 187·10308
D Diethyl amino-1-butyrothioamide	$C_8H_{17}NS$	obs. 159·108168 calc. 159·108165

PART FOUR - DISCUSSION OF THE MASS SPECTRA

Previous studies of the mass spectra of organosulphur compounds have been concerned mainly with dithiocarboxylic acid esters (203) (S-alkyl thioesters $R-\overset{\overset{O}{\|}}{C}-SR$, alkylthioesters $R-\overset{\overset{S}{\|}}{C}-OR'$ and dithioesters $R-\overset{\overset{S}{\|}}{C}-SR'$) dialkyl sulphites (185), dimethyl thioncarbamates ($ArO-\overset{\overset{S}{\|}}{C}-OAr$) (204) and substituted thioureas (205). In two cases (203,185) the occurrence of McLafferty rearrangement has been reported as a major fragment and an intermediate process.

The present investigation reports the mass spectra of an amide and some thioamides which are presented in Table (2) and figures 1 and 2.


MORPHOLINO-1-VALEROTHIOAMIDE
DIETHYLAMINO-1-BUTYROTHIOAMIDE
RELATIVE INTENSITY
100
80
60
40
20
57
87
100
80
60
40
20
30
44
58
73
0
20
40
60
80
100
120
140
160
180
m/e

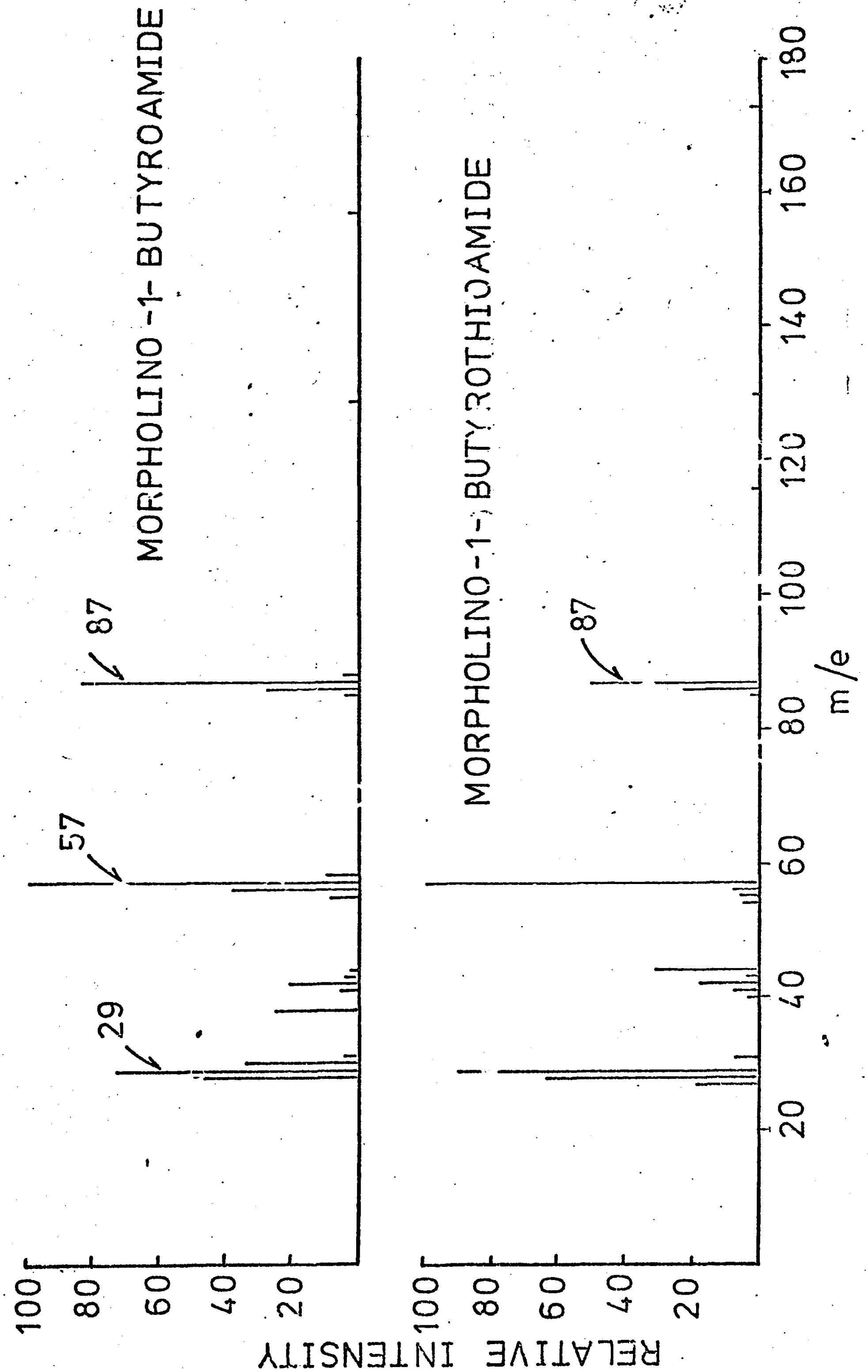

MORPHOLINO-1- BUTYROAMIDE
MORPHOLINO-1-, BUTYROTHIOAMIDE
29
57
87
87
RELATIVE INTENSITY
100
80
60
40
20
100
80
60
40
20
m/e
20
40
60
80
100
120
140
160
180

TABLE No. 2

COMPOUND

m/e	Morpholino-1-butyroamide relative abundance %	Morpholino-1-butyro-thioamide relative abundance %	Morpholino-1-valero-thioamide relative abundance %	Diethyl amino-1-butyro thioamide relative abundance %
27	13.55	19.50	14.25	13.90
28	44.45	63.30	47.22	21.50
29	72.00	90.00	66.60	16.25
30	35.60	45.00	32.20	66.70
31	4.50	8.20	9.45	-
32	-	5.60	4.30	3.60
34	-	1.20	1.40	2.10
37	5.45	-	-	-
38	8.65	-	-	-
40	-	2.85	3.70	6.45
41	5.40	7.45	6.70	8.20
42	21.35	18.30	20.75	11.30
43	4.90	4.15	5.90	4.60
44	-	32.60	39.20	33.50
45	3.55	4.10	2.80	-
48	-	6.65	2.80	10.20
55	4.90	5.30	7.20	-
56	31.10	8.20	35.30	5.45
57	100.00	100.00	100.00	4.20
58	6.25	8.50	7.70	100.00
59	-	-	-	4.40
60	-	-	-	2.50
64	-	2.80	3.20	3.60
70	-	0.50	0.65	2.75

TABLE No. 2 (cont)

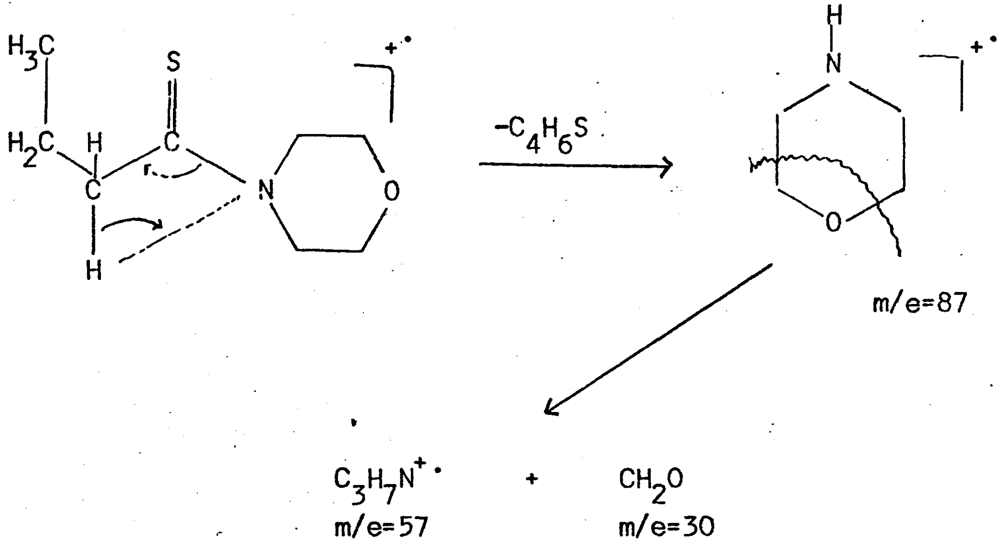
m/e	A	B	C	D
72	-	0.70	0.75	19.65
73	-	-	-	27.50
74	-	-	-	2.80
85	1.50	0.90	2.50	-
86	28.45	24.50	44.50	-
87	79.65	51.00	85.40	-
88	2.3	2.8	4.35	2.25
115	-	0.50	0.80	-
129	-	3.5	3.7	5.4
130	-	-	--	1.70
131	-	-	-	1.75
157	3.50	-	-	-
159	-	-	-	2.20
173	-	2.6	-	-
183	-	-	0.70	-
187	-	-	0.20	-

TABLE No. 3

Ion	m/e	Accurate Masses
C_4H_9ON	87	Obs. 87.068069 calc. 87.068410
C_4H_8ON	86	obs. 86.059881 calc. 86.060385
C_4H_7ON	85	obs. 85.052827 calc. 85.052761
$C_4H_{10}N$	72	obs. 72.081082 calc. 72.081320

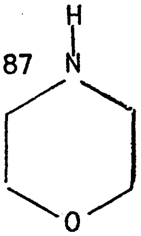
It appears that the main route of the breakdown is: molecule ⟶ molecular ion ⟶ alkyl or morpholine ion. No confirmatory metastable peaks could be detected (fig. 3).

(3)



RESULTS OF MASS MEASUREMENT

m/e=87



obs.	87.068069
calc.	87.068410

m/e=57

C_3H_7N

obs.	57.057108
calc.	57.057846

Metastable transition

$87^{+\cdot} \longrightarrow 57^{+}$

m.s. obs.	37.40
calc.	37.34

THE McLAFFERTY REARRANGEMENT

In every case the occurrence of C-N bond cleavage, accompanied by a hydrogen migration to the amine part, was observed. A four-membered ring transition state can be assumed as a probable mechanism. Accurate mass measurement at m/e=87 ion supports the route of the above fragmentation.

The base peak at m/e=57 is common to the spectra of A, B and C, which arises from separated morpholine ring by loss of CH_2O. There is a well defined metastable ion at m/e=37.34 corresponding to the transition state of $87^+ \longrightarrow 57^{+\cdot}$. Accurate mass measurement gives evidence to prove the pathway (fig.3).

Decomposition of base peak (C_3H_7N) in the first three spectra is a likely route to form two significant ions at m/e=28 and m/e=29. This is supported by the appearance of two intense metastable ions at m/e=13.76 and m/e=14.75 respectively. However, the results of mass measurement is a little evidence to this mechanism. (fig. 4).

$$C_3H_7N \overset{+\cdot}{\longrightarrow} CH_2N^+ + C_2H_5 \qquad (1) \qquad\qquad (4)$$

$$C_3H_7N \longrightarrow \cdot CH_3N + C_2H_4 \qquad (2)$$

METASTABLE TRANSITION

	M_1		M_2			
1)	57^+	$\longrightarrow$	28^+	m.s.	obs.	13.75
					calc.	13.75
2)	57^+	$\longrightarrow$	29^+		obs.	14.75
					calc.	14.75

RESULTS OF MASS MEASUREMENT

m/e = 28

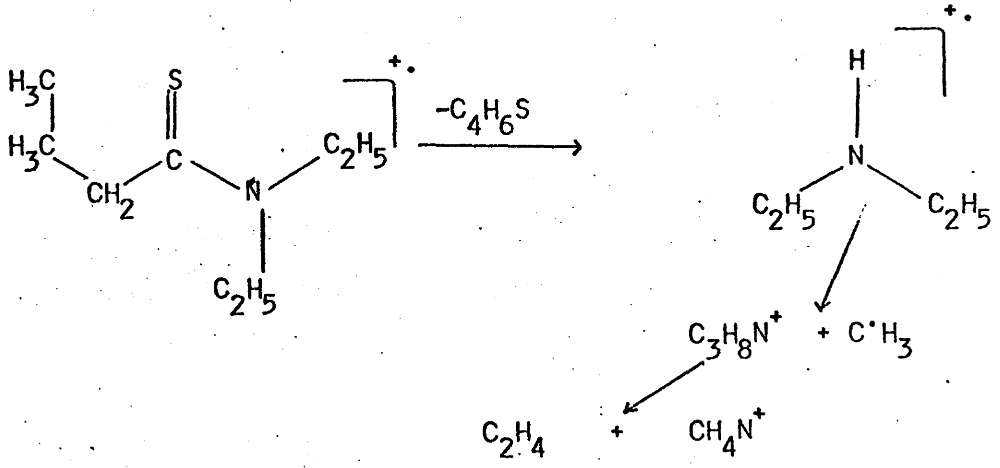
1)	large peak	obs.	28.01874
	CH_2N	calc.	28.018723
2)	small peak	obs.	28.03131
	C_2H_4	calc.	28.031298

m/e = 29

1)	large peak	obs.	29.02665
	CH_3N	calc.	29.026547
2)	small peak	obs.	29.039173
	C_2H_5	calc.	29.039123

Finally, a similar fragmentation for diethylamino-1-butyrothioamide was observed (fig.5).

(5)



1) $73^+ \longrightarrow 58^+ + 15$ m.s. obs. 46.15, calc. 46.08

2) $58^+ \longrightarrow 30^+$

metastable transition m.s. obs. 15.52, calc. 15.51

RESULTS OF MASS MEASUREMENT

m/e = 73	obs. 73.08905
$C_4H_{11}N$	calc. 73.089145
m/e = 58	obs. 58.065483
C_3H_8N	calc. 58.065671
m/e = 30	obs. 30.034323
cH_4N	calc. 30.034371

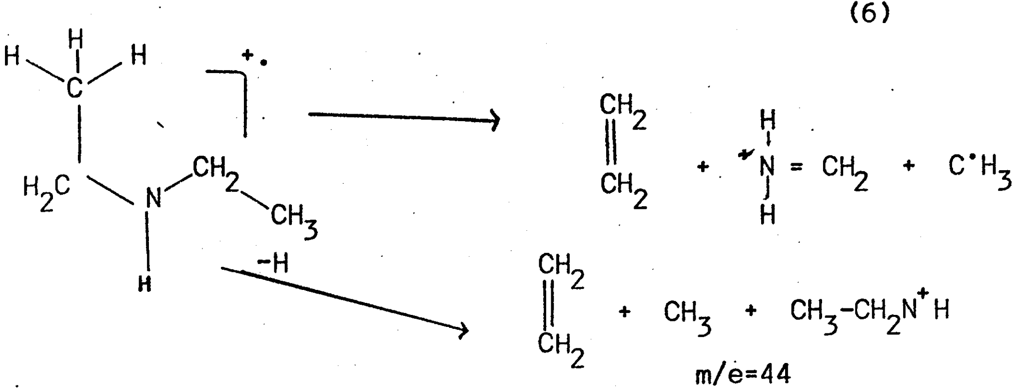
LOSS OF HYDROGEN

The peak of high intensity at m/e=86 corresponds to the loss of a hydrogen from separated morpholine; further process induces a peak of low abundance at m/e=85.

A similar fragment at m/e=72 for diethyl amino-i-butyro-thioamide was obtained (fig.6). An interesting dissociation with loss of ten hydrogen atoms from molecular ion at higher temperature (206) (150°) for two compounds (B and C) has been observed. The same process had been reported previously for piperidine (207).

All these ions were accurately mass-measured, and the result is illustrated in table 3 and figures 3-9.

(6)



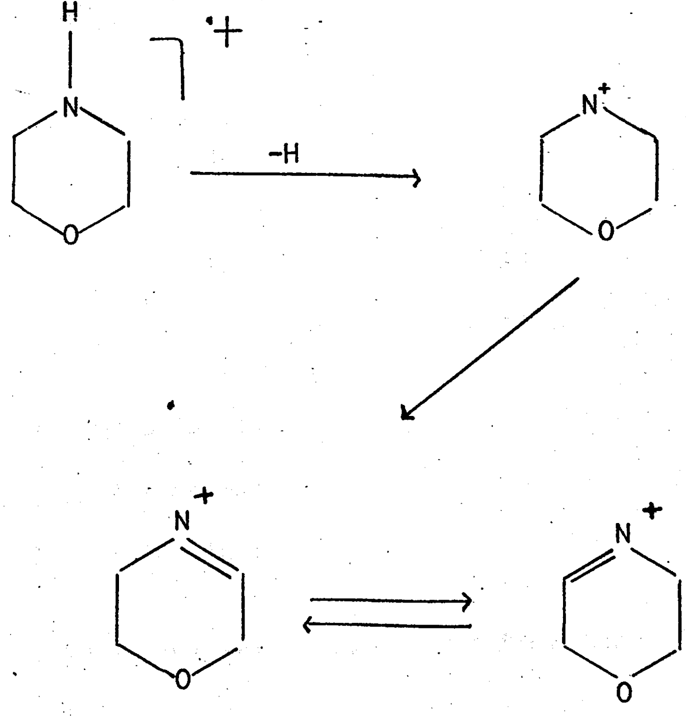
$72^+ \longrightarrow 44^+ + 28$

metastable ion

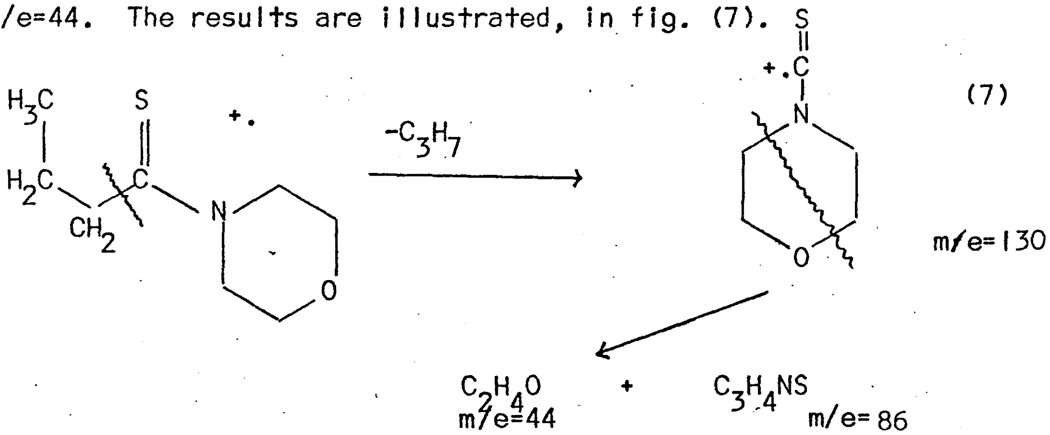
	obs.	26.93
	calc.	26.89

result of mass measurement at m/e = 44

C_2H_6N	obs.	44.05090
	calc.	44.05002

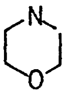


High resolution technique shows that the peak at m/e=86 comprises two ions; the larger one is due to the cleavage of the C-N< bond followed by elimination of a hydrogen atom, and the second one presumably arises from the expulsion of $C_3H_7^{\bullet}$ from the molecular ion, followed by decomposition of the ring and formation of ethylene oxide at m/e=44. The results are illustrated, in fig. (7).



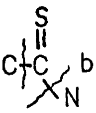
(7)

RESULTS OF MASS MEASUREMENT AT m/e 86

No 1		Obs.	86.059881
		Calc.	86.060385
No 2	C_3H_4NS	Obs.	86.005938
		Calc.	86.006445

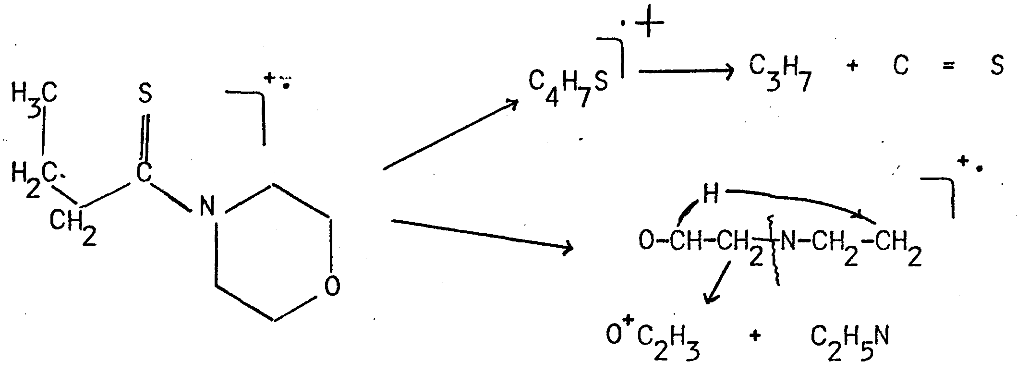
The peak at m/e=43 comprises three ions, the largest one is due to $C_2H_3O^+$, the medium feature corresponding to $C_2H_5N^+$ and the third one is related to the $C_3H_7^+$ ion.

The possibility of this fragment can be assumed in the rupture of



bonds at once followed by decomposition of the separated morpholine ring (fig.8).

(8)



RESULTS OF MASS MEASUREMENT AT m/e=43

43

	C_2H_3O	C_2H_5N	C_3H_7
obs.	43.018774	43.042735	43.05693
calc.	43.018387	43.042197	43.05477

The use of high resolution method shows two significant ions at m/e=32 in the three sulphur compounds. The larger one arises from the expulsion of sulphur and the other one is due to the presence of an oxygen molecule; these ions were accurately mass-measured (fig.9).

ACCURATE MASSES AT m/e=32 (9)

^{32}S	obs.	31.971998
	calc.	31.9720727
$^{16}O_2$	obs.	31.989667
	calc.	31.989828

- o O o -

CHAPTER (4)

IDENTIFICATION OF ORGANIC COMPOUNDS

I. USE OF HIGH RESOLUTION MASS SPECTROMETRY

Elucidation of the structure of various types of organic compounds relies on an interpretation of their high resolution mass spectra and a certain elemental composition of the ions under investigation (208).

Composition of the molecular ion gives a piece of information about the structure of organic compounds, which is not generally abundant. An adequately high resolving power is required to produce a sufficiently well-defined ion beam for accurate mass measurement, also reveals any multiplicity caused by the presence of more than one ion of the same nominal mass.

The mass measurement itself involves the determination of the precise mass of the important fragments, necessary for interpretation. Each mass measurement requires the measurement of standard mass peak and the unknown by adjusting the ratio of the two accelerating voltage potentials and the signal amplitude to equalize the height of the two peaks.

Attempting to do a number of mass measurement is not only rather tedious, but also lengthy. A constant vapour pressure of the sample must be attained in the source over the entire period. It requires therefore a relatively large sample and is technically difficult with a compound that is either temperature sensitive or has to be introduced directly into the ion source without the intermediate reservoir.

A fluorocarbon is a suitable standard because it produces ions of known mass relatively evenly spaced over the entire mass range up to about mass 1000. Furthermore, the absence of hydrogen, a relatively heavy element, as far as the mass excess over the integral mass is concerned, causes most fluorocarbon ions to be of lowest mass in a given multiple of nominal mass and is thus easily recognized if the unknown is a compound relatively rich in hydrogen. Because of the chemical inertness, thermal stability and high volatility of fluorocarbons, they are easily handled in a mass spectrometer in spite of their high molecular weight. Beynon (209) was the first who used such a compound for his work.

In practice, selecting of two predetermined two-standard ions of higher and lower mass, respectively, than the unknown ion and measuring their relative distances, the mass of the unknown ion could then be computed by interpolation. However, it seems that this process is not very rapid and a tedious work is involved, accompanied by human error, so that the automation of this procedure becomes desirable.

2. COMPUTER MATCHING TECHNIQUE

A computer can be used in a wide variety of applications involved in the various steps of data processing. Large numbers of authentic spectra can be tabulated, examined and indexed by computer, as well as stored in a computer-accessible form. In many cases the use of computer may give a greater knowledge of fragmentation. Hamming and Eisenbraun (210) illustrated the assemblage of a large volume of data associated with an exercise in correlation studies, in searching for characteristic fragmentation of organic compounds.

More than thirty five thousand reference spectra are now available in the form of mass to charge values and intensities, stored on magnetic tape or discs. Such large libraries of spectra can then be searched by means of a computer for the "best fit" of an unknown spectrum against the reference spectra. One difficulty (211) which is encountered is that the spectrum of the same compound may vary from one mass spectrometer to another. Reed (212) has reported a different spectra for farnesol obtained on four different instruments.

Several workers have employed a library file for correlation studies Talroze (213) et al. studied nine hundred spectra from the American Petroleum Institute collection to find out the best match for the unknown compound, the intensity ratio of a few pairs of lines were sufficiently different to give a useful identification.

Abrahamsson (214-216) and co-workers have transferred the mass spectra from the American Petroleum Institute, American Standard for Testing and Material, and Dow Chemical Company collection, to magnetic tape to form the basis of a library for matching purposes. They suggested five most intense peaks as a useful key. Smith, Knock and co-workers (217-219) developed four methods of matching and their comparison with different approaches. They presented a general formula for each method and obtained a successful result. Terpene identification was searched for by these methods and similar results gained.

Hites and co-workers (220,221) used the largest or, two largest in each successive fourteen mass units. They have been particularly concerned with the problem of handling data from a Gas Chromatography - Mass Spectrometry combination by a directly coupled computer. The results obtained with Gas Chromatograph-Mass Spectrometer, scans taken continuously every four seconds indicated that such procedures could show up the effects of unresolved Gas Chromatograph peaks and indicate where subtraction technique were useful. It was demonstrated that this method is very effective when applied to Gas Chromatography-Mass Spectrometer analysis of mixture.

Patterson and Ryhage (222) studied three different methods for identification of unknown compounds. In method one when the molecular weight of the unknown was found equal with the library compound, the six most intense are compared. The relative intensities are regarded as equal if they are within ±15%. If four (or six) of these peaks match, the identified compound is printed out. This method was effective only about one quarter of the time for molecular weights above two hundred. Below this mass the system was satisfactory but too many compounds were retrieved. In method two the same approach is followed but, instead of selecting the six most intense peaks for all cases, a change to ten peaks is made for molecular weights above two hundred. A file of data containing two thousand spectra was used and several successful trials of method two were made including Gas Chromatography-Mass Spectrometry analysis of an unknown five-component mixture. In method three the six highest peaks are first examined as in method two and only those spectra with four or more matches are accepted. Then the complete spectra, including all peaks equal to or higher than three per cent of the base peak, are compared. However, for an identity between the unknown and library spectrum sixty per cent of the peak must agree.

In 1970 Grotch (223) studied a statistical examination of matching large groups of mass spectra in library matching search technique. This study derived from the statistics and information theory. The results obtained indicated that low-resolution spectra are specific signatures even when encoded to only one bit. Several tests have been carried out on how well such a programme can identify a substance.

One problem is that the reference standards put into the programme must be free of errors and impurities.

Reed *et al.* (224) studied a matching method to identify an unknown compound by using information theory and finding the minimum divergence between the unknown and reference spectra. However, they reported that when the same compound is run in various mass spectrometers the divergence between the different spectra of the same compound can be greater than between different isomers of the compound on the same instrument.

An Approach to the Problem of Identification

INTRODUCTION

The present study reports a method of correlation based on the eight individual fragments and the position of each peak in the file. The idea is to avoid the customary practice of using the molecular weight in the recognition of the unknown spectra. It was considered that a mass spectrum of an unknown compound should give valuable information about its structure.

Theoretical

The peaks of a mass spectrum may be expressed by a_1, a_2, a_3, ...a_n, and their heights by ha_1, ha_2, ha_3, ...ha_n. The sum of the peak heights is:

$$ha_1 + ha_2 + ha_3 + \ldots\ldots + ha_n \text{ or } \sum_{a_n}^{a_1} h_n$$

If the eight most intense peaks are used, their sums will be $\sum_{a_8}^{a_1} h_m u$ and $\sum_{a_8}^{a_1} h_m f$ for the unknown spectrum and the known spectrum respectively. Therefore their correlation could be derived as follows:

$$\text{Correlation} = \frac{\sum_{a_8}^{a_1} h_m f}{\sum_{a_8}^{a_1} h_m u} \times 100 \qquad (1)$$

When both masses and heights of these eight peaks are exactly matched, the correlation is a hundred, therefore the compounds are identical. In the case of similar compounds, the same process is repeated, but, only the common peaks are treated and the results will be printed.

EXPERIMENTAL

The system included an AEI-MS902 high resolution mass spectrometer combined with a data system. The spectra were scanned by sweeping the magnetic field to cover a selected high-mass to low-mass range. The voltage output of an electron multiplier-amplifier system was digitized by an analogue to digital convertor. The output is linked to an Elliott Data System, which consists of peak voltage profiles, recorded on paper tape , and was processed subsequently. Masses were calculated with reference to a known standard (perfluorokerosene).

Description of the File

A set of high resolution mass spectral data was available (at the University of Strathclyde, Chemistry Dept.) on paper tape. A programme was developed to transfer two thousand spectra to a magnetic tape; subsequently, each spectrum was normalised with respect to the base peak (area and width are combined to give the intensity). The normalised spectrum was stored in descending order of mass to charge ratios (see Appendix).

EIGHT PEAK TAPE

Due to the computertime taken to make the comparison between an unknown and the compounds in the tape, it proved necessary to reorganize the complete file. As a first step it was decided to keep only the eight largest peaks of each spectrum, or all if there were less than eight and ordered in decreasing order of intensity. The programme was written in such a manner to select the eight most intense peaks from each spectrum stored in the complete file.

INDEX FILE

As was discussed earlier the spectra were identified only by a serial number, therefore it was essential to create a file containing all necessary information, such as: name, mol.Wt. and elemental composition (number of atoms of carbon, hydrogen, oxygen, nitrogen, sulphur etc.). These data were punched on cards and a programme was written to read and transfer these data to a magnetic tape. After each search the complete information of those compounds related to the unknown was printed out.

RESULTS

Several spectra were selected as unknown compounds without prior knowledge of their structure. The search proceeded for the best fit against the library file.

The first compound that was used had a serial No. of (555); according to the equation (1), the unique peaks were calculated and the correlation was printed out (tables No 1, 2) and subsequently the INDEX FILE was used to find out the exact structure of the unknown molecule. However, the final test gave the same compound ($C_{22}H_{26}N_3OCl$) for three different spectra which had been run on different occasions.

TABLE No. I

Unknown		Library file					
Ser. No. 555		Ser. No. 4254		4258		4260	
m/e	I	m/e	I	m/e	I	m/e	I
83	100	83	100	* 83	100	*283	100
426	89	426	89	*283	76	*426	76
283	66	283	66	*426	33	*366	45
366	53	366	53	*139	29	*139	45
139	50	139	50	*366	28	284	31
427	39	427	39	81	20	282	31
143	30	143	30	282	18	*427	29
145	29	145	29	284	17	*145	24
$\sum_{a_8}^{a} I$	456		456		266		319

* The peaks which are present in the unknown or unique peak for calculation.

Using the equation (1) gives the following results:

TABLE No. 2

Spectrum No.		Correlation	
Unknown	File	Observed	Calculated
555	4254	100	100
	4258	57	58
	4260	68	69

APPENDIX

Contents

1 - Programme.

2 - High resolution mass spectral data (including P.F.K.).

3 - Calculated mass spectral data in descending order of mass to charge ratios.

4 - Calculated eight most intense peaks in descending order of intensity.

5 - Result of correlation.

```
#LISTING OF :CBAS12.CAFBORHANI1(1/E1BD) PRODUCED ON  5MAY75 AT 16.45.02

#OUTPUT BY LISTFILE IN ':CBAS12.CAFBORHANI1' ON  5MAY75 AT 16.56.36

DOCUMENT     :CBAS12.CAFBORHANI1(/B1BD)


STARTED :CBAS12,CAFBORHANI1, 5MAY75  16.23.53 TYPE:BACK
16.23.53* JOB CAFBORHANI1,:CBAS12
16.23.53* CAFBORHANI1
16.23.53* SFORTRAN *CR/EBCDIC/
16.23.56* BOX CONTEXT=FORT
16.23.58* TA FB,CM
END OF MACRO
16.23.59* TA AB,CM
FILES ALREADY ONLINE: :MACROS.CONSOLIDATE(3/) :LIB.SUBGROUPSRF4(1/MA25)
:LIB.PROGRAM XFIV(1/MYC1) IS ALREADY ONLINE
16.24.03 0.02 USED URGENCY M
16.24.03 JOB IS NOW FULLY STARTED
16.24.10 0.03 CORE GIVEN 32512

FORTRAN COMPILATION BY #XFIV MK 3A     DATE  05/05/75  TIME  16/24/16



PROGRAM(MSDH)
INPUT3=CR0
INPUT5=CR1
OUTPUT6=LP0
USE 7=MT1/UNFORMATTED(COMPLETE)/1500
USE 8=ED1/DIRECT(RESERVEDA)/128
CREATE 9=MT1/UNFORMATTED(COMPLETE)/1500
CREATE 10=ED1/DIRECT(RESERVEDA)/128
COMPRESS INTEGER AND LOGICAL
END




MASTER MSDH
  DEVICE OR CHANNEL NO.S USED ARE AS FOLLOWSO-
3- CARD READER
5- PAPER TAPE READER
6- LINE PRINTER
7- MAGNETIC TAPE(I/O) FOR COMPLETE SPECTRA, NAME, AND CONDITIONS
8- MAGNETIC TAPE(I/O) FOR SPECTRAL INDEX BASED ON TEN MOST INTENSE PEAKS
  THE PROGRAM CAN EXECUTE THE FOLLOWING NUMBERED OPTIONSO-
1- STORE THIS SPECTRUM ONLY
2- COMPARE THIS SPECTRUM ONLY
3- COMPARE AND STORE THIS SPECTRUM
4- COMPARE AND STORE THIS SPECTRUM IF NO SIGNIFICANT SIMILARITY FOUND
6PRINT TOP TEN FROM TAPE LIBRARY
8- STORE TOP TEN IN COMPLETE SPEC LIBRARY
9PRINT COMPLETE SPECTRUM FROM THE TAPE LIBRARY
1000-INITIALISE FILES
1001-PRINT INDEX FOR GIVEN MASS

  THE OPTION NUMBER IS READ FROM THE FIRST CARD IN I8 FORMAT.
  IF THIS = 5, CONTROL JUMPS TO THE LAST SECTION IN MASTER SEGMENT
  WITH THE OTHER OPTIONS THE PROGRAM READS FROM PAPER TAPE, THE
```

```
   SPECTRUM SERIAL NO.(FORMAT I8), AND THE FIRST 999(OR LESS) SAMPLE P
   INTENSITIES,AND WIDTHS(FORMAT 9X,F11.6,X,I7,X,I7).
   THE ARRAYS ARE REARRANGED TO GIVE THE TEN MOST INTENSE PEAKS AT THE TO
   AFTER NORMALISATION TO 100. COMPARISON AND/OR STORING TAKES PLACE.
INTEGER OPTION,SPEC NO,SPEC NU,NO LIST(500,2),NAME(10),COND(20),
1      WIDTH
REAL MASS,INDX 10,NEXT PK
COMMON MASS(1000),AREA(1000),INDX 10(170,3)

OPTION- AS SPECIFIED ABOVE.
SPEC NO,SPEC NU- SPECTRUM SERIAL NO.S (DO NOT CONFUSE WITH NO SPEC
                 WHICH STANDS FOR NUMBER OF SPECTRA).
NO LIST- A COMPARISON ARRAY/WHICH IS TO CONTAIN ALL THE SPECTRUM NO.S
      HAVING AT LEAST ONE OF THE TOP TEN MOST INTENSE PEAKS AND THEIR
      CORRELATION BASED ON RELATIVE POSITIONS FROM ONE TO TEN.
NAME   - ONE CARD REQUIRED (OPTIONS 1,3,&4) WHICH HAS COMPOUND NAME.
COND   - TWO CARDS REQD. AS PREVIOUS HAVING SPECTROMETER CONDITIONS,ETC.
      NAME & COND ARE REQUIRED ONLY IN STORING AND MAY BE BLANK OR IN
      ANY FORMAT.
MASS   - MASS TO CHARGE RATIOS (FORMAT F11.6 FOR PEAK)
AREA   - ACTUALLY INTENSITY    (FORMATS I7,I7 FOR NTNSTY & WIDTH)
INDX 10- TEN PEAK INDEX BASED ON TRUNCATED MASS CONTAINING ACCURATE MASS
      SPECTRUM NO. & POSITION OF THE PEAK IN THAT SPECTRUMS TOP TEN.


   READ OPTION FROM CARDS(I8)0 ALL RUNS STOP WITH NEGATIVE OPTION (900-
   BLOCK); IF PRINT ONLY IS REQUIRED(OPTION 5 OR LATER OPTIONS) GOTO 500.
DEFINE FILE 8(999,62,U,III),10(999,62,U,JJJ)
FORMAT(I8)
READ(3,1) OPTION
IF (OPTION.EQ.1001) GOTO  1000
IF (OPTION .NE. 1000) GOTO 222
ENDFILE 9
J=1
DO 223 I=1,999
WRITE(10'I) J,I,X,X,X
STOP
CONTINUE
DIF1=0.0127
DIF2=0.93
IF (OPTION .LT. 0) GOTO 900
IF (OPTION .EQ. 5) GOTO500
IF (OPTION .EQ. 9) GOTO 500
IF (OPTION .EQ. 6) GOTO 600
READ(5,12) SPEC NO
FORMAT (I0)
THE ABOVE STATEMENT IS NON STANDARD********************************
WRITE(6,224) SPEC NO
FORMAT(8H SPEC NO,I5)
```

```
 HAVING READ SPECTRUM SERIAL NO. FROM PAPER TAPE,CONTINUE ON THAT MEDIUM
 WITH M/E, AREA,& WIDTH. THE INDEX,I, IS A COUNT OF THE NO. OF SAMPLE PEAKS
 IF M/E IS CLOSE TO INTEGRAL THEN ITS TREATED AS PFK REFERENCE PEAK. THE
 SPECTRYM IS TERMINATED BY ZERO M/E. AREA & WIDTH ARE COMBINED TO GIVE
 INTENSITY (SEE A.MCLACHLAN,B.SC. THESIS FOR BASIS)
3FORMAT(I0,F0.0,I0,I0)
 THE ABOVE STATEMENT IS NON STANDARD*********************************
 DO 5  I=2,1000
 READ (5,3) IDUMMY,PEAK,NTNSTY,WIDTH
 IF (PEAK .EQ. 0.0) GOTO  8
 DIFFCE=PEAK-AINT(PEAK)
 IF (DIFFCE .LT. DIF1 .OR. DIFFCE .GT. DIF2) GOTO 4
 MASS(I)=PEAK
 J=WIDTH/1024
 AREA(I)=FLOAT(NTNSTY)*2**J
5CONTINUE

   AT THIS POINT THERE ARE MORE THAN 999 SAMPLE PEAKS. THE REST ARE
   IGNORED & A WARNING PRINTED TO THIS EFFECT. THE PROGRAM THEN BUBBLE
   SORTS THE FIRST TEN PEAKS INTO THE MOST INTENSE INDESCENDING ORDER,
   I.E. MASS(2) IS THE BASE PEAK (THE PRACTICE OF USING THE FIRST ELEMENT
   TO SAY HOW MANY            ELEMENTS ARE VALID IS ADOPTED).
 I=1000
 FORMAT(69H1WARNING0 MORE THAN 999 PEAKS OR INCORRECT TERMINATOR IN
1SPECTRUM NO. ,I8)
 WRITE(6,6) SPEC NO
 READ (5,3) IDUMMY,PEAK,NTNSTY,WIDTH
 IF (PEAK .NE. 0.0) GOTO 7
 MASS(1)=I
 K=I
 DO 10  J=2,11
 NEXT PK=AREA(J)
 JJ=J+1
 DO 9  I=JJ,K
 A=AREA(I)
 IF (A .LE. NEXT PK) GOTO 9
 B=MASS(J)
 MASS(J)=MASS(I)
 MASS(I)=B
 AREA(I)=NEXT PK
 AREA(J)=A
 NEXT PK =A
 CONTINUE
 CONTINUE
```

```
   AREAS (I.E.INTENSITIES) WILL BE NORMALISED TO 100. OPTION CHECKEDO-
   200 BLOCK IS COMPARISON; 100 BLOCK IS STORING.
BASE PK=AREA(2)
DO 11 I=2,K
AREA(I)=AREA(I)/BASE PK*100
IF (OPTION .LT. 2 .OR. OPTION .GT. 4) GOTO 100


CONTINUE
NO LIST(1,1)=1
DO 204  I=2,9
   PEAK=MASS(I)
   M OVER E=PEAK
   CALL READ 10(M OVER E)
   NO SPEC=INDX 10(1,1)
   IF (NO SPEC .EQ .1) GOTO 204
   DO 203 J=2,NO SPEC
        NO SAME=NO LIST(1,1)
        SPEC NU=INDX 10(J,2)
        DO 202 L=2,NO SAME
        IF (NO SAME .EQ .1) GOTO 202
            IF (NO LIST(L,1)-SPEC NU) 202,201,202
            NO LIST(L,2)=NO LIST(L,2)+10-ABS(I-1-INDX 10(J,3))
            GOTO 203
        CONTINUE
        NO SAME=NO SAME+1
        NO LIST(NO SAME,1)=SPEC NU
        NO LIST(NO SAME,2)=10-ABS(I-1-INDX 10(J,3))
        NO LIST(1,1)=NO SAME
   CONTINUE
CONTINUE
DO  2041 I=2,NOSAME
NO LIST(I,2)= FLOAT(NO LIST(I,2))/80.0*100.0



FORMAT(1H1)
WRITE(6,205)
FORMAT(100(1H ,10(10H  SPEC COR)/1X,10(I6,I4)/))
IF (NO SAME. EQ .1) GOTO 211
WRITE(6,210) (NO LIST(I,1),NO LIST(I,2),I=2,NO SAME)
CONTINUE
IF (OPTION .EQ. 2) GOTO 2
IF (OPTION .EQ. 3) GOTO 100
OPTION = 4 SO CHECK IF CORRELATION >20; IF SO DISCARD NAME & COND
IF (NO SAME .EQ .1) GOTO 100
DO 220 I=2,NO SAME
IF (NO LIST(I,2) .GT. 20) GOTO 221
CONTINUE
GOTO 100
CONTINUE
GOTO 2
```

```
      CONTINUE
      IF (OPTION .EQ. 8)GOTO 800
      FORMAT (10A8)
      READ (7,END=103)
      GOTO 102
      CONTINUE
      BACKSPACE 7
      III = MASS(1)
      XXX = AREA(1)
      WRITE(7)SPEC NO,NAME,COND,III,XXX,(MASS(I),AREA(I),I=2,K)
      CONTINUE
      ENDFILE 7
      REWIND 7
      SPECTRUM INSERTED IN COMPLETE SPECTRUM LIBRARY,NOW UPDATE TEN PEAK INDEX.
      DO 130 I=2,9
      M OVER E=MASS(I)
      CALL READ 10(M OVER E)
      NO SPEC=INDX 10(1,1)+1
      INDX 10(1,1)=NO SPEC
      INDX 10(NO SPEC,1)=MASS(I)
      INDX 10(NO SPEC,2)=SPEC NO
      INDX 10(NO SPEC,3)=I-1
      GOTO 126
      THE FOLLOWING WERE IN THE ORIGINAL
      MM=MOVERE-1
      DO 125 J=1,MM
      READ(8)
      WRITE(8)((INDX 10(I,J),J=1,3),I=1,NO SPEC)
      REWIND 8
      INT1= INDX 10 (1,1)
      INT2=INDX 10 (1,2)
      INT3=INDX 10 (1,3)
      WRITE (8'MOVERE) INT1,INT2,INT3,
     1  ((INDX 10(II,J),J=1,3),II=2,NO SPEC)
      CONTINUE
      GOTO 2


      CONTINUE
      READ(5,1) SPEC NO
      WRITE(6,516) SPEC NO
      READ (7,END=514) SPEC NU,NAME,COND,L,A,(MASS(I),AREA(I),I=2,L)
      IF (SPEC NU .NE. SPEC NO) GOTO 510
      FORMAT(1H1)
```

```
K =L
I = 2
IF (I .GE. K) GOTO 540
L = I
BIG = MASS (I)
IP1 = I+1
DO 539 J = IP1,K
IF (MASS (J).LE. BIG) GOTO 539
BIG =MASS(J)
L = J
CONTINUE
IF (I .EQ. L) GOTO 542
MASS (L) =MASS (I)
MASS(I) = BIG
TEMP = AREA (I)
AREA (I) = AREA(L)
AREA (L) = TEMP
I= I+1
GOTO 538
CONTINUE
FORMAT(1H ,6(20H      M/E          I  )/6(F13.6,F7.2))
NL=(K+4)/6
WRITE (6,512)
DO 518 L=1,NL
III=L+1
JJJ=III+5*NL
IF (JJJ.LE.K) GO TO 518
JJJ=JJJ-NL
GOTO 517
WRITE (6,513) (MASS(KKK),AREA(KKK),KKK=III,JJJ,NL)
REWIND 7
GOTO 2
REWIND 7
FORMAT(13H1SPECTRUM NO.,I8,11H NOT STORED)
FORMAT (6(F13.4,F7.2))
FORMAT(8H1SPEC NO,I8)
WRITE(6,515) SPEC NO
GOTO 2
```

```
CONTINUE
READ (3,1) SPEC NO
WRITE (6,611) SPEC NO
READ (7,END=614) SPEC NU,NAME,COND,L,A,(MASS(I),AREA(I),I=2,L)
IF (SPEC NU .NE. SPEC NO) GOTO 610
FORMAT(1H1,'SPECTRUM NO.',I10)
FORMAT(1H  , 20H     M/E          I  ,10(/F13.0,F7.0))
WRITE (6,612)
DO 613 I=2,9
IMASS=MASS(I)
IAREA=AREA(I)
WRITE (6,616) IMASS,IAREA
FORMAT (I9,I10)
REWIND 7
GOTO 2
REWIND 7
FORMAT(13H1SPECTRUM NO.,I8,11H NOT STORED)
WRITE(6,615) SPEC NO
GOTO 2


CONTINUE
FORMAT (10A8)
READ(7,END=803)
GOTO 802
CONTINUE


BACKSPACE 7
MASS(1)=11
III = MASS(1)
XXX = AREA(1)
WRITE(7)SPEC NO,NAME,COND,III,XXX,(MASS(I),AREA(I),I=2,11)
GOTO 104
```

```
00 CONTINUE
   REWIND 7
   REWIND 8 IN ORIGINAL
   CALL EXIT
00 READ(3,12) M OVER E
   CALL READ 10(M OVER E)
   WRITE (6,1001) M OVER E
   L=INDX 10(1,1)
   IF (L.EQ.1) WRITE (6,1002)
   IF (L.EQ.1) GOTO 2
   DO 1004 I=2,L
   SPEC NO =INDX 10(I,2)
   IPOS= INDX 10(I,3)
4  WRITE (6,1003) INDX 10(I,1),SPEC NO,IPOS
3  FORMAT (1H ,F20.6,2I10)
   GO TO  2
1  FORMAT(' INDEX FOR MASS',I10)
2  FORMAT(' NOTHING THERE')
   END



TH  1075, NAME  MSDH


   SUBROUTINE READ 10(M)
   REAL MASS, INDX 10
   COMMON MASS(1000), AREA(1000), INDX 10(170,3)
   GOTO 2
   THE FOLLOWING WERE IN THE ORIGINAL
   MM=M-1
   DO 1 I=1,MM
1  READ(8)
   READ(9) L,K,X,((INDX 10(I,J),J=1,3),I=2,L)
2  READ(8'M)L,K,X,((INDX 10(I,J),J=1,3),I=2,L)
   INDX 10(1,1)=L
   INDX 10(1,2)=K
   REWIND 8 IN THE ORIGINAL
   RETURN
   END
```

```
+ZZZZZZZZZZZZZZZZZZZZZZZZZZZZZZZZZZZZZZZZZZZZZZZZZZZZZZZZZZZZZZZZZZZZZZ

#LISTING OF :CBAS12.MASSDATA(97)    PRODUCED ON 19MAR75 AT 15.31.03

#OUTPUT BY LISTFILE IN ':CBAS12.TELEBOR' ON  1MAY75 AT 13.54.02

DOCUMENT     MASSDATA


     0     4242
     1      133   366.295837       624         36
     2      134   365.291588      2843         54
     3      135   364.281739       560         26
     4      136   363.276313      1151         40
     5      146   347.281663      1368         40
     6      154   332.259510       462         29
     7      161   321.242437       400         26
     8      162   320.236279      1177         44
     9      169   306.218921       834         43
    10      171   305.211841       773         40
    11      173   303.226639       375         24
    12      174   302.225009      1688         49
    13      181   291.228025      1622         48
    14      183   290.224627      7224         69
    15      184   289.216100      1450         46
    16      185   287.201733      1428         44
    17      188   285.219292       630         30
    18      189   284.214152      1773         46
    19      196   273.216419       533         34
    20      197   272.212072      3827         58
    21      198   271.205649      5868         61
    22      199   270.197539       374         21
    23      201   269.190915       910         38
    24      209   258.195309       461         25
    25      210   257.190682      1514         48
    26      214   254.203011      1951         49
    27      215   253.195221      2609         53
    28      224   239.180100       792         36
    29      230   229.160060       350         25
    30      232   226.172891       521         29
    31      240   213.164082      1452         51
    32      243   211.149002       686         31
    33      250   199.148960       735         38
    34      252   198.139530       282         21
    35      254   197.132469       831         44
    36      256   195.138950       587         32
    37      260   189.128431       381         28
    38      263   185.134102       628         38
    39      264   183.120031       444         26
    40      270   178.135192       835         42
    41      271   177.128052      1460         49
    42      272   176.119529       576         34
    43      273   175.147951       863         40
    44      274   175.111735       659         34
    45      276   174.140461       577         36
    46      278   173.132370       898         34
    47      279   172.121790       296         20
    48      280   171.117561      1076         47
    49      282   169.102408       492         34
    50      286   164.929871       712         38
    51      288   163.111811      1100         44
    52      291   162.103220       269         20
    53      293   161.132562      1490         59
    54      294   161.096208      1334         45
```

```
 55     295    160.122941      1261        52
 56     296    159.116708      2860        57
 57     297    158.109080      2055        55
 58     298    157.101742      1578        48
 59     301    155.085933       351        22
 60     305    150.104620       320        25
 61     307    149.132391      3321        63
 62     308    149.095570       607        36
 63     309    149.050131       779        44
 64     310    149.023620      1591        52
 65     311    148.123190      2664        69
 66     312    147.116561      6764        74
 67     313    147.079491       360        22
 68     315    146.108468      3478        65
 69     316    145.101420      3080        59
 70     318    144.094089      1222        41
 71     320    143.085611      1623        53
 72     322    137.096050       634        32
 73     324    136.089609      1010        43
 74     326    135.117602      1485        52
 75     327    135.081480       709        36
 76     329    134.109241      1192        57
 77     330    134.027601       987        44
 78     331    133.101922      3422        71
 79     333    132.093300       733        36
 80     335    131.085910      3105        63
 81     337    130.076610       280        20
 82     338    129.070702       985        43
 83     339    128.063960       408        27
 84     340    127.018771       371        27
 85       0      0.000000         0         0
 86    4176
 87      42    357.275162      2073        54
 88      43    356.271841      7595        76
 89      47    338.261361      1235        45
 90      53    323.235248      1169        41
 91      59    301.253913      1328        42
 92      61    299.236982      1407        47
 93      68    285.221212       544        26
 94      69    284.246711       880        34
 95      70    283.242031      4288        58
 96      73    281.227120      1155        39
 97      78    272.213588       979        38
 98      83    259.205349       710        31
 99      88    247.201169      1445        47
100      89    246.198209      8102        67
101      90    245.189663      1049        44
102      94    241.195731      1210        49
103      96    239.179632       696        37
104      97    237.162931       660        32
105     101    232.181022       854        38
106     103    231.176023      1642        47
107     105    230.163273       743        34
108     106    229.193163       932        31
109     107    229.160000      2798        47
110     109    228.188070      5037        60
111     110    227.180584       920        39
112     111    225.164291       636        28
113     117    217.159238       385        23
114     119    215.141891       470        26
115     120    214.169180      2151        56
116     121    213.163931      6823        64
117     123    212.155343       533        26
118     125    211.147611      1492        42
119     127    209.133532       372        23
120     130    201.164602       478        22
```

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121    132    200.154669     372     26
122    134    199.148918    2021     53
123    136    197.133631    1121     41
124    140    189.163559     879     38
125    141    187.149621    2423     50
126    143    186.140100     821     39
127    145    185.133469    1467     42
128    146    183.117439     556     30
129    151    177.163670     348     22
130    152    176.120522    1082     45
131    153    175.148782    1159     41
132    154    175.112650     951     38
133    156    174.138919     890     42
134    158    173.133621    3145     57
135    159    172.124401     685     33
136    160    171.117593    1767     47
137    162    169.101861     701     37
138    166    163.149231    1206     47
139    167    163.112561    1545     49
140    171    161.132460    2501     54
141    172    160.123810    1517     53
142    173    159.117162    5863     71
143    174    158.109230    3905     63
144    175    157.101620    2775     60
145    177    155.086201     666     30
146    179    151.112760     929     37
147    182    149.134251     832     34
148    183    148.123172    1012     42
149    184    147.117340    3963     58
150    186    146.108371    1837     60
151    187    145.101672    6577     68
152    189    144.093021    1674     58
153    191    143.086081    2906     57
154    193    142.078390     592     31
155    194    141.070480     764     36
156    195    137.133681     959     41
157    196    137.097592     925     36
158    198    135.117792    2883     53
159    199    135.081110     550     30
160    201    134.107669    1798     62
161    202    133.101702    5325     66
162    204    132.092711    1656     62
163    206    131.085870    4090     69
164    208    130.077861     976     41
165    209    129.070451    1897     58
166    210    128.062730    1138     47
167    211    125.096972    5035     69
168    213    124.088722    2556     58
169    215    123.117520    2894     61
170    216    123.081402    1648     53
171    217    122.107921    1104     39
172    218    121.101681    5822     69
173    219    120.093351    3346     70
174    221    119.086021    5814     64
175    223    118.077720    1721     54
176    224    117.070281    2818     63
177    226    116.062701     684     39
178    227    115.054940     898     34
179    229    112.084431    3602     95
180    231    111.081401   32867     87
181    232    110.105381     438     25
182    233    110.075042     439     23
183    234    110.070860     397     23
184    235    109.102172    4555     63
185    236    109.065971    2418     53
186    237    108.093151    3129     74
```

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188     239   106.077591     1962      65
189     240   105.070821     8515      71
190     242   104.062492      630      31
191     245    98.061390      381      20
192     246    97.064936     1028      47
193     247    96.091341      741      41
194     249    95.085409     5745      73
195     250    95.047994      397      23
196     251    95.010429     3221      62
197     252    94.077272     1532      60
198     254    93.070472     6568      73
199     256    92.061501     1987      73
200     257    91.054928     8980      74
201     259    86.097553     1990      57
202     263    83.087188     2797      61
203     264    83.050461     1341      47
204     265    83.011125     1272      49
205     266    82.075847      760      35
206     268    81.925080     6340      77
207     269    81.071188     8852      77
208     271    80.917292     3039      62
209     272    80.061734      917      49
210     273    79.927072     5963      76
211     274    79.055948     7049      76
212     275    78.919834     2979      68
213       0     0.000000        0       0
214    4230
215      66   436.186807     2023      72
216      68   434.166504      559      37
217      74   421.160524      572      35
218      75   420.154577     1891      65
219      80   406.141171      640      40
220      82   405.134169     3309      84
221      86   394.140739      554      31
222      88   393.134330     3099      83
223      90   391.123072      520      36
224      95   381.130971      860      49
225      97   380.128170      270      21
226      98   379.115738     1479      72
227     100   377.100839      725      44
228     104   368.122749      468      31
229     106   365.106238      630      40
230     115   338.115931      541      35
231     116   337.067310      980      49
232     118   336.101044      345      24
233     125   325.068340     1339      65
234     128   321.075011     1121      56
235     139   296.064288      351      25
236     140   295.062183     2509      89
237     161   188.087810      346      24
238     169   161.060961      313      20
239     182   115.053441      590      42
240     187    95.011137     1585      81
241       0     0.000000        0       0
242    4230
243       9   730.896791      322      26
244      11   716.919718      344      27
245      60   437.187129     1222      75
246      63   436.185391     4558     109
247      65   434.181256      695      44
248      66   434.154463      599      33
249      72   422.167884     1385      80
250      73   421.168686      487      33
251      74   421.144684      294      21
252      75   420.152993     2426     103
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253      76    419.156632       286        23
254      81    405.132381      3131       107
255      84    394.139214      1204        67
256      86    393.133073      5836       120
257      88    391.126041       815        49
258      89    391.104240       288        23
259      92    381.134041      2022        98
260      94    380.122371       870        62
261      95    379.117430      3011       103
262      98    377.094955       324        24
263     102    368.123739      1985        94
264     103    367.120071       275        21
265     105    366.107230       451        33
266     106    365.098227      1540        85
267     114    338.113327      1853        96
268     115    337.072690      2485       101
269     116    336.103149       627        44
270     119    335.071681       364        26
271     125    325.070698      3725       105
272     128    323.075289       452        35
273     129    321.080191      1210        60
274     130    321.052291       845        47
275     135    311.068980       342        22
276     136    311.057441       425        26
277     142    296.068237       356        26
278     143    295.060439      4290       111
279     148    283.059849      1635        93
280     156    270.056460       409        31
281     162    257.011131       396        30
282     189    203.045151       450        33
283     190    203.034860       289        25
284     197    190.102010      3233       105
285     198    189.096321       672        48
286     199    188.086532      6107       121
287     214    162.070831       477        32
288     216    161.059440      3457       112
289     217    160.087411      1901        96
290     218    160.058991       780        37
291     219    160.047152      1245        60
292     220    159.082961      2403        99
293     224    147.047571       445        32
294     226    145.070242       937        53
295     227    145.010521      2287       103
296     228    144.064620       262        23
297     236    129.070292      1424        91
298     237    128.065099       347        26
299     242    115.055792      1965        96
300       0      0.000000         0         0
301    4124
302      16    778.919426       403        29
303      24    755.921652       283        21
304     198    426.921421       923        58
305     200    424.920467      1674        73
306     263    321.107172      4125       111
307     264    320.103638     18306       134
308     303    265.081682      2251        95
309     304    264.078159     10851       127
310     336    216.073681      1923        90
311     337    215.070483     12049       142
312     338    215.018211       400        28
313     348    200.074722       621        41
314     350    199.072679      7995       128
315     352    198.068383     38545       165
316     354    197.060942      1449        75
317     356    196.059071       294        22
318     357    196.049119       386        26
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319     361   187.082211      470      30
320     362   187.073941      343      26
321     371   177.018031      271      21
322     375   171.078461     1704     102
323     376   170.072391     6562     125
324     377   170.036652     2820     118
325     379   169.065982     3042     111
326     388   160.058562      263      21
327     389   159.052220      319      24
328     390   159.039160      285      21
329     395   153.071820     2438     102
330     396   152.072670      267      21
331     397   152.066160      268      21
332     407   144.063311      317      25
333     409   143.084869      338      24
334     411   142.077632     4955     129
335     412   141.070452     3752     129
336     418   133.034811      423      26
337     420   132.060110      270      21
338     422   131.049481     6289     143
339     424   129.065451      269      21
340     425   128.061809     4188     133
341     426   127.060021      632      43
342     427   127.050582      517      37
343     428   126.013492      291      21
344     431   124.038171      673      48
345     432   124.028951      590      41
346     434   123.029141      435      31
347     435   122.042502      627      41
348     436   122.035659      397      26
349     440   116.059681     1216      80
350     443   115.054660     5582     124
351     444   115.023881      329      24
352     445   114.013002      458      31
353     449   106.037952    10480     146
354     451   105.034631   119514     211
355     453   103.053791     4648     145
356     454   102.046440     2194     119
357     457    96.038371     1387      97
358     458    95.012005     7587     141
359     461    91.060546      684      43
360     462    91.054961      567      31
361     463    91.049077      680      45
362     464    89.041456     1551      97
363       0     0.000000        0       0
364    4121
365     204   426.907503      323      24
366     206   424.916515      795      44
367     335   215.012804      213      22
368     352   185.139810      836      52
369     360   170.118463     1081      53
370     388   129.078452     1798      67
371     389   128.107219     4740      88
372     396   114.092141      749      51
373     397   114.056582      902      58
374     402   100.076391     1391      72
375     404    95.010973     3826      91
376     408    88.071758     2181      78
377     409    87.067931    47297     133
378     411    86.060043    16578     114
379     412    85.051729     1192      60
380       0     0.000000        0       0
381    4254
382      22   512.337167     1902      62
383      23   511.333456    11196     101
384      24   510.329829    31664     122
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386	29	468.325803	1333	61
387	31	456.327082	363	21
388	33	444.323742	1119	55
389	34	443.314274	4819	95
390	36	442.306304	4429	95
391	37	441.330483	2130	69
392	38	440.326003	8085	109
393	40	429.318720	6018	109
394	41	428.318889	41047	137
395	42	427.315758	232876	184
396	43	427.239773	473	27
397	44	426.485190	1424	86
398	45	426.295725	526088	580
399	46	426.051585	650	35
400	47	426.021164	398	30
401	50	425.303006	2918	89
402	51	424.298191	954	62
403	54	413.300232	1938	65
404	55	412.292720	11809	115
405	56	411.288065	28981	126
406	57	408.305371	931	47
407	59	398.288090	518	28
408	60	396.305938	499	28
409	62	385.305001	1795	72
410	63	385.270505	290	21
411	64	384.298413	7918	120
412	65	383.296181	961	50
413	67	380.312104	1140	52
414	68	380.276168	543	32
415	69	373.263479	911	56
416	70	372.260431	7049	100
417	71	371.256290	28174	136
418	72	370.262931	4996	127
419	73	369.280313	7357	148
420	75	368.291550	20372	150
421	76	367.291881	105369	165
422	78	366.386392	293	21
423	79	366.369361	574	35
424	80	366.287111	312048	289
425	81	366.180752	290	21
426	82	365.284913	1387	63
427	83	364.282353	303	21
428	84	359.260373	421	27
429	85	358.254606	793	36
430	86	357.246414	768	43
431	87	356.236358	655	42
432	88	355.230183	1827	67
433	90	353.273191	1972	89
434	91	352.271313	12769	121
435	92	351.268143	43467	139
436	93	349.286721	3107	79
437	94	348.281442	10986	121
438	95	343.247120	3148	129
439	97	342.253963	2503	81
440	98	341.248105	6002	108
441	99	340.246730	713	43
442	100	333.257173	2589	90
443	102	328.239570	1940	72
444	103	327.236463	9024	168
445	104	326.258861	6175	118
446	105	325.254649	1222	62
447	108	315.440471	491	33
448	109	315.422118	269	21
449	110	315.398662	298	23
450	111	315.292664	380	28

451	112	315.277551	357	27
452	113	315.229981	2663	146
453	114	315.177484	376	27
454	115	315.124000	564	40
455	116	315.037409	573	39
456	121	314.928949	331	23
457	122	314.904042	517	31
458	123	314.880111	669	40
459	124	314.863841	327	23
460	125	314.841429	421	28
461	126	314.814950	436	28
462	127	314.790540	414	28
463	128	314.769701	341	26
464	129	314.696908	297	21
465	130	314.681683	574	39
466	131	314.604858	400	30
467	132	314.549961	353	27
468	133	314.477772	312	23
469	134	314.288691	301	22
470	135	314.226691	1842	81
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486	153	286.258931	642	44
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1184     303     157.030130      2740        67
1185     304     156.092961      4784        90
1186     305     155.109209      1736        64
1187     306     155.086390      6052        94
1188     308     154.133690      1667        57
1189     309     154.079380       893        48
1190     310     153.129940     15993        97
1191     311     153.093450      1156        48
1192     312     153.071952      1256        56
1193     313     152.153731       461        31
1194     314     152.122271      8868        85
1195     315     152.064120       694        47
1196     316     151.150831      5576        86
1197     317     151.113821      1975        54
1198     319     150.140251      1236        55
1199     320     150.104960       899        50
1200     322     149.133550     10446       101
1201     323     149.097992      2074        69
1202     324     149.025441      4422        76
1203     325     148.123119     10051       101
1204     326     147.118181     51435       138
1205     327     147.082130      1764        60
1206     328     146.108039     19814       116
1207     329     145.102280     92510       182
1208     330     145.068171       491        32
1209     331     145.053260       389        27
1210     332     144.088708     21236       158
1211     333     143.077570     88928       189
1212     335     142.125570       735        43
1213     336     142.078231      6823       107
1214     337     141.622670      2404        61
1215     338     141.122460      2086        93
1216     339     141.092301      3526        84
1217     340     141.070321      6037        99
1218     341     140.117500     16043        99
1219     342     140.084279       284        20
1220     343     139.113292    172378       159
1221     344     138.137690      1278        54
1222     345     138.102889      1930        61
1223     346     137.133800     11617        99
1224     347     137.096953     10982       103
1225     348     136.123501      2595        76
1226     349     136.088751      1544        59
1227     350     135.117401     16304       108
1228     351     135.081530      1333        53
1229     352     134.107260     11345       105
1230     353     133.606520       853        43
1231     354     133.101881     62757       141
1232     355     133.064131       359        26
1233     357     132.092550      9441       105
1234     359     131.085731     34829       131
1235     360     131.050711      3027        64
1236     362     130.077079      8479       110
1237     363     129.069420     15575       120
1238     364     128.061541      7807       127
1239     365     127.055251      1668        59
1240     366     127.040493      5338        88
1241     367     126.100511      2258        54
1242     368     125.155521       502        31
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1243     369   125.097716     26420       101
1244     370   125.061761       946        48
1245     371   124.121921      3089        81
1246     372   124.088922      2574        70
1247     374   123.117960     24728       110
1248     375   123.081581      6472        90
1249     376   122.108432      8529       100
1250     377   122.072921       673        46
1251     378   121.101751     32659       132
1252     379   121.065932      1121        51
1253     380   120.093042     24230       121
1254     381   119.085620     32393       120
1255     383   118.076953      8932       101
1256     384   117.069652     22368       135
1257     385   116.060592      4295       108
1258     386   115.076710       791        46
1259     387   115.054320      5851        85
1260     388   113.590640      1694        59
1261     389   113.095092       698        48
1262     391   112.088731      4129        74
1263     393   111.117440      3031        74
1264     394   111.081012      1647        59
1265     395   110.105670      3413        78
1266     396   110.073051       978        49
1267     397   109.101511     27756       120
1268     398   109.065569      2587        65
1269     399   108.092541     10188       110
1270     400   108.058161       311        22
1271     401   107.086132     37098       135
1272     402   107.050481       538        35
1273     403   106.076781     11152       108
1274     404   105.070341     52331       139
1275     405   104.062571      3639        80
1276     406   103.054361      3660        77
1277     407   102.047661       604        38
1278     408   102.030321       271        21
1279     409   101.059250      4884       101
1280     412    99.081737      1663        57
1281     413    99.045238       764        46
1282     414    98.074016       911        42
1283     415    97.102300      3338        75
1284     416    97.065717      5961        92
1285     417    96.091994      3703        98
1286     418    96.058346      8243        93
1287     419    95.086498     29368       121
1288     420    95.050499      1030        48
1289     421    94.076471      6094       101
1290     422    93.070812     36193       130
1291     424    92.061302      8512       108
1292     425    91.055307     37823       141
1293       0     0.000000         0         0
1294     555
1295      22   512.337187      1902        62
1296      23   511.333456     11196       101
1297      24   510.329829     31664       122
1298      28   471.314067       846        42
1299      29   468.325803      1333        61
1300      31   456.327082       363        21
1301      33   444.323742      1119        55
1302      34   443.314274      4819        95
1303      36   442.306304      4429        95
1304      37   441.330483      2130        69
1305      38   440.326003      8085       109
1306      40   429.318720      6018       109
1307      41   428.318889     41049       137
1308      42   427.315758    237876       184
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SPEC NO      4124
  M/E           I        M/E         I        M/E         I        M/E         I        M/E         I

 778.9194     0.34    200.0747     0.52    170.0367     2.36    142.0776     4.15    124.0290     0.49
 755.9217     0.24    199.0727     6.69    169.0660     2.55    141.0705     3.14    123.0291     0.36
 426.9214     0.77    198.0684    32.25    160.0586     0.22    133.0348     0.35    122.0425     0.52
 424.9205     1.40    197.0609     1.21    159.0522     0.27    132.0601     0.23    122.0357     0.33
 321.1072     3.45    196.0591     0.25    159.0392     0.24    131.0495     5.26    116.0597     1.02
 320.1036    15.32    196.0491     0.32    153.0718     2.04    129.0655     0.23    115.0547     4.67
 265.0817     1.88    187.0822     0.39    152.0727     0.22    128.0618     3.50    115.0249     0.28
 264.0782     9.08    187.0739     0.29    152.0662     0.22    127.0600     0.53    114.0130     0.35
 216.0737     1.61    177.0180     0.23    149.1343     0.00    127.0506     0.43    106.0380     8.77
 215.0705    10.08    171.0785     1.43    144.0633     0.27    126.0135     0.24    105.0346   100.00
 215.0182     0.33    170.0724     5.49    143.0849     0.28    124.0382     0.56    103.0538     3.89

SPEC NO      4121
  M/E           I        M/E         I        M/E         I        M/E         I        M/E         I

 426.9214     0.00    215.0128     0.45    129.0785     3.80    114.0566     1.91     87.0679   100.00
 426.9075     0.68    185.1398     1.77    128.1072    10.02    100.0764     2.94     86.0600    35.05
 424.9165     1.68    170.1185     2.29    114.0921     1.58     88.0718     4.61     85.0517     2.52

SPEC NO      4230
  M/E           I        M/E         I        M/E         I        M/E         I        M/E         I

 436.1868    61.14    405.1342   100.00    380.1282     8.16    338.1159    16.35    296.0643    10.61
 434.1665    16.89    394.1407    16.74    379.1157    44.70    337.0673    29.62    295.0622    75.82
 421.1605    17.29    393.1343    93.65    377.1008    21.91    336.1010    10.43    225.1643     0.06
 420.1546    57.15    391.1231    15.71    368.1227    14.14    325.0683    40.47    188.0878    10.46
 406.1412    19.34    381.1310    25.99    365.1062    19.04    321.0750    33.88    161.0610     9.46
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SPEC NC     4258
   M/E          I          M/E          I          M/E          I          M/E          I          M/E          I

 511.3355     1.03      283.2424    76.13      212.1555     1.31      158.1088    11.17      133.1022     7.55
 510.3328     3.64      282.2349    18.33      211.1486     1.89      157.1012     4.39      131.0857     3.69
 428.3204     1.34      281.2272     2.99      199.1430     4.92      157.0284     1.68      131.0507     1.11
 427.3158    10.09      268.2181     2.26      197.1326     1.31      153.1277     2.62      129.0700     1.12
 426.3133    33.62      267.2113     7.41      189.1647     1.24      149.1320     1.35      125.0967     2.70
 411.2866     1.13      254.2033     1.94      187.1509     1.12      148.1210     0.67      123.1209     0.01
 384.3016     1.49      253.1958     0.43      185.1334     1.29      147.1172     8.08      123.1178     2.90
 371.2577     2.04      242.2033     3.11      165.0828     2.82      146.1071     2.63      122.1102     0.49
 368.3002     1.04      241.1972     0.47      183.1146     0.46      145.1013    12.53      121.1015     4.13
 367.2936     8.13      237.1631     0.77      179.1796     1.19      144.0920     1.57      120.0955     2.59
 366.2908    28.81      229.1909     0.99      177.1641     1.64      143.0759    12.73      119.0858     3.92
 351.2702     2.27      228.1846     7.26      175.1485     1.97      141.0694     0.51      117.0708     2.34
 326.2605     3.65      227.1803     1.29      173.1322     3.51      140.1148     2.38      117.0583     0.93
 311.2346     2.72      227.0933     2.50      171.1176     1.31      139.1116    29.97      109.1031     4.12
 310.2297     8.72      225.1725     0.73      163.1477     3.51      137.1319     1.93      108.0949     0.75
 295.2081     0.59      215.1794     0.64      161.1321     3.32      137.0960     1.61      107.0851     9.28
 285.2516     1.57      214.1681     2.36      160.1218     1.55      135.1181     1.86      106.0760     2.14
 284.2464    17.47      213.1642    11.62      159.1164    10.68      134.1084     0.70      105.0694    11.63
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SPEC NO    4242
     M/E          I          M/E         I          M/E         I          M/E         I          M/E         I

     366.2958   8.64       287.2017  19.77       213.1641  20.10       173.1324  12.43       149.1324  45.97
     365.2916  39.55       285.2193   8.72       211.1490   9.50       172.1218   4.10       149.0956   8.40
     364.2817   7.75       284.2142  24.54       199.1490  10.17       171.1176  14.89       149.0501  10.78
     363.2763  15.93       273.2164   7.38       198.1395   3.90       169.1024   6.81       149.0236  22.02
     347.2817  18.94       272.2121  52.98       197.1325  11.50       164.9299   9.86       148.1232  36.88
     332.2595   6.40       271.2056  81.23       195.1389   8.13       163.1118  15.23       147.1166  93.63
     321.2424   5.54       270.1975   5.18       189.1284   5.27       162.1052   3.72       147.0795   4.98
     320.2363  16.29       269.1909  12.60       185.1341   8.69       161.1325  20.63       146.1085  48.15
     306.2189  11.54       258.1953   6.38       183.1200   6.15       161.0962  18.47       145.1014  42.64
     305.2118  10.70       257.1907  20.96       178.1352  11.56       160.1229  17.73       144.0941  16.92
     303.2266   5.19       254.2030  27.01       177.1281  20.21       159.1167  39.59       143.0856  22.47
     302.2250  23.37       253.1952  36.12       176.1195   7.97       158.1091  28.45       137.0960   8.78
     291.2280  22.45       239.1801  10.96       175.1480  11.95       157.1017  21.84       136.0896  13.98
     290.2246 100.00       229.1601   4.84       175.1117   9.12       155.0859   4.86       135.1176  20.56
     289.2161  20.07       226.1729   7.21       174.1405   7.99       150.1046   4.43       135.0815   9.81
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SPEC NO     4176
  M/E          I          M/E         I          M/E          I          M/E         I          M/E         I

 357.2752    6.31      229.1932    2.84      177.1637    1.06      146.1084    5.59      122.1079    3.56
 356.2718   23.11      229.1600    8.51      176.1205    3.29      145.1017   20.01      121.1017   17.71
 338.2614    3.76      228.1881   15.33      175.1488    3.53      144.0930    5.09      120.0934   10.18
 323.2352    3.56      227.1806    2.80      175.1126    2.89      143.0861    8.84      119.0860   17.69
 301.2539    4.04      225.1643    1.94      174.1389    2.71      142.0784    1.80      118.0777    5.24
 299.2370    4.28      217.1592    1.17      173.1336    9.57      141.0705    2.32      117.0703    8.57
 285.2212    1.66      215.1419    1.43      172.1244    2.08      137.1337    2.92      116.0627    2.08
 284.2467    2.68      214.1692    6.54      171.1176    5.38      137.0976    2.81      115.0549    2.73
 283.2420   13.05      213.1639   20.76      169.1019    2.13      135.1178    8.77      112.0844   10.96
 281.2271    3.51      212.1553    1.62      163.1492    3.67      135.0811    1.67      111.0814  100.00
 272.2136    2.98      211.1476    4.54      163.1126    4.70      134.1077    5.47      110.1054    1.33
 259.2053    2.16      209.1335    1.13      161.1325    7.61      133.1017   16.20      110.0750    1.34
 247.2012    4.40      201.1646    1.45      160.1238    4.62      132.0927    5.04      110.0709    1.21
 246.1962   24.65      200.1546    1.74      159.1172   17.84      131.0859   12.44      109.1022   13.86
 245.1897    3.19      199.1489    6.15      158.1092   11.88      130.0779    2.97      109.0660    7.36
 241.1957    3.68      197.1338    3.41      157.1016    8.44      129.0705    5.77      108.0932    9.52
 239.1796    2.12      189.1636    2.67      155.0862    2.03      128.0627    3.46      107.0865   22.75
 237.1629    2.01      187.1496    7.37      151.1128    2.83      125.0970   15.32      106.0776    5.97
 232.1810    2.60      186.1401    2.50      149.1343    2.53      124.0887    7.78      105.0768   25.91
 231.1760    5.00      185.1335    4.46      148.1232    3.08      123.1175    8.81      104.0625    1.92
 230.1633    2.26      183.1174    1.69      147.1173   12.06      123.0814    5.01       98.0614    1.16
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SPEC NC     4254
    M/E            I           M/E          I          M/E          I          M/E          I          M/E          I

  512.3372      0.32       351.2681      7.41      284.2473    21.39      181.1027      0.06      142.0785      2.13
  511.3335      1.91       349.2867      0.53      283.2394    66.16      179.1817      0.30      141.6245      0.96
  510.3298      5.40       348.2814      1.87      282.2344    21.33      177.1657      0.60      141.1243      0.63
  471.3141      0.14       343.2471      0.54      281.2263     3.99      176.1574      0.17      141.0799      3.41
  468.3258      0.23       342.2540      0.43      280.2218     0.25      175.1492      0.99      140.1182      6.19
  456.3271      0.06       341.2481      1.02      279.2136     0.31      174.1402      0.46      140.0876      0.07
  444.3237      0.19       340.2467      0.12      277.1981     0.25      173.1330      1.62      139.1139     50.40
  443.3143      0.82       333.2572      0.44      269.2188     1.03      172.1240      0.43      138.1395      0.38
  442.3063      0.76       328.2396      0.33      268.2131     3.86      171.1164      1.04      138.1048      0.57
  441.3305      0.36       327.2365      1.54      267.2094     8.78      170.1088      0.25      137.1351      3.98
  440.3260      1.38       326.2589      1.05      266.2027     0.14      169.1007      0.54      137.0980      3.65
  429.3187      1.03       325.2546      0.21      255.2108     0.58      167.0856      0.07      136.1249      0.78
  428.3189      7.00       315.4405      0.08      254.2048     1.59      165.1650      0.13      136.0906      0.39
  427.3158     39.71       315.4221      0.05      253.1935     1.49      165.1295      0.16      135.1189      5.59
  427.2398      0.08       315.3987      0.05      252.1913     0.44      165.0704      0.05      135.0828      0.35
  426.4552      0.24       315.2927      0.06      251.1664     0.08      164.1528      0.16      134.1086      3.68
  426.2957     89.72       315.2774      0.06      243.2108     0.15      163.1489      1.73      134.0770      0.06
  426.0516      0.11       315.2300      0.45      242.2034     1.01      163.1137      0.09      133.6091      0.28
  426.0212      0.07       315.1775      0.06      241.1931     0.77      162.1404      0.30      133.1030     21.95
  425.3030      0.50       315.1240      0.10      240.1834     0.73      161.1334      1.66      132.0951      3.51
  424.2982      0.16       315.0374      0.10      239.1789     0.44      160.1238      0.94      132.0570      0.07
  413.3002      0.33       314.9289      0.06      238.1718     0.14      159.1182      4.21      131.0863     12.35
  412.2927      2.01       314.9040      0.09      237.1639     0.58      158.1117      1.50      131.0522      1.02
  411.2881      4.94       314.8801      0.11      229.1913     0.50      157.1257      0.21      130.0780      2.83
  408.3054      0.16       314.8638      0.06      228.1859     2.52      157.1026      4.65      129.0696      5.44
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398.2881	0.09	314.8414	0.07	227.1763	0.98	157.0326	0.27	128.0621	2.65
396.3059	0.09	314.8150	0.07	227.0923	0.35	156.0936	0.99	127.0444	2.77
385.3050	0.31	314.7905	0.07	226.1699	0.97	155.0911	2.08	126.1017	0.76
385.2705	0.05	314.7697	0.06	225.1623	0.41	154.1327	0.60	125.1346	0.16
384.2964	1.35	314.6969	0.05	223.1477	0.04	154.0779	0.21	125.0989	6.45
383.2962	0.16	314.6817	0.10	217.1948	0.24	153.1291	5.51	125.0623	0.32
380.3121	0.19	314.6049	0.07	215.1768	0.46	153.0932	0.32	124.1228	0.90
380.2762	0.09	314.5500	0.06	214.1666	1.34	153.0706	0.42	124.0894	0.95
373.2635	0.16	314.4778	0.05	213.1620	4.96	152.1548	0.17	123.1182	10.13
372.2604	1.20	314.2887	0.05	212.1544	0.97	152.1221	2.88	123.0816	2.24
371.2563	4.80	314.2267	0.31	211.1469	1.24	152.0643	0.13	122.1083	3.55
370.2629	0.85	314.1957	0.11	209.1345	0.13	151.1561	1.68	122.0744	0.18
369.2803	1.25	312.2354	0.74	203.1803	0.31	151.1139	0.56	121.1018	12.95
368.2915	3.47	311.2312	4.67	201.1632	0.48	150.1397	0.36	121.0668	0.33
367.2919	17.97	310.2271	16.03	200.1504	0.57	150.1062	0.17	120.6000	0.27
366.3844	0.05	309.2236	0.19	199.1419	2.74	149.1342	3.53	120.0929	9.52
366.3694	0.10	308.2492	0.11	198.1370	0.55	149.0974	0.63	119.0855	13.45
366.2871	53.22	300.2418	0.15	197.1315	1.09	149.0257	1.03	118.0767	3.44
366.1808	0.05	299.2352	0.52	195.1164	0.08	148.1230	3.17	117.0692	8.26
365.2849	0.24	298.2290	0.08	189.1642	0.74	148.0931	0.09	116.0594	1.59
364.2824	0.05	297.2212	0.41	189.1284	0.10	147.1175	17.90	115.0772	0.24
359.2604	0.07	296.2124	0.50	188.1543	0.08	146.1085	6.43	115.0539	2.11
358.2546	0.14	295.2056	1.82	187.1487	0.63	145.1022	29.29	114.0932	0.18
357.2464	0.13	294.2354	0.05	186.1389	0.34	145.0544	0.18	113.5916	0.79
356.2364	0.11	293.2313	0.23	185.1325	1.13	144.0899	6.55	113.0945	0.25
355.2302	0.31	292.2212	0.27	185.0823	0.93	143.0780	30.73	112.1245	0.08
353.2732	0.34	286.2589	0.11	184.1251	0.29	142.1270	0.23	112.0893	1.52
352.2713	2.18	285.2498	2.55	183.1176	0.83	142.0971	0.05	111.1175	1.02

SPEC NC 4256

M/E	I	M/E	I	M/E	I	M/E	I	M/E	I
510.3360	1.61	269.2236	0.79	201.1644	0.72	158.1094	19.12	135.1177	3.67
428.3199	2.45	268.2157	3.51	200.1536	0.81	157.1018	6.46	134.1077	2.28
427.3156	15.02	267.2111	10.07	199.1410	8.63	157.0293	0.76	133.1018	16.74
416.3129	53.00	255.2059	0.50	198.1417	0.65	155.0864	0.60	132.0931	1.95
411.2878	1.64	254.2023	2.82	197.1324	2.35	153.1282	4.24	131.0862	7.22
384.3041	1.24	253.1963	0.94	189.1647	2.11	152.1205	1.65	131.0503	1.67
372.2623	0.67	242.2032	3.60	187.1491	2.58	151.1493	0.64	130.0784	1.34
371.2588	2.64	241.1966	1.28	186.1410	0.38	149.1322	1.97	129.0707	2.79
368.3009	1.28	239.1804	0.47	185.1342	2.03	149.0244	0.94	128.0640	0.93
367.2957	9.35	237.1653	1.25	185.0827	4.23	148.1223	1.83	127.0413	2.14
366.2912	33.54	229.1921	1.57	183.1179	1.57	147.1171	12.79	125.0989	5.93
352.2723	0.58	228.1878	8.91	179.1789	1.92	146.1075	3.36	123.1209	7.36
351.2673	3.29	227.1796	2.12	177.1637	2.42	145.1018	19.55	123.0849	1.37
348.2811	0.82	227.0923	3.26	175.1484	3.53	144.0928	2.68	122.1121	2.16
341.2462	0.39	226.1720	1.90	174.1396	1.37	144.0742	0.87	121.1061	9.13
326.2607	0.94	225.1651	0.47	173.1324	5.59	143.0764	21.91	120.0984	5.49
311.2337	4.06	217.1947	0.73	172.1235	0.96	142.0782	0.92	119.0859	23.20
310.2281	13.09	215.1798	0.98	171.1176	2.16	141.6218	0.57	118.0808	4.58
295.2076	1.39	214.1694	3.15	169.1029	0.74	141.0927	0.47	117.0723	12.38
285.2503	2.45	213.1642	13.93	165.1627	0.33	141.0710	0.96	116.0658	1.32
284.2466	22.94	213.1620	0.01	163.1488	5.72	140.1163	4.56	116.0546	0.42
283.2421	100.00	212.1562	2.19	161.1331	5.43	139.1125	46.12	115.0619	1.84
282.2347	23.06	211.1491	2.55	160.1228	2.74	137.1337	2.89	113.5994	0.99
281.2275	4.24	203.1798	0.64	159.1168	16.10	137.0970	2.11	112.1004	2.04

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SPEC NO     4260
  M/E            I           M/E           I           M/E           I           M/E           I           M/E           I

 512.3383     0.12      327.2389     1.64      255.2096     1.62      193.1016     0.10      157.1008     8.73
 511.3371     0.58      326.2597     1.48      255.1822     0.09      191.1802     0.45      157.0301     0.72
 510.3320     1.74      325.2539     0.24      254.2037     5.05      191.1431     0.21      156.0930     1.25
 471.3120     0.11      318.2196     0.10      253.1937     2.65      190.1695     0.57      155.1092     0.45
 468.3258     0.09      315.3165     0.08      252.1883     1.46      190.1356     0.37      155.0864     1.58
 444.3232     0.15      315.2248     0.31      251.1819     0.42      189.1648     3.00      154.1337     0.44
 443.3157     0.74      315.1570     0.09      246.2003     0.13      189.1287     0.88      154.0794     0.23
 442.3109     0.76      315.1194     0.13      245.1928     0.22      189.0571     0.45      153.1299     4.18
 441.3325     0.32      315.0420     0.09      244.2128     0.17      188.1542     0.67      153.0935     0.30
 440.3275     1.06      315.0155     0.07      244.1852     0.13      187.1491     2.74      153.0720     0.33
 429.3189     0.78      314.8781     0.10      243.2083     1.18      186.1382     1.09      152.1537     0.12
 428.3207     5.01      314.8073     0.12      242.2039     4.85      186.0858     0.29      152.1223     2.32
 427.3165    29.79      314.7885     0.10      242.1687     0.07      185.1323     3.33      152.0641     0.18
 426.4573     0.11      314.7590     0.10      241.1953     2.70      185.0823     3.10      151.1508     1.46
 426.4369     0.11      314.7387     0.08      240.1857     1.55      184.1223     0.95      151.1158     0.52
 426.3077    76.76      314.7163     0.12      239.1794     1.65      183.1164     2.46      150.1403     0.32
 426.1182     0.09      314.6481     0.07      238.1705     0.80      182.1081     0.28      150.1050     0.23
 426.0661     0.06      314.5790     0.07      237.1646     2.44      181.1016     0.43      149.1335     2.73
 425.3057     0.45      314.2212     0.45      230.1972     0.32      180.1840     0.22      149.0980     0.54
 424.2923     0.11      312.2374     0.86      229.1923     2.88      179.1807     1.98      149.0254     1.16
 413.2984     0.30      311.2328     5.00      229.1623     0.17      179.0865     0.18      148.1231     2.63
 412.2942     1.47      310.2289    17.07      228.1875    13.60      178.1699     0.63      147.1182    13.43
 411.2885     3.79      309.2232     0.21      228.0957     0.32      177.1650     3.13      147.0821     0.46
 408.3064     0.14      308.2529     0.15      227.1789     3.56      177.1282     0.18      146.1080     5.18
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398.2816    0.07     305.1078    0.09     227.1447    0.17     176.1534    0.96     145.1023   24.16
385.3075    0.23     300.2436    0.35     227.0923    2.29     176.1203    0.09     145.0682    0.13
384.3009    0.97     299.2379    0.73     226.1715    3.51     175.1485    4.28     145.0573    0.10
384.2640    0.11     298.2301    0.30     225.1634    1.49     175.1127    0.31     144.0887    5.55
383.2936    0.15     297.2211    0.67     224.1555    0.47     174.1392    2.29     143.0776   23.23
380.3075    0.29     296.2107    0.71     223.1460    0.56     173.1329    6.47     142.1256    0.19
372.2610    1.00     295.2055    2.20     221.1902    0.27     173.0986    0.17     142.0782    1.78
371.2573    3.57     294.2335    0.22     218.2007    0.23     172.1238    1.64     141.6227    0.63
370.2842    0.24     293.2266    0.40     217.1946    1.50     171.1170    3.32     141.1225    0.54
370.2509    0.43     292.2183    0.41     216.1838    0.45     170.1061    0.89     141.0923    0.92
369.2838    1.02     286.2539    0.29     215.1779    2.51     169.1217    0.27     141.0703    1.58
368.2926    2.67     285.2478    3.95     215.1398    0.09     169.1010    1.62     140.1175    4.19
367.2939   14.61     284.2460   31.89     214.1684    5.40     168.1167    0.27     140.0843    0.07
366.2906   45.95     283.3588    0.10     213.1638   21.90     168.0925    0.39     139.1133   45.02
366.1907    0.07     283.3317    0.29     213.1300    0.13     167.1456    0.17     138.1377    0.33
365.2829    0.24     283.2342  100.00     212.1548    4.00     167.0813    0.63     138.1029    0.50
364.2755    0.12     282.2342   31.55     211.1484    4.59     167.0352    0.26     137.1338    3.03
359.2583    0.13     281.2271    6.17     210.1397    0.40     166.1702    0.12     137.0970    2.87
358.2499    0.24     281.1910    0.15     209.1332    0.68     166.1350    0.30     136.1235    0.68
357.2444    0.19     280.2183    0.62     207.1184    0.20     165.1645    1.00     136.0888    0.40
356.2345    0.13     279.2121    0.72     205.1615    0.12     165.1282    1.14     135.1174    4.26
355.2257    0.31     279.1605    0.24     204.1854    0.28     165.0699    0.40     135.0815    0.35
353.2740    0.27     278.2013    0.22     203.1810    1.78     164.1529    1.00     134.1073    2.96
352.2719    1.56     277.1957    0.63     203.1437    0.19     163.1487    7.66     133.6065    0.22
351.2680    5.40     270.2278    0.29     202.1705    0.50     163.1126    0.52     133.1019   16.39
349.2868    0.43     270.1975    0.11     202.1379    0.34     162.1374    1.58     133.0641    0.09
348.2809    1.44     269.2219    1.91     201.1641    1.91     162.1026    0.09     132.0926    2.47
343.2632    0.19     269.1899    0.16     201.1318    0.24     161.1319    6.69     131.0857    9.10
343.2261    0.31     268.2149    6.19     200.1504    2.28     161.0962    0.44     131.0507    0.79
342.2533    0.40     267.2091   15.77     199.1429   11.15     160.1223    4.24     130.0771    2.21
341.2484    0.91     266.2012    0.41     198.1393    1.63     159.1162   20.07     129.0694    4.07
340.2392    0.15     265.1927    0.29     197.1335    3.79     159.0817    0.14     128.0615    2.04
333.2582    0.37     263.1803    0.17     196.1257    0.28     158.1100   22.44     127.0553    0.44
328.2357    0.41     256.2154    0.25     195.1185    0.48     157.1231    0.52     127.0405    1.39
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SPECTRUM NO.       4176          SPECTRUM NO.       4260
     M/E            I                 M/E             I

     111           100                283           100
      91            27                426            76
      81            26                366            45
     105            25                139            45
     246            24                284            31
     356            23                282            31
     107            22                427            29
      79            21                145            24


SPECTRUM NO.       4230          SPECTRUM NO.       4256
     M/E            I                 M/E             I

     405           100                283           100
     393            93                426            53
     295            75                139            46
     436            61                366            33
     420            57                105            27
     379            44                100            25
     325            40                119            23
     321            33                282            23


SPECTRUM NO.       4121           SPECTRUM NO.       4258
     M/E            I                  M/E             I

      87           100                  83           100
      86            35                 283            76
     128            10                 426            33
      98             4                 139            29
     129             3                 366            28
     100             2                  81            20
      85             2                 282            18
     170             2                 284            17


SPECTRUM NO.       4254           SPECTRUM NO.       555
     M/E            I                  M/E             I

      83           100                  83           100
     426            89                 426            89
     283            66                 283            66
     366            54                 366            53
     139            50                 139            50
     427            39                 427            39
     143            30                 143            30
     145            29                 145            29

                                  *ZZZZZZZZZZZZZZZZZZZZZZZZZZZZZZZ
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TABLE NO. 4

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TNNNNNNNNNNNNNNNNNNNNNNNNNNNNNNNNNNNNNNNNNNNNNNNNNNNNNNNNNNNNNNNNNNNNNNNNNNNNNNNNNNNNNNNNNNN

#LISTING OF :WORKFILE.AAA00010256(1/)  PRODUCED ON 18APR75 AT 17.26.13

#OUTPUT BY LISTFILE IN ':CBAS12.CAFBORHAN11' ON 18APR75 AT 17.26.17

DOCUMENT     1

SPEC NO     4242
SPEC NO     4176
SPEC NO     4230
SPEC NO     4230
SPEC NO     4124
SPEC NO     4121
SPEC NO     4234
SPEC NO     4256
SPEC NO     4258
SPEC NO     4240
SPEC NO      555


  SPEC COR  SPEC COR  SPEC COR  SPEC COR  SPEC COR  SPEC COR  SPEC COR  SPEC COR  SPEC COR  SPEC COR
  4254 100  4258  57  4256  45  4260  68

TNNNNNNNNNNNNNNNNNNNNNNNNNNNNNNNNNNNNNNNNNNNNNNNNNNNNNNNNNNNNNNNNNNNNNNNNNNNNNNNNNNNNNNNNNNNNN
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CHAPTER FIVE

The Anlysis of Mixtures

INTRODUCTION

While the elucidation of the electron impact mass spectra of individual compounds has been extensively studied for about fifty years, studies of mixtures have remained relatively neglected.

This problem, that of analysing mixtures of compounds, although difficult, has received some attention in the past by Barnard (225). The first successful approach was reported by Meyerson (226), this represented the resolution of the two components of a binary mixture. It was also suggested that by extension of the same technique one could resolve a ternary mixture.

The next approach was made by Monteiro and Reed (227), using a rather different method. These authors discussed the problem of analysis of a four component mixture.

The matter was re-examined by Halket and Reed (228, 229) in a series of papers and it is now further extended with the aim of finding a method whereby the number and type of compounds contained in an arbitrary mixture can be determined. Once the number of components has been determined, the individual spectra are dissected from the combined data.

THEORETICAL

The mass spectra of n pure compounds may be used to form a mixture array. This is done by mixing four mass spectral vectors, (A_1 A_2 ..... A_8),

$(B_1\ B_2 \cdots\cdots B_8)$ etc., together; each vector has eight elements (peaks).

The mixture array $\underline{M}$, is formed by multiplication of the following matrix:

$$\underset{X}{\begin{pmatrix} X_{a_1} & X_{b_1} & X_{c_1} & X_{d_1} \\ X_{a_2} & X_{b_2} & X_{c_2} & X_{d_2} \\ \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot \\ X_{a_4} & X_{b_4} & X_{c_4} & X_{d_4} \end{pmatrix}} \times \underset{A}{\begin{pmatrix} A_1 & A_2 & \cdots & A_8 \\ B_1 & B_2 & \cdots & B_8 \\ C_1 & C_2 & \cdots & C_8 \\ D_1 & D_2 & \cdots & D_8 \end{pmatrix}} = \underset{M}{\begin{pmatrix} M_{11} & M_{12} & \cdots\cdots & M_{18} \\ M_{21} & M_{22} & \cdots\cdots & M_{28} \\ \cdot & \cdot & & \cdot \\ \cdot & \cdot & & \cdot \\ \cdot & \cdot & & \cdot \\ M_{41} & M_{42} & & M_{48} \end{pmatrix}}$$

The elements of $\underline{X}$ are the composites of this matrix, elements M_{11} consist of:

$$X_{a_1} \cdot A_1 + X_{b_1} \cdot B_1 + X_{c_1} \cdot C_1 + X_{d_1} \cdot D_1$$

and the element M_{12} is:

$$X_{a_1} \cdot A_2 + X_{b_1} \cdot B_2 + X_{c_1} \cdot C_2 + X_{d_1} \cdot D_2$$

etc., so that, the first mixture spectrum is formed by mixing the four spectra of matrix $\underline{A}$ together in relative amounts given by the first row of matrix $\underline{X}$. The second mixture, $(M_{21}\ M_{22} \cdots\cdots M_{28})$, is formed by mixing according to the second row of X, and so on. The four spectra will then be mixed up linearly within all four mixtures spectra. If the rows of $\underline{X}$ are all linearly independent (230), then the rows of $\underline{M}$ will be different but only four of them will be linearly independent. It is assumed, of course, that the rows of matrix $\underline{A}$ are linearly independent, like mass spectra. The rank of the matrix, $\underline{M}$, is then four (227, 230) and this may be determined experimentally by well known methods (231).

Calculation of the eigenvalues from the above matrix gives the number of components in the mixture. Various methods of computation were used by Halket (232) to analyse some mixtures by mass spectrometry. He identified the unique peaks by different subroutines and isolated the spectra of each component but, he noted that his results indicated the presence of some apparent impurities.

The present investigation reports the extension of the previous study, firstly to identify the origin of the extra products, secondly to clarify the mechanism of their formation.

EXPERIMENTAL

A four component mixture was prepared by mixing together equal weights of N-methylmorpholine, cyclohexanethiol, n-nonane and p-xylene, and was analysed in a mass spectrometer.

The spectra were obtained by the following method: The sample (0.6 ml) was introduced via the cold inlet system and de-gassed with liquid nitrogen in the usual manner. The fractionation technique was employed within the mass spectrometer itself. The spectra were immediately visible after adjustment of the gain control. A series of spectra were taken at a constant monitor pressure. Spectra were recorded at about 45-minuts intervals until some fourteen spectra had been obtained (table No. 1) and the sample was exhausted.

The experiments were carried out upon a GEC - AEI MS 902S with a source pressure less than 10^{-5} Torr, and source temperature of 135°C.

m/e	I	I	I	I	I	I	I
27	13.400	12.900	12.300	13.100	12.900	14.800	22.600
28	33.500	32.300	65.200	65.600	70.700	56.200	79.200
29.	12.300	11.800	11.600	11.500	12.100	14.400	22.300
32	8.900	8.600	16.700	16.700	17.600	14.000	19.800
39	8.900	9.100	8.700	9.800	8.600	12.700	21.700
40	3.400	3.200	3.600	3.300	3.400	4.100	9.400
41	19.000	18.800	17.400	18.000	18.100	28.100	46.200
42	33.000	32.300	30.400	30.300	33.300	28.800	23.600
43	100.000	100.000	100.000	100.000	100.000	100.000	100.000
44	6.700	7.000	7.200	7.400	6.900	6.800	5.300
45	0.0	0.0	0.0	0.0	0.0	0.0	0.0
51	7.800	7.800	8.000	8.300	7.800	9.600	10.400
52	4.500	4.300	4.800	4.800	4.300	5.200	5.700
53	0.0	0.0	0.0	0.0	0.0	0.0	0.0
54	0.0	0.0	0.0	0.0	0.0	0.0	0.0
55	10.100	10.200	10.100	11.500	12.100	24.000	36.800
56	12.000	12.100	11.400	11.500	11.700	15.100	16.000
57	33.200	32.000	31.900	32.800	32.300	49.300	62.300
65	3.900	3.900	4.300	4.800	4.800	5.200	6.600
67	4.200	4.000	4.800	5.400	6.000	13.000	20.800
70	8.400	8.900	8.000	9.000	8.600	11.600	12.300
71	24.300	25.500	23.200	23.800	24.100	27.400	18.900
77	7.800	8.600	7.800	8.900	9.000	12.300	10.900
78	0.0	0.0	0.0	0.0	0.0	0.0	0.0
79	4.500	4.600	4.800	4.900	5.200	6.800	7.500
82	0.0	0.0	0.0	0.0	0.0	13.000	16.000
83	0.0	0.0	0.0	0.0	0.0	13.000	15.100
84	4.500	4.600	4.300	4.900	5.200	6.800	9.400
85	12.800	13.700	12.000	13.100	13.800	20.500	20.800
91	56.400	60.800	56.500	63.100	64.100	84.900	79.200
92	5.000	5.000	4.900	5.700	5.200	6.200	5.700
99	4.500	5.100	4.600	4.900	5.200	6.800	7.900
100	7.300	9.100	8.000	8.200	8.600	8.200	2.800
101	33.000	39.500	34.800	37.400	37.100	31.500	7.200
105	17.900	25.000	18.800	20.000	19.700	27.400	18.900
106	36.300	48.600	40.400	45.000	44.800	63.000	40.600
107	3.400	4.300	4.200	4.900	4.800	5.500	4.700
116	2.200	2.700	2.800	4.600	5.200	9.600	11.300
128	4.500	5.900	5.500	6.300	5.700	8.500	8.500

I	I	I	I	I	I	I
22.000	55.600	43.500	18.800	44.800	22.900	25.300
68.300	26.700	24.000	35.700	40.000	39.600	47.800
19.200	55.600	80.700	21.200	42.000	33.700	28.400
17.500	6.700	6.000	8.900	10.000	9.600	11.900
20.000	51.100	54.000	16.700	48.000	25.300	23.900
13.300	63.300	100.000	6.700	10.000	7.800	9.000
38.300	84.400	67.700	40.200	98.000	62.700	52.200
40.000	30.000	30.600	25.700	32.000	29.300	32.800
100.000	96.700	74.200	100.000	100.000	100.000	100.000
6.700	11.100	19.400	6.700	10.000	7.000	7.500
0.0	13.300	12.300	4.500	18.000	7.200	7.100
8.300	17.800	17.700	9.500	20.000	9.400	10.900
4.700	10.000	9.700	5.400	11.200	5.800	6.700
0.0	15.600	12.900	6.500	21.600	9.000	9.700
0.0	26.700	24.200	12.300	50.000	22.900	20.900
28.300	71.100	48.400	39.600	97.600	63.900	51.500
11.700	20.000	16.200	15.600	36.000	21.100	20.200
29.200	60.000	42.000	53.600	98.000	72.300	62.700
5.000	13.300	12.900	5.000	12.000	6.000	6.000
18.300	47.800	40.300	23.400	96.000	42.200	38.800
9.200	13.800	9.000	9.800	26.000	13.300	12.700
20.000	20.000	16.200	20.300	42.000	22.000	23.200
8.300	18.400	16.200	8.900	12.000	9.600	10.400
0.0	11.100	11.300	5.000	14.000	5.400	6.000
6.700	15.100	12.900	6.000	0.0	6.600	8.700
11.700	32.200	22.600	21.900	97.200	37.400	31.300
10.800	26.700	17.800	19.500	96.800	32.500	28.100
5.000	10.000	9.000	7.300	24.000	10.600	10.500
10.000	21.100	12.900	16.700	52.000	24.100	22.400
42.500	100.000	64.500	68.100	96.000	55.400	62.700
4.200	8.900	9.400	5.400	12.000	4.800	65.700
4.600	8.900	8.000	5.900	12.000	8.400	10.500
5.000	4.000	3.200	5.000	4.000	3.400	5.700
14.200	7.100	5.800	17.900	10.000	8.400	13.400
9.200	21.100	16.200	19.000	36.000	16.900	19.100
19.200	41.100	29.700	45.800	78.000	35.500	40.300
2.500	4.400	3.300	4.500	10.000	4.200	5.200
8.000	20.000	12.900	14.500	86.000	21.100	21.600
4.200	8.400	6.500	6.700	28.000	9.400	10.200

Measurements and Computation

A series of 39 peaks common to all were selected and analysed for the eigenvalues . The number of these indicates the number of compounds present; in this instance. The result of this calculation is shown in the following table.

TABLE No. 2

```
PRINCIPAL COMPONENTS ANALYSIS

  14VARIABLES
  39OBSERVATIONS

MEANS
      14.04098       14.92815       15.10250       15.88455       16.12555       19.59737       20.67683
      29.97684       26.25890       19.59480       41.82561       23.89223       25.15378

STANDARD DEVIATIONS
      19.09857       19.95197       20.56328       21.08504       21.51219       22.56540       23.35611
      25.90529       23.84615       19.89377       34.08072       22.05502       21.42403

CORRELATION COEFFICIENTS

ROW    1
    1.00000     0.99244     0.96717     0.96787     0.96001     0.94824     0.85678     0.87439     0.60876
    0.89964     0.41380     0.71426     0.74420

ROW    2
    0.99244     1.00000     0.95836     0.96378     0.95443     0.95510     0.83047     0.83035     0.58316
    0.88570     0.40506     0.67994     0.71494

ROW    3
    0.96717     0.95836     1.00000     0.99836     0.99795     0.94859     0.89139     0.90890     0.54060
    0.86080     0.36860     0.67292     0.71973

ROW    4
    0.96787     0.96378     0.99836     1.00000     0.99902     0.95976     0.89317     0.89570     0.54865
    0.86583     0.38047     0.67063     0.72038

ROW    5
    0.96001     0.95443     0.99795     0.99902     1.00000     0.95507     0.89477     0.90105     0.54088
    0.85797     0.37598     0.66568     0.71569

ROW    6
    0.94824     0.95510     0.94859     0.95976     0.95507     1.00000     0.92993     0.85231     0.66160
    0.93643     0.56067     0.76987     0.70657
```

```
ROW  8
    0.87439     0.83035     0.90890     0.89570     0.90105     0.85231     0.92278     1.00000     0.69269
    0.87135     0.50975     0.80901     0.79642

ROW  9
    0.60876     0.58316     0.54060     0.54865     0.54088     0.66160     0.75725     0.69269     1.00000
    0.81522     0.72490     0.85325     0.74564

ROW 10
    0.42937     0.39929     0.37524     0.37354     0.36866     0.43449     0.54853     0.55515     0.89397
    0.57852     0.47707     0.62959     0.53339

ROW 11
    0.89964     0.88570     0.86080     0.86583     0.85797     0.93843     0.93459     0.87135     0.81522
    1.00000     0.73782     0.93025     0.88210

ROW 12
    0.41380     0.40506     0.36860     0.38047     0.37598     0.56067     0.63480     0.50975     0.72490
    0.73782     1.00000     0.86053     0.72023

ROW 13
    0.71426     0.67994     0.67292     0.67063     0.66568     0.76987     0.86559     0.80901     0.85325
    0.93025     0.86053     1.00000     0.87900

ROW 14
    0.74420     0.71494     0.71973     0.72038     0.71569     0.78657     0.84383     0.79642     0.74564
    0.88210     0.72023     0.87900     1.00000


EIGENVALUES
   10.92932     1.76922     0.67402     0.24264     0.17219     0.10139     0.06197     0.02684     0.01085

CUMULATIVE PERCENTAGE OF EIGENVALUES
    0.78067     0.90704     0.95518     0.97251     0.98481     0.99206     0.99648     0.99840     0.99917
```

The next step is to derive their spectra. These results are now shown in the following table.

TABLE No. 3

29 32 39 8 10 34 12 23 30 35 36 5 15 16 20 26 27 3
37 11 14
7 12 19 22 24

27.0	0.0	0.0	0.0	0.0	63.95	0.0
28.0	26.70	34.60	13.21	8.14	29.47	27.12
29.0	0.08	4.75	11.68	5.40	38.40	2.41
32.0	11.47	22.40	25.59	21.69	32.58	15.59
39.0	0.0	0.0	0.0	51.97	0.0	0.0
40.0	90.55	32.59	65.37	22.64	34.25	50.71
41.0	0.0	0.0	0.0	0.0	89.88	0.0
42.0	0.0	49.11	0.0	0.0	0.0	0.0
43.0	59.17	21.76	81.33	5.84	3.87	29.11
44.0	0.0	10.91	0.0	0.0	0.0	0.0
45.0	0.0	0.0	0.0	0.0	0.0	1.62
51.0	0.0	0.0	11.97	0.0	0.0	0.0
52.0	12.26	13.48	13.23	7.34	0.18	14.37
53.0	0.0	0.0	0.0	0.0	0.0	39.22
54.0	0.0	0.0	0.0	26.07	0.0	0.0
55.0	0.0	0.0	0.0	33.65	0.0	0.0
56.0	29.57	41.09	48.66	41.61	34.88	49.18
57.0	100.00	0.0	0.0	0.0	0.0	0.0
65.0	54.35	52.18	55.02	38.44	27.93	59.07
67.0	0.0	0.0	0.0	100.00	0.0	0.0
70.0	8.52	13.26	16.76	12.33	5.85	16.39
71.0	29.18	21.70	0.65	14.00	6.87	21.25
77.0	0.0	0.0	19.88	0.0	0.0	0.0
78.0	16.72	24.07	29.46	17.25	28.85	21.74
79.0	77.90	86.12	82.22	57.69	43.02	89.26
82.0	0.0	0.0	0.0	76.76	0.0	0.0
83.0	0.0	0.0	0.0	22.42	0.0	0.0
84.0	27.02	41.27	4.76	8.60	11.20	40.16
85.0	26.55	0.0	0.0	0.0	0.0	0.0
91.0	0.0	0.0	88.52	0.0	0.0	0.0
92.0	96.84	49.72	62.06	1.03	2.34	51.55
99.0	12.36	0.0	0.0	0.0	0.0	0.0
100.0	2.93	3.90	2.50	4.70	2.19	4.74
101.0	0.0	26.95	0.0	0.0	0.0	0.0
105.0	0.0	0.0	67.58	0.0	0.0	0.0
106.0	0.0	0.0	17.42	0.0	0.0	0.0
107.0	0.0	0.0	0.0	0.0	52.20	0.0
116.0	0.0	0.0	0.0	17.60	0.0	0.0
128.0	14.71	0.0	0.0	0.0	0.0	0.0
	NONANE	N.METHYL MORPHOLINE	PXYLENE	CYCLOHEXANETHIOL		

It is of some considerable interest to note that the number of compounds deduced is greater than the number incorporated in the initial mixture and it is important to isolate the extra new spectra and, if possible, to identify the compound(s) which give rise to them.

As the original four components are known, so also are their mass spectra and thus the original conponents can be identified in the mixture analysis as is shown in the following table.

TABLE No. 9

m/e	I	I	I	I
27.0	0.0	0.0	0.0	0.0
28.0	26.70	34.60	13.21	8.14
29.0	0.08	4.75	11.68	5.40
32.0	11.47	22.40	25.59	21.69
39.0	0.0	0.0	0.0	51.97
40.0	90.55	32.59	65.37	22.64
41.0	0.0	0.0	0.0	0.0
42.0	0.0	49.11	0.0	0.0
43.0	59.17	21.76	81.33	5.84
44.0	0.0	10.91	0.0	0.0
45.0	0.0	0.0	0.0	0.0
51.0	0.0	0.0	11.97	0.0
52.0	12.26	13.48	13.23	7.34
53.0	0.0	0.0	0.0	0.0
54.0	0.0	0.0	0.0	26.07
55.0	0.0	0.0	0.0	33.65
56.0	29.57	41.09	48.66	41.61
57.0	100.00	0.0	0.0	0.0
65.0	54.35	52.18	55.02	38.44
67.0	0.0	0.0	0.0	100.00
70.0	8.52	13.26	16.76	12.33
71.0	29.18	21.70	0.65	14.00
77.0	0.0	0.0	19.88	0.0
78.0	18.72	24.07	29.46	17.25
79.0	77.90	86.12	82.22	57.69
82.0	0.0	0.0	0.0	76.76
83.0	0.0	0.0	0.0	22.42
84.0	27.02	41.27	4.76	8.60
85.0	26.55	0.0	0.0	0.0
91.0	0.0	0.0	88.52	0.0
92.0	96.84	49.72	62.06	1.03
99.0	12.36	0.0	0.0	0.0
100.0	2.93	3.90	2.50	4.70
101.0	0.0	26.95	0.0	0.0
105.0	0.0	0.0	67.58	0.0
106.0	0.0	0.0	17.42	0.0
107.0	0.0	0.0	0.0	0.0
116.0	0.0	0.0	0.0	17.60
128.0	14.71	0.0	0.0	0.0
	NONANE	N.METHYL MORPHOLINE	P XYLENE	CYCLOHEXANE THIOL

In practice the resolved spectra are only a fraction of those reported for the pure organic compounds and an extra product which was isolated is as follows:

TABLE No. 5

TABLE No. 5

me	I	I
27.0	63.95	0.0
28.0	29.47	27.12
29.0	38.40	2.41
32.0	32.58	15.59
39.0	0.0	0.0
40.0	34.25	50.71
41.0	89.88	0.0
42.0	0.0	0.0
43.0	3.87	29.11
44.0	0.0	0.0
45.0	0.0	1.62
51.0	0.0	0.0
52.0	0.18	14.37
53.0	0.0	89.22
54.0	0.0	0.0
55.0	0.0	0.0
56.0	34.88	49.18
57.0	0.0	0.0
65.0	27.93	59.07
67.0	0.0	0.0
70.0	5.85	16.39
71.0	6.87	21.25
77.0	0.0	0.0
78.0	28.85	21.74
79.0	43.02	89.26
82.0	0.0	0.0
83.0	0.0	0.0
84.0	11.20	40.16
85.0	0.0	0.0
91.0	0.0	0.0
92.0	2.34	51.55
99.0	0.0	0.0
100.0	2.19	4.74
101.0	0.0	0.0
105.0	0.0	0.0
106.0	0.0	0.0
107.0	52.20	0.0
116.0	0.0	0.0
128.0	0.0	0.0

Using the published work on the identification of the organic compounds from a data bank (233) an attempt was made to match the present spectra to those in the library file.

The search was carried out, but no satisfactory result was obtained. It was assumed that these products could be a mixture of some ions or molecules which does not exist in the file, therefore their structure cannot be identified.

However, it was decided to employ a high resolution technique and investigate the origin of the extra products.

Mechanism of the Formation of Additional Products

The second approach is to clarify the mechanism of the formation and the origin of the extra products. Use was made of a high resolution mass spectrometer (MS 902) combined with a data system by which it was possible to resolve all the ions and to print out the elemental composition of each individual fragment together with its accurate mass. The experiment was repeated by analysing the same mixture in different concentration.

Table No. 7

Name	Wt %	Mol.Wt.	b.p.°C
n-nonane	35	128	150
p-xylene	30	106	138
cyclohexanethiol	15	116	158-60
N-methylmorpholine	20	101	115-6

Mixture No. 2 run at Strathclyde University.

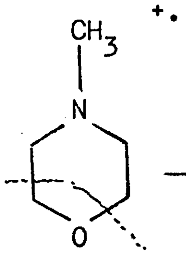
Ten different spectra were obtained on paper tape and transferred to the printed format (see the Appendix).

It may be helpful to observe the separation pattern of each component of the mixture measured under the same conditions to specify the contribution of their ions produced by electron impact, and subsequently to trace the formation of new products (table No. 8)

The Mass Spectra of a Single Component

1 - N-Methylmorpholine

The mass spectrum shows intense peaks at 42, 43, 71 and 101, the structure is similar to those of related analogues (234). The following pathway can be assumed for its breakdown:



$$\longrightarrow CH_2O + C_4H_9N^{+\cdot}$$

101 30 71

$$C_4H_9N^{+\cdot} \rightarrow C_2H_4 + C_2H_5N^{+\cdot}$$

$$C_4H_9N^{+\cdot} \rightarrow CH_2N^{+} + {}^{\cdot}C_3H_7$$

28 43 base peak

2 - p-Xylene

Fragmentation of p-xylene has been studied by Meyerson and Rylander (235): the formation of a tropylium ion was suggested.

$$C_8H_{10}^{+\cdot} \longrightarrow C_7H_7^{+} + {}^{\cdot}CH_3$$

106 91 15

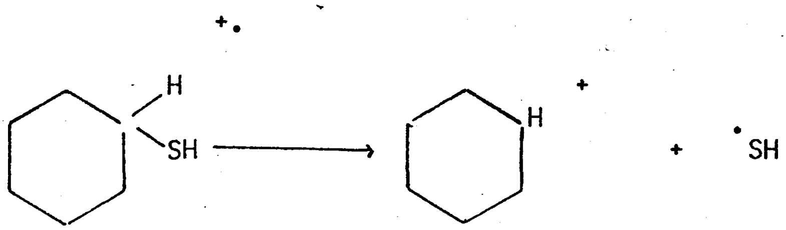
The other significant ions are at m/e = 105, 79, 78, 77, 65 and 39, which are a mixture of carbon and hydrogen.

3 - n-Nonane

The fragmentation patterns of aliphatic hydrocarbons are well established (236). Groups of peaks occur, spaced fourteen mass units apart, (corresponding to a difference of CH_2 -). In the case of n-nonane the base peak occurs at m/e = 43. The other intense ions have the general formula of $C_nH_{2n+1}^{+}$ and $C_nH_{2n}^{+}$ e.g. $C_5H_{11}^{+}$, $C_3H_6^{+}$, etc.

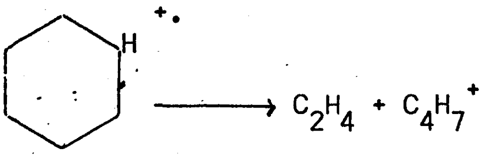
4-Cyclohexanethiol

Separation of ·SH and ·CSH radicals in the mass spectra of sulphur compounds are relatively common (237). An abundant ion at m/e = 83 could be the result of this cleavage.



116 83 33

Decomposition of the ring yields the base peak at m/e = 55, and this is supported by the appearance of a metastable ion, at m/e 36.3.



83 28 55

Table No. 8

m/e	n-Nonane	N-Methyl Morpholine	p-Xylene	Cyclohexanethiol
27	14.17	9.10	6.29	18.33
28	32.50	20.50	28.50	20.50
29	22.38	5.34	2.31	10.33
30		3.00		
32	8.00	5.10	7.20	5.20
39	8.20	1.44	9.60	21.66
40	2.98	2.06	1.38	5.83
41	35.87	6.23	3.31	59.16
42	14.17	44.90	4.30	5.00
43	100.00	100.00	12.91	8.33
44	4.30	9.67	1.13	1.65
50			4.30	
51			12.25	
52			6.29	
53			3.9	10.0
54		1.60		36.65
55	13.14	1.40	0.66	100.00
56	20.15	6.68	1.15	6.66
57	88.05	1.60	3.64	3.35
58	4.47	1.87		3.83
60				10.80
63			4.30	
65			6.29	
67				83.50
68				5.00
69	4.47			3.35
70	15.67	4.54	0.66	

Cont. Table No. 8

m/e	n-Nonane	N-Methyl Morpholine	p-Xylene	Cyclohexanethiol
71	23.13	26.73	2.64	
77			14.56	
78			6.95	
79			6.80	
81				12.45
82				85.00
83				77.50
84	10.44			5.85
85	31.34	0.55		
91			<u>100.00</u>	
92			8.60	
98	4.47			
99	31.34			
101		58.28	7.20	
103			6.95	
104			4.30	
105			36.40	
106			77.45	
107			7.25	
116				51.60
128	14.18			

Results and Discussion

To interpret the mass spectra of this mixture it was considered to distinguish the extra products from the collected spectra,(see Appendix) and classify them in different groups (tablesNo. 9, 10)

The results observed show the occurrence of some synthetic reactions in the mass spectrometer. In view of the low ion source pressure, the occurrence of ion molecule reactions is more likely to be due to surface reactions than to reactions occurring in the gas phase. For instance the formation of 1-pentanethiol ion (table No. 9) could result from the reaction of the following species:

$$C_5H_{11}^+ + {}^\bullet SH \longrightarrow C_5H_{12}S^{+\bullet}$$

The above assumption may be rationalized to include homologous series, such as n-propylmercaptan, n-butylmercaptan, etc. However, a general formula can be derived as follows:

$$C_nH_{2n+1}^+ + {}^\bullet SH \longrightarrow C_nH_{2n+1}SH^{+\bullet}$$

The same argument may be extended to unsaturated molecules, or sequential loss of hydrogen atoms from saturated ions could be the origin of these species.

The formation of aniline or its isomers may be due to a reaction between the following ions:

$$C_5H_5^+ + CH_2N \longrightarrow C_6H_7N^+$$ or

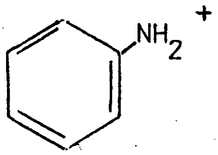


Table No.9

Identified extra Compounds

No.	Name	Molecular formula	Mol.Wt.
1	Ethylmercaptan	C_2H_6S	62
2	Allylmercaptan	C_3H_6S	74
3	n-Propylmercaptan	C_3H_8S	76
4	n-Butylmercaptan	$C_4H_{10}S$	90
5	2- or 3-Methylthiophen	C_5H_6S	98
6	Pentamethylene Sulphide	$C_5H_{10}S$	102
7	1-Pentanethiol	$C_5H_{12}S$	104
8	Aniline	C_6H_7N	93
9	n-Propyl aldehyde	C_3H_6O	58
10	Benzaldehyde	C_7H_6O	106
11	Benzylalcohol	C_7H_8O	108
12	Butylisocyanate	C_5H_9ON	99
13	2-Methylthiazoline	C_4H_7NS	101
14	Ethyl 2-hydroxyethyl Sulphide	$C_4H_{10}OS$	106
15	2-Oxazolidinethione	C_3H_5ONS	103

Table No. 10

Protonated Ions

No.	Formula	Mol.Wt.
1	CH_6S	50
2	C_2H_8S	64
3	$C_3H_{10}S$	78
4	$C_5H_{14}S$	106
5	SNH_5	51
6	C_2H_9NS	79
7	$C_3H_{11}NS$	93
8	$C_4H_{13}NS$	107
9	CH_6OS	66
10	$C_4H_{12}OS$	108

It is clear that the above molecule cannot be a fragment of N-methylmorpholine, therefore, it must have other origins.

The identification of the ion $C_7H_6O^+$ as arising from benzaldehyde is supported by the intense ion at C_7H_5O as expected for loss of $^{\bullet}H$.

$$C_7H_6O^{+\bullet} \xrightarrow{-^{\bullet}H} C_7H_5O^+ \text{ or } PhC{\equiv}O^+$$

The formation of an intense ion $(C_4H_7NS)^+$ at m/e = 101 represents the molecular ion of 2-Methylthiazoline or its isomers which can only be the result of synthesis in the ion source.

$$C_3H_6N^{+\bullet} \quad + \quad C^{\bullet}SH \longrightarrow C_4H_7NS^{+\bullet}$$

The presence of a significant peak at m/e = 106 is characteristic of the molecular ion of ethyl 2-hydroxyethyl sulphide $(C_4H_{10}OS)^+$. It seems that the formation of this molecule is very low and is completed only after several hours. The prominent peak at m/e = 103 shows the molecular ion of 2-oxazolidinethione $(C_3H_5ONS)^+$ with the intensity of 9.6% of the base peak. The formation of this product may be the result of the following reaction:

$$C_2H_4ON^+ + {}^{\bullet}CSH \longrightarrow C_3H_5ONS^{+\bullet}$$

The interesting products are some protonated ions (table No.10) with the formula of C_2H_9NS, $C_3H_{11}NS$ and $C_4H_{13}NS$ and the following reactions may account for their presence.

$$C_4H_9^+ + {}^{\bullet}SH + NH_3 \longrightarrow C_4H_{13}NS^{+\bullet}$$

$$C_3H_7^+ + {}^{\bullet}SH + CH_2N + H_2 + {}^{\bullet}H \longrightarrow C_4H_{13}NS^{+\bullet}$$

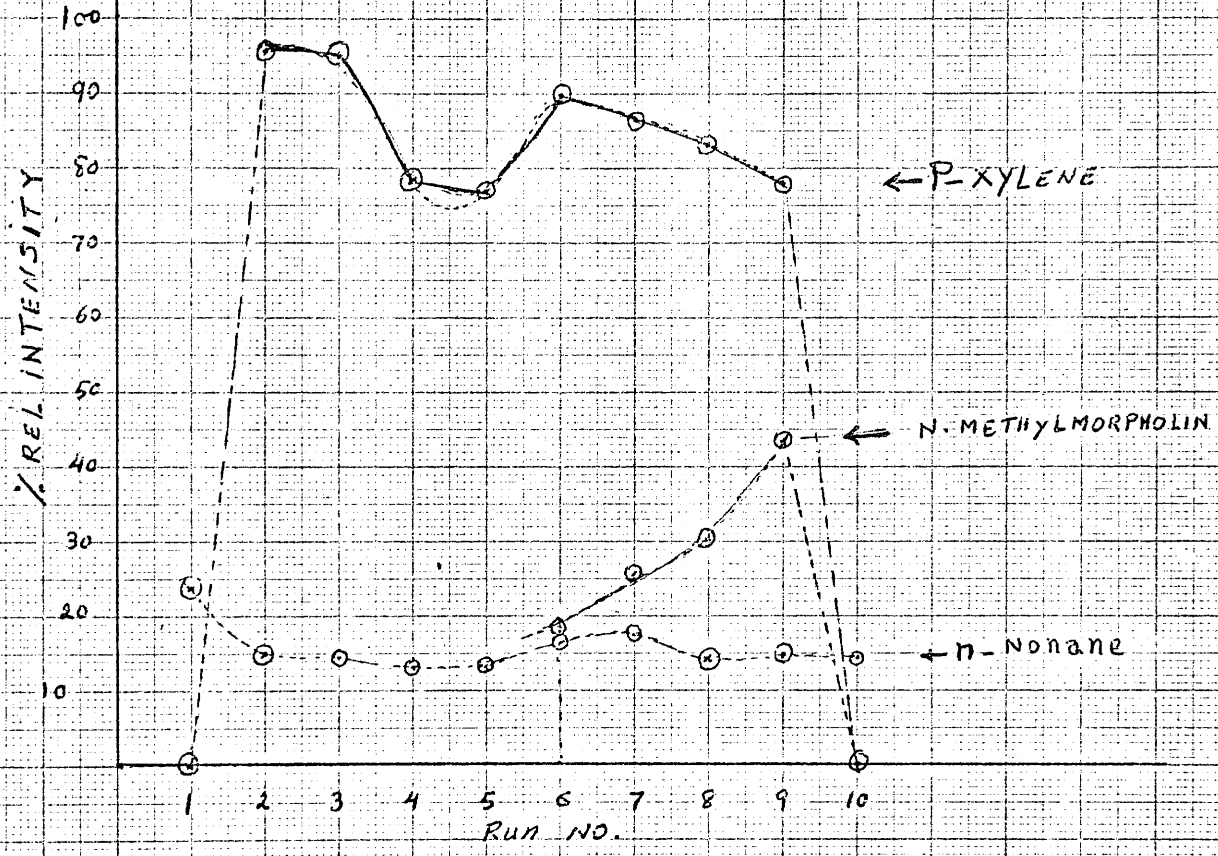
$$\overset{\bullet}{C}_4H_8 + SNH_5^+ \longrightarrow C_4H_{13}NS^{+\bullet}$$

On further bombardment these products could lose ammonia to give $C_4H_{10}S$, C_3H_8S and C_2H_6S.

The experimental method showed that the results were affected by variation of the concentration of the components, this was supported by the absence of the molecular ion of cyclohexanethiol in the second experiment, but it is significant in the first observation (table No.1). On the other hand the sulphur products appear at run six. These may be due to an adsorption of cyclohexanethiol and subsequent desorption after a few hours.

In the case of the other three major components, their molecular ions are quite intense, but vary from run to run. (Fig. 1).

(FIG 1)



% REL INTENSITY
100
90
80
70
60
50
40
30
20
10
1
2
3
4
5
6
7
8
9
10
Run NO.
←P-XYLENE
← N-METHYLMORPHOLIN
← n-Nonane

CONCLUSION

Use of high resolution mass spectrometry clarified the composition of fifteen extra compounds and also ten protonated ions, induced by electron impact of a four component mixture (table No. 7). Evidence suggests some synthetic reactions occur by recombination of fragment ions from different parents.

The adsorption of cyclohexanethiol on the surface of the source was proved by the absence of its molecular ion in the mass spectra of the mixture (see Appendix). Decomposition of the new products has been shown by loss of hydrogen from their parent ions and the existence of some fragments related to the products. From the results obtained it can be proposed that the analysis of mixtures by mass spectrometry may not be an efficient technique , particularly when the mixture contains some sulphur species.

APPENDIX

High Resolution Mass Spectral Data

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                      PAGE    1

           UNIVERSITY OF STRATHCLYDE


        DEPARTMENT OF PURE AND APPLIED CHEMISTRY


         MASS SPECTROMETRY LABORATORY


       CALCULATION OF HIGH RESOLUTION MASS SPECTRUM


OUR COMPONENET MIXTURE.


UBMITTED BY
 BORHANI.


ECTRUM REFERENCE NO.      4218






          ELEMENT   MAX NO.  ATOMIC WEIGHT

              *C        2         13.00336
               O        1         15.99491
               N        1         14.00307
               S        1         31.97207


AX. ALLOWED ERROR    10.0 PPM,    OR    0.007


AX. NO. OF CARBON ATOMS      10
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                              PAGE     2

          CALCULATION OF HIGH RESOLUTION MASS SPECTRUM

SPECTRUM REFERENCE NO.       4218
  RUN NO.       1

   FOUND        THEORY       C     H     *C     O     N     S     ERROR      AREA

  129.1605     129.1643      9    21     0     0     0     0     -29.5       2.5
               129.1598      8    20     1     0     0     0       5.1       2.5
  128.1569     128.1565      9    20     0     0     0     0       3.0      24.8
  108.0852     108.0813      7    10     0     0     1     0      35.9       0.6
  107.0817     107.0861      8    11     0     0     0     0     -41.3      15.6
  106.0705     106.0657      7     8     0     0     1     0      45.7      92.9
  105.0686     105.0704      8     9     0     0     0     0     -17.0      57.6
               105.0660      7     8     1     0     0     0      25.5      57.6
  104.0619     104.0626      8     8     0     0     0     0      -7.0       7.6
               104.0581      7     7     1     0     0     0      36.8       7.6
  103.0544     103.0548      8     7     0     0     0     0      -4.0      13.4
               103.0503      7     6     1     0     0     0      39.4      13.4
  102.0468     102.0469      8     6     0     0     0     0      -1.7       3.1
               102.0425      7     5     1     0     0     0      42.1       3.1
  101.0390     101.0391      8     5     0     0     0     0      -1.3       0.5
  100.1203     100.1252      7    16     0     0     0     0     -49.0       0.9
               100.1207      6    15     1     0     0     0      -4.3       0.9
   99.1171      99.1174      7    15     0     0     0     0      -2.8      11.1
                99.1129      6    14     1     0     0     0      42.2      11.1
   98.1096      98.1095      7    14     0     0     0     0       0.2       6.4
                98.1051      6    13     1     0     0     0      45.8       6.4
   98.0156      98.0156      8     2     0     0     0     0      -0.9       0.5
   97.1018      97.1017      7    13     0     0     0     0       0.8       1.2
   93.0624      93.0578      6     7     0     0     1     0      49.4       0.7
   92.0581      92.0626      7     8     0     0     0     0     -48.7      16.4
   91.0475      91.0422      6     5     0     0     1     0      58.1     100.0
   90.0455      90.0469      7     6     0     0     0     0     -15.6       1.5
   89.0379      89.0391      7     5     0     0     0     0     -14.3       4.0
   87.0218      87.0235      7     3     0     0     0     0     -19.2       0.7
   86.1035      86.1095      6    14     0     0     0     0     -70.4       3.6
                86.0970      5    12     0     0     1     0      75.6       3.6
   86.0135      86.0156      7     2     0     0     0     0     -24.8       0.7
   85.0999      85.1017      6    13     0     0     0     0     -21.6      45.6
   84.0917      84.0939      6    12     0     0     0     0     -26.1      14.9
   83.0831      83.0861      6    11     0     0     0     0     -35.6       0.8
   82.0752      82.0782      6    10     0     0     0     0     -36.8       0.6
   80.0550      80.0500      5     6     0     0     1     0      62.8       0.9
   79.0507      79.0548      6     7     0     0     0     0     -51.4      12.7
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      CALCULATION OF HIGH RESOLUTION MASS SPECTRUM

ECTRUM REFERENCE NO.        4218
 RUN NO.        2

  FOUND       THEORY      C     H    *C     O     N     S    ERROR     AREA

128.1572    128.1565      9    20     0     0     0     0      5.7     15.8
107.0816    107.0861      8    11     0     0     0     0    -42.0      9.4
            107.0816      7    10     1     0     0     0     -0.3      9.4
106.0776    106.0782      8    10     0     0     0     0     -5.8     95.7
            106.0738      7     9     1     0     0     0     36.3     95.7
105.0702    105.0704      8     9     0     0     0     0     -2.1     41.3
104.0615    104.0626      8     8     0     0     0     0    -10.9      4.5
            104.0581      7     7     1     0     0     0     32.0      4.5
103.0541    103.0548      8     7     0     0     0     0     -6.9      8.2
 99.1170     99.1174      7    15     0     0     0     0     -4.2      7.5
             99.1129      6    14     1     0     0     0     40.9      7.5
 98.1092     98.1095      7    14     0     0     0     0     -3.1      4.3
 92.0584     92.0626      7     8     0     0     0     0    -45.7      9.8
             92.0581      6     7     1     0     0     0      2.9      9.8
 91.0548     91.0548      7     7     0     0     0     0      0.5    100.0
 89.0397     89.0391      7     5     0     0     0     0      6.5      2.3
 86.1059     86.1095      6    14     0     0     0     0    -42.0      2.3
 85.1028     85.1017      6    13     0     0     0     0     12.4     31.8
             85.0972      5    12     1     0     0     0     64.9     31.8
 84.0947     84.0939      6    12     0     0     0     0     10.1      9.0
 79.0553     79.0548      6     7     0     0     0     0      6.5      7.3
             79.0503      5     6     1     0     0     0     63.0      7.3
 78.0469     78.0469      6     6     0     0     0     0     -0.2      7.0
 77.0400     77.0391      6     5     0     0     0     0     10.8     16.2
 71.0869     71.0861      5    11     0     0     0     0     11.1     23.9
 70.0794     70.0782      5    10     0     0     0     0     16.7     14.8
 69.0713     69.0704      5     9     0     0     0     0     12.7      2.9
 65.0403     65.0391      5     5     0     0     0     0     17.6      7.7
 63.0246     63.0235      5     3     0     0     0     0     17.5      5.2
 58.0747     58.0782      4    10     0     0     0     0    -61.2      3.7
 58.0430     58.0419      3     6     0     1     0     0     19.1      4.3
 57.0710     57.0704      4     9     0     0     0     0     10.5     73.8
             57.0660      3     8     1     0     0     0     88.8     73.8
 56.0632     56.0626      4     8     0     0     0     0     10.0     18.7
             56.0581      3     7     1     0     0     0     89.7     18.7
 55.0552     55.0548      4     7     0     0     0     0      8.6     18.7
 53.0394     53.0391      4     5     0     0     0     0      4.4      5.9
             53.0347      3     4     1     0     0     0     88.7      5.9
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         CALCULATION OF HIGH RESOLUTION MASS SPECTRUM

SPECTRUM REFERENCE NO.       4218
  RUN NO.        2


  FOUND       THEORY      C     H    *C     O     N     S   ERROR     AREA

 52.0312     52.0313     4     4     0     0     0     0    -1.3      7.6
             52.0268     3     3     1     0     0     0    84.6      7.6
 51.0237     51.0235     4     3     0     0     0     0     4.9     15.0
             51.0190     3     2     1     0     0     0    92.5     15.0
 50.0159     50.0156     4     2     0     0     0     0     4.3      5.1
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CALCULATION OF HIGH RESOLUTION MASS SPECTRUM

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SPECTRUM REFERENCE NO.      4218
 RUN NO.       3

 FOUND       THEORY      C     H    *C     O     N     S     ERROR     AREA

129.1599    129.1643     9    21     0     0     0     0     -34.0      1.5
            129.1598     8    20     1     0     0     0       0.6      1.5
128.1563    128.1565     9    20     0     0     0     0      -1.7     14.5
107.0822    107.0861     8    11     0     0     0     0     -36.1     11.9
106.0755    106.0782     8    10     0     0     0     0     -25.5     95.5
            106.0738     7     9     1     0     0     0      16.6     95.5
105.0707    105.0704     8     9     0     0     0     0       2.6     45.2
            105.0660     7     8     1     0     0     0      45.1     45.2
104.0617    104.0626     8     8     0     0     0     0      -8.6      5.5
            104.0581     7     7     1     0     0     0      34.3      5.5
103.0547    103.0548     8     7     0     0     0     0      -0.4     10.1
            103.0503     7     6     1     0     0     0      43.0     10.1
102.0468    102.0469     8     6     0     0     0     0      -1.3      1.9
 99.1169     99.1174     7    15     0     0     0     0      -4.9      7.4
             99.1129     6    14     1     0     0     0      40.2      7.4
 98.1093     98.1095     7    14     0     0     0     0      -2.9      4.1
 92.0585     92.0626     7     8     0     0     0     0     -44.8     12.9
 91.0522     91.0548     7     7     0     0     0     0     -27.9    100.0
             91.0503     6     6     1     0     0     0      21.2    100.0
 90.0468     90.0469     7     6     0     0     0     0      -1.8      1.1
             90.0425     6     5     1     0     0     0      47.8      1.1
 89.0395     89.0391     7     5     0     0     0     0       4.4      2.8
 86.1056     86.1095     6    14     0     0     0     0     -45.7      2.4
             86.1051     5    13     1     0     0     0       6.2      2.4
 85.1021     85.1017     6    13     0     0     0     0       4.4     35.4
 84.0948     84.0939     6    12     0     0     0     0      10.8      9.6
 79.0552     79.0548     6     7     0     0     0     0       5.9      9.6
             79.0503     5     6     1     0     0     0      62.4      9.6
 78.0466     78.0469     6     6     0     0     0     0      -3.9      7.6
             78.0425     5     5     1     0     0     0      53.3      7.6
 77.0395     77.0391     6     5     0     0     0     0       5.5     19.4
             77.0347     5     4     1     0     0     0      63.5     19.4
 76.0316     76.0313     6     4     0     0     0     0       3.5      1.3
             76.0268     5     3     1     0     0     0      62.3      1.3
 75.0236     75.0235     6     3     0     0     0     0       1.3      1.2
             75.0190     5     2     1     0     0     0      60.8      1.2
 74.0163     74.0156     6     2     0     0     0     0       8.5      1.7
 72.0900     72.0939     5    12     0     0     0     0     -53.6      1.4
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         CALCULATION OF HIGH RESOLUTION MASS SPECTRUM


ECTRUM REFERENCE NO.        4218
 RUN NO.        3


 FOUND        THEORY      C     H    *C     O     N     S    ERROR      AREA

              72.0894     4    11     1     0     0     0      8.4       1.4
71.0864       71.0861     5    11     0     0     0     0      3.9      24.2
              71.0816     4    10     1     0     0     0     66.8      24.2
70.0785       70.0782     5    10     0     0     0     0      4.0      15.3
              70.0738     4    -9     1     0     0     0     67.8      15.3
69.0710       69.0704     5     9     0     0     0     0      7.9       2.9
67.0548       67.0548     5     7     0     0     0     0      0.9       1.1
66.0458       66.0469     5     6     0     0     0     0    -18.1       1.4
              66.0425     4     5     1     0     0     0     49.6       1.4
65.0397       65.0391     5     5     0     0     0     0      8.8       8.7
64.0306       64.0313     5     4     0     0     0     0    -11.4       1.4
              64.0268     4     3     1     0     0     0     58.4       1.4
63.0237       63.0235     5     3     0     0     0     0      3.8       6.7
              63.0190     4     2     1     0     0     0     74.7       6.7
62.0154       62.0156     5     2     0     0     0     0     -4.4       2.3
58.0736       58.0782     4    10     0     0     0     0    -80.3       3.8
58.0416       58.0419     3     6     0     1     0     0     -5.1      13.0
57.0693       57.0704     4     9     0     0     0     0    -19.0      71.7
56.0619       56.0626     4     8     0     0     0     0    -12.7      18.6
              56.0581     3     7     1     0     0     0     67.8      18.6
55.0542       55.0548     4     7     0     0     0     0    -10.1      11.4
54.0458       54.0469     4     6     0     0     0     0    -21.2       1.5
              54.0425     3     5     1     0     0     0     61.5       1.5
53.0386       53.0391     4     5     0     0     0     0    -10.0       7.5
52.0304       52.0313     4     4     0     0     0     0    -16.7      11.0
              52.0268     3     3     1     0     0     0     69.2      11.0
51.0233       51.0235     4     3     0     0     0     0     -4.1      19.2
              51.0190     3     2     1     0     0     0     83.5      19.2
50.0157       50.0156     4     2     0     0     0     0      0.8       5.8
45.0361       45.0340     2     5     0     1     0     0     46.2       1.4
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         CALCULATION OF HIGH RESOLUTION MASS SPECTRUM

ECTRUM REFERENCE NO.       4218
RUN NO.        4

 FOUND       THEORY      C      H     *C      O      N      S     ERROR      AREA

129.1602   129.1643      9     21      0      0      0      0     -32.0       1.3
           129.1598      8     20      1      0      0      0       2.6       1.3
128.1570   128.1565      9     20      0      0      0      0       4.0      13.4
107.0819   107.0861      8     11      0      0      0      0     -38.9       9.5
106.0761   106.0782      8     10      0      0      0      0     -19.9      78.2
           106.0738      7      9      1      0      0      0      22.2      78.2
105.0708   105.0704      8      9      0      0      0      0       3.2      45.9
           105.0660      7      8      1      0      0      0      45.8      45.9
104.0623   104.0626      8      8      0      0      0      0      -2.9       4.5
           104.0581      7      7      1      0      0      0      40.1       4.5
103.0546   103.0548      8      7      0      0      0      0      -1.6       8.2
           103.0503      7      6      1      0      0      0      41.8       8.2
102.0472   102.0469      8      6      0      0      0      0       2.5       1.8
 99.1169    99.1174      7     13      0      0      0      0      -4.7       7.2
            99.1129      6     14      1      0      0      0      40.4       7.2
 98.1098    98.1095      7     14      6      0      0      0       2.8       3.9
 32.0584    32.0626      7      8      0      0      0      0     -45.7      11.2
 91.0516    91.0548      7      7      0      0      0      0     -34.4     100.0
            91.0503      6      6      1      0      0      0      14.7     100.0
 90.0463    90.0469      7      6      0      0      0      0      -7.1       1.1
            90.0425      6      5      1      0      0      0      42.5       1.1
 89.0399    89.0391      7      5      0      0      0      0       8.8       2.6
 86.1060    86.1095      6     14      0      0      0      0     -40.8       2.3
            86.1051      5     13      1      0      0      0      11.1       2.3
 85.1025    85.1017      6     13      0      0      0      0       8.9      31.8
            85.0972      5     12      1      0      0      0      61.5      31.8
 84.0942    84.0939      6     12      0      0      0      0       3.8      10.1
 79.0549    79.0548      6      7      0      0      0      0       1.6       8.6
            79.0503      5      6      1      0      0      0      58.1       8.6
 78.0466    78.0469      6      6      0      0      0      0      -4.3       8.1
            78.0425      5      5      1      0      0      0      52.9       8.1
 77.0396    77.0391      6      5      0      0      0      0       5.7      18.9
            77.0347      5      4      1      0      0      0      63.8      18.9
 76.0311    76.0313      6      4      0      0      0      0      -2.2       1.2
            76.0268      5      3      1      0      0      0      56.6       1.2
 75.0235    75.0235      6      3      0      0      0      0      -0.1       1.2
            75.0190      5      2      1      0      0      0      59.5       1.2
 74.0157    74.0156      6      2      0      0      0      0       1.4       1.5
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        CALCULATION OF HIGH RESOLUTION MASS SPECTRUM


ECTRUM REFERENCE NO.      4218
 RUN NO.        4


 FOUND      THEORY      C    H    *C    O    N    S    ERROR    AREA

72.0893    72.0939      5   12    0     0    0    0    -63.6     1.4
71.0850    71.0861      5   11    0     0    0    0    -14.9    27.5
           71.0816      4   10    1     0    0    0     48.0    27.5
70.0785    70.0782      5   10    0     0    0    0      3.6    16.0
           70.0738      4    9    1     0    0    0     67.3    16.0
69.0704    69.0704      5    9    0     0    0    0     -0.8     2.9
66.0454    66.0469      5    6    0     0    0    0    -24.8     1.3
           66.0425      4    5    1     0    0    0     43.6     1.3
65.0389    65.0391      5    5    0     0    0    0     -3.3     8.2
64.0303    64.0313      5    4    0     0    0    0    -16.3     1.5
           64.0268      4    3    1     0    0    0     53.5     1.5
63.0237    63.0235      5    3    0     0    0    0      2.8     5.9
           63.0190      4    2    1     0    0    0     73.8     5.9
62.0162    62.0156      5    2    0     0    0    0      8.7     2.2
58.0735    58.0782      4   10    0     0    0    0    -82.4     4.1
           58.0738      3    9    1     0    0    0     -5.4     4.1
58.0421    58.0419      3    6    0     1    0    0      4.9     7.5
57.0701    57.0704      4    9    0     0    0    0     -5.7    69.2
           57.0660      3    8    1     0    0    0     72.6    69.2
56.0626    56.0626      4    8    0     0    0    0      0.8    20.0
           56.0581      3    7    1     0    0    0     80.5    20.0
55.0552    55.0548      4    7    0     0    0    0      8.2    10.9
           55.0503      3    6    1     0    0    0     89.4    10.9
54.0466    54.0469      4    6    0     0    0    0     -6.4     1.4
           54.0425      3    5    1     0    0    0     76.3     1.4
53.0395    53.0391      4    5    0     0    0    0      7.6     6.4
           53.0347      3    4    1     0    0    0     91.9     6.4
52.0313    52.0313      4    4    0     0    0    0     -0.1    10.5
           52.0268      3    3    1     0    0    0     85.8    10.5
51.0238    51.0235      4    3    0     0    0    0      6.0    17.9
           51.0190      3    2    1     0    0    0     93.6    17.9
50.0159    50.0156      4    2    0     0    0    0      4.1     5.3
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           CALCULATION OF HIGH RESOLUTION MASS SPECTRUM

PECTRUM REFERENCE NO.        4218
 RUN NO.       5

 FOUND       THEORY       C      H     *C      O      N      S     ERROR     AREA

129.1603    129.1643      9     21      0      0      0      0     -30.7      1.4
            129.1598      8     20      1      0      0      0       3.9      1.4
128.1566    128.1565      9     20      0      0      0      0       0.8     13.4
107.0822    107.0861      8     11      0      0      0      0     -35.9      9.3
106.0766    106.0782      8     10      0      0      0      0     -15.2     77.1
            106.0738      7      9      1      0      0      0      26.9     77.1
105.0707    105.0704      8      9      0      0      0      0       3.0     45.1
            105.0660      7      8      1      0      0      0      45.6     45.1
104.0621    104.0626      8      8      0      0      0      0      -4.7      4.2
            104.0581      7      7      1      0      0      0      38.3      4.2
103.0546    103.0548      8      7      0      0      0      0      -1.7      8.3
            103.0503      7      6      1      0      0      0      41.7      8.3
102.0469    102.0469      8      6      0      0      0      0      -0.9      1.6
 99.1169     99.1174      7     15      0      0      0      0      -4.7      7.1
             99.1129      6     14      1      0      0      0      40.3      7.1
 98.1090     98.1095      7     14      0      0      0      0      -5.9      3.8
 92.0583     92.0626      7      8      0      0      0      0     -47.2     10.1
 91.0518     91.0548      7      7      0      0      0      0     -32.5    100.0
 90.0459     90.0469      7      6      0      0      0      0     -12.1      0.9
             90.0425      6      5      1      0      0      0      37.5      0.9
 89.0394     89.0391      7      5      0      0      0      0       3.6      2.6
 86.1051     86.1095      6     14      0      0      0      0     -51.6      2.3
             86.1051      5     13      1      0      0      0       0.3      2.3
 85.1018     85.1017      6     13      0      0      0      0       1.2     32.5
             85.0972      5     12      1      0      0      0      53.8     32.5
 84.0942     84.0939      6     12      0      0      0      0       3.9      9.2
 79.0549     79.0548      6      7      0      0      0      0       1.5      8.5
             79.0503      5      6      1      0      0      0      58.1      8.5
 78.0463     78.0469      6      6      0      0      0      0      -8.2      7.3
             78.0425      5      5      1      0      0      0      49.1      7.3
 77.0391     77.0391      6      5      0      0      0      0      -0.2     17.9
             77.0347      5      4      1      0      0      0      57.9     17.9
 76.0309     76.0313      6      4      0      0      0      0      -5.0      1.1
             76.0268      5      3      1      0      0      0      53.8      1.1
 75.0236     75.0235      6      3      0      0      0      0       1.7      1.2
             75.0190      5      2      1      0      0      0      61.2      1.2
 74.0156     74.0156      6      2      0      0      0      0      -0.4      1.4
 72.0897     72.0939      5     12      0      0      0      0     -58.8      1.3
 71.0844     71.0861      5     11      0      0      0      0     -23.4     29.3
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        CALCULATION OF HIGH RESOLUTION MASS SPECTRUM

ECTRUM REFERENCE NO.      4218
 RUN NO.       5


 FOUND        THEORY       C      H      *C      O      N      S     ERROR     AREA

              71.0816      4     10       1      0      0      0      39.5     29.3
 70.0783      70.0782      5     10       0      0      0      0       0.3     14.3
              70.0738      4      9       1      0      0      0      64.1     14.3
 70.0660      70.0657      4      8       0      0      1      0       4.0      0.9
 69.0705      69.0704      5      9       0      0      0      0       0.9      2.7
 67.0549      67.0548      5      7       0      0      0      0       1.4      0.8
 66.0457      66.0469      5      6       0      0      0      0     -19.6      1.1
              66.0425      4      5       1      0      0      0      48.0      1.1
 65.0396      65.0391      5      5       0      0      0      0       7.0      7.9
              65.0347      4      4       1      0      0      0      75.7      7.9
 64.0309      64.0313      5      4       0      0      0      0      -6.9      1.4
              64.0269      4      3       1      0      0      0      62.9      1.4
 63.0236      63.0235      5      3       0      0      0      0       1.3      5.3
              63.0190      4      2       1      0      0      0      72.2      5.3
 62.0157      62.0156      5      2       0      0      0      0       1.1      1.9
 58.0742      58.0782      4     10       0      0      0      0     -69.3      3.8
              58.0738      3      9       1      0      0      0       7.7      3.8
 58.0423      58.0419      3      6       0      1      0      0       7.8      6.4
 57.0706      57.0704      4      9       0      0      0      0       2.5     73.3
              57.0660      3      8       1      0      0      0      80.9     73.3
 56.0630      56.0626      4      8       0      0      0      0       7.4     18.9
              56.0581      3      7       1      0      0      0      87.1     18.9
 56.0509      56.0500      3      6       0      0      1      0      15.4      1.2
 55.0553      55.0548      4      7       0      0      0      0       9.8     10.1
              55.0503      3      6       1      0      0      0      91.0     10.1
 54.0468      54.0469      4      6       0      0      0      0      -2.0      1.3
              54.0425      3      5       1      0      0      0      80.7      1.3
 53.0392      53.0391      4      5       0      0      0      0       1.4      6.5
              53.0347      3      4       1      0      0      0      85.7      6.5
 52.0310      52.0313      4      4       0      0      0      0      -5.6      9.4
              52.0268      3      3       1      0      0      0      80.3      9.4
 51.0231      51.0235      4      3       0      0      0      0      -7.4     16.8
              51.0190      3      2       1      0      0      0      80.2     16.8
 50.0156      50.0156      4      2       0      0      0      0      -0.9      5.6
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        CALCULATION OF HIGH RESOLUTION MASS SPECTRUM

PECTRUM REFERENCE NO.       4218
 RUN NO.    6


  FOUND       THEORY     C     H    *C     O     N     S    ERROR      AREA

129.1607    129.1643     9    21     0     0     0     0    -28.3       1.6
            129.1598     8    20     1     0     0     0      6.3       1.6
128.1570    128.1565     9    20     0     0     0     0      3.7      16.4
126.1411    126.1408     9    18     0     0     0     0      2.0       0.2
108.0858    108.0813     7    10     0     0     1     0     41.4       0.4
107.0822    107.0861     8    11     0     0     0     0    -36.1      10.8
            107.0769     4    13     0     0     1     1     49.9      10.8
106.0763    106.0782     8    10     0     0     0     0    -18.0      89.9
            106.0738     7     9     1     0     0     0     24.2      89.9
            106.0816     5    14     0     0     0     1    -49.7      89.9
106.0483    106.0419     7     6     0     1     0     0     60.6       0.2
            106.0452     4    10     0     1     0     1     28.8       0.2
105.0709    105.0704     8     9     0     0     0     0      4.2      43.2
            105.0660     7     8     1     0     0     0     46.7      43.2
            105.0738     5    13     0     0     0     1    -27.9      43.2
104.0623    104.0626     8     8     0     0     0     0     -2.9       5.3
            104.0581     7     7     1     0     0     0     40.1       5.3
            104.0660     5    12     0     0     0     1    -35.2       5.3
103.0552    103.0548     8     7     0     0     0     0      4.4       9.5
            103.0503     7     6     1     0     0     0     47.8       9.5
            103.0581     5    11     0     0     0     1    -28.3       9.5
102.0858    102.0919     5    12     0     1     1     0    -59.9       1.7
            102.0874     4    11     1     1     1     0    -16.1       1.7
102.0469    102.0469     8     6     0     0     0     0     -0.8       2.0
            102.0425     7     5     1     0     0     0     43.0       2.0
            102.0503     5    10     0     0     0     1    -33.8       2.0
101.0837    101.0841     5    11     0     1     1     0     -3.3      18.3
            101.0796     4    10     1     1     1     0     41.0      18.3
101.0395    101.0391     8     5     0     0     0     0      3.6       0.3
            101.0425     5     9     0     0     0     1    -29.7       0.3
100.1211    100.1252     7    16     0     0     0     0    -41.3       0.6
            100.1207     6    15     1     0     0     0      3.4       0.6
100.0761    100.0762     5    10     0     1     1     0     -1.8       3.2
 99.1170     99.1174     7    15     0     0     0     0     -4.0       7.7
             99.1129     6    14     1     0     0     0     41.1       7.7
 98.1091     98.1095     7    14     0     0     0     0     -4.4       4.6
             98.1051     6    13     1     0     0     0     41.2       4.6
 98.0156     98.0156     8     2     0     0     0     0     -0.9       0.4
             98.0190     5     6     0     0     0     1    -35.3       0.4
 97.1020     97.1017     7    13     0     0     0     0      2.9       0.7
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        CALCULATION OF HIGH RESOLUTION MASS SPECTRUM

SPECTRUM REFERENCE NO.      4218
  RUN NO.       6


  FOUND      THEORY      C     H    *C     O     N     S     ERROR     AREA

 93.0612    93.0578      6     7     0     0     1     0      36.6      0.4
            93.0612      3    11     0     0     1     1       0.3      0.4
 92.0583    92.0626      7     8     0     0     0     0     -46.9     10.9
            92.0534      3    10     0     0     1     1      53.1     10.9
 91.0516    91.0548      7     7     0     0     0     0     -35.3    100.0
            91.0503      6     6     1     0     0     0      13.8    100.0
            91.0581      4    11     0     0     0     1     -72.3    100.0
            91.0456      3     9     0     0     1     1      65.8    100.0
 90.0461    90.0469      7     6     0     0     0     0      -9.4      1.0
            90.0425      6     5     1     0     0     0      40.3      1.0
            90.0503      4    10     0     0     0     1     -46.8      1.0
 89.0394    89.0391      7     5     0     0     0     0       3.4      2.8
            89.0425      4     9     0     0     0     1     -34.5      2.8
 87.0235    87.0235      7     3     0     0     0     0       0.7      0.5
            87.0190      6     2     1     0     0     0      52.1      0.5
            87.0268      4     7     0     0     0     1     -38.0      0.5
 86.1058    86.1095      6    14     0     0     0     0     -43.9      2.6
            86.1051      5    13     1     0     0     0       8.0      2.6
 86.0608    86.0606      4     8     0     1     1     0       2.8      0.1
 86.0163    86.0156      7     2     0     0     0     0       7.9      0.5
            86.0112      6     1     1     0     0     0      59.9      0.5
            86.0190      4     6     0     0     0     1     -31.3      0.5
 85.1024    85.1017      6    13     0     0     0     0       7.7     36.0
            85.0972      5    12     1     0     0     0      60.3     36.0
 84.0942    84.0939      6    12     0     0     0     0       4.1     10.7
            84.0894      5    11     1     0     0     0      57.3     10.7
 83.0865    83.0861      6    11     0     0     0     0       5.6      0.5
            83.0816      5    10     1     0     0     0      59.4      0.5
 82.0787    82.0782      6    10     0     0     0     0       5.4      0.2
            82.0738      5     9     1     0     0     0      59.9      0.2
 81.0710    81.0704      6     9     0     0     0     0       7.2      0.1
 80.0591    80.0626      6     8     0     0     0     0     -43.9      0.7
            80.0581      5     7     1     0     0     0      12.0      0.7
 79.0549    79.0548      6     7     0     0     0     0       1.5      8.3
            79.0503      5     6     1     0     0     0      58.1      8.3
 78.0470    78.0469      6     6     0     0     0     0       0.3      8.2
            78.0503      3    10     0     0     0     1     -42.9      8.2
 77.0406    77.0391      6     5     0     0     0     0      11.8     18.7
            77.0347      5     4     1     0     0     0      69.8     18.7
            77.0425      3     9     0     0     0     1     -31.9     18.7
 76.0317    76.0313      6     4     0     0     0     0       5.4      1.3
            76.0347      3     8     0     0     0     1     -38.9      1.3
 75.0242    75.0235      6     3     0     0     0     0      10.2      1.4
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          CALCULATION OF HIGH RESOLUTION MASS SPECTRUM

SPECTRUM REFERENCE NO.        4210
  RUN NO.        6


  FOUND       THEORY     C    H   *C    O    N    S    ERROR    AREA

             75.0268     3    7    0    0    0    1    -34.7     1.4
 74.0165     74.0156     6    2    0    0    0    0     11.3     1.7
             74 0112     5    1    1    0    0    0     71.7     1.7
             74.0190     3    6    0    0    0    1    -34.2     1.7
 72.0898     72.0939     5   12    0    0    0    0    -56.3     1.7
 72.0787     72.0813     4   10    0    0    1    0    -35.7     0.4
 71.0841     71.0861     5   11    0    0    0    0    -28.3    34.6
             71.0816     4   10    1    0    0    0     34.6    34.6
 70.0777     70.0782     5   10    0    0    0    0     -7.1    18.0
             70.0738     4    9    1    0    0    0     56.7    18.0
 69.0707     69.0704     5    9    0    0    0    0      4.2     3.3
             69.0660     4    8    1    0    0    0     68.9     3.3
 68.0631     68.0626     5    8    0    0    0    0      7.2     0.3
             68.0581     4    7    1    0    0    0     72.9     0.3
 67.0545     67.0548     5    7    0    0    0    0     -2.2     0.8
 66.0452     66.0469     5    6    0    0    0    0    -25.9     1.4
             66.0425     4    5    1    0    0    0     41.8     1.4
 65.0392     65.0391     5    5    0    0    0    0      1.3     0.9
 65.0286     65.0265     4    3    0    0    1    0    -31.5     0.5
 64.0304     64.0313     5    4    0    0    0    0    -13.4     1.4
             64.0268     4    3    1    0    0    0     56.4     1.4
             64 0347     2    8    0    0    0    1    -66.1     1.4
 63.0236     63.0235     5    3    0    0    0    0      2.4     6.0
             63.0190     4    2    1    0    0    0     73.3     6.0
             63.0269     2    7    0    0    0    1    -51.1     6.0
 62.0157     62.0156     5    2    0    0    0    0      1.2     2.2
             62.0112     4    1    1    0    0    0     73.3     2.2
             62.0190     2    6    0    0    0    1    -53.1     2.2
 59.0453     59.0497     3    7    0    1    0    0    -73.8     0.2
             59.0452     2    6    1    1    0    0      1.9     0.2
 58.0731     58.0782     4   10    0    0    0    0    -88.4     4.6
 58.0419     58.0419     3    6    0    1    0    0      0.5     6.2
             58.0374     2    5    1    1    0    0     77.5     6.2
 57.0697     57.0704     4    9    0    0    0    0    -13.3    74.3
             57.0660     3    8    1    0    0    0     65.0    74.3
 57.0338     57.0340     3    5    0    1    0    0     -4.1     0.2
 56.0625     56.0626     4    8    0    0    0    0     -1.8    21.0
             56.0581     3    7    1    0    0    0     77.9    21.0
 56.0500     56.0500     3    6    0    0    1    0     -0.4     2.0
             56.0456     2    5    1    0    1    0     79.3     2.0
 55.0547     55.0548     4    7    0    0    0    0     -0.8    12.0
 55.0424     55.0422     3    5    0    0    1    0      3.1     0.4
             55.0377     2    4    1    0    1    0     84.3     0.4
```

CALCULATION OF HIGH RESOLUTION MASS SPECTRUM

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ECTRUM REFERENCE NO.       4218
 RUN NO.       6

 FOUND       THEORY     C    H    *C    O    N    S    ERROR    AREA

 54.0459    54.0469     4    6    0     0    0    0    -20.1     1.4
            54.0425     3    5    1     0    0    0     62.6     1.4
 54.0342    54.0344     3    4    0     0    1    0     -3.6     0.5
 53.0390    53.0391     4    5    0     0    0    0     -2.1     7.4
            53.0347     3    4    1     0    0    0     82.2     7.4
 52.0308    52.0313     4    4    0     0    0    0     -9.1     9.8
            52.0268     3    3    1     0    0    0     76.8     9.8
 51.0233    51.0235     4    3    0     0    0    0     -3.5    19.2
            51.0190     3    2    1     0    0    0     84.1    19.2
 51.0128    51.0190     3    2    1     0    0    0   -122.3     0.2
            51.0109     3    1    0     0    1    0     36.6     0.2
            51.0143     0    5    0     0    1    1    -29.5     0.2
 50.0155    50.0156     4    2    0     0    0    0     -2.6     6.2
            50.0112     3    1    1     0    0    0     86.8     6.2
            50.0190     1    6    0     0    0    1    -70.0     6.2
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                    PAGE    15

        CALCULATION OF HIGH RESOLUTION MASS SPECTRUM

SPECTRUM REFERENCE NO.      4218
  RUN NO.      7

  FOUND      THEORY     C    H   *C    O    N    S    ERROR     AREA

129.1603   129.1643     9   21    0    0    0    0    -30.9      1.7
           129.1598     8   20    1    0    0    0      3.7      1.7
128.1573   128.1565     9   20    0    0    0    0      5.9     17.4
126.1414   126.1408     9   18    0    0    0    0      4.3      0.1
108.0852   108.0813     7   10    0    0    1    0     35.6      0.4
107.0820   107.0861     8   11    0    0    0    0    -38.3     10.5
           107.0769     4   13    0    0    1    1     47.7     10.5
106.0766   106.0782     8   10    0    0    0    0    -15.1     86.2
           106.0738     7    9    1    0    0    0     27.0     86.2
           106.0816     5   14    0    0    0    1    -46.9     86.2
106.0512   106.0452     4   10    0    1    0    1     56.6      0.3
105.0701   105.0704     8    9    0    0    0    0     -2.7     47.0
           105.0660     7    8    1    0    0    0     39.9     47.0
           105.0738     5   13    0    0    0    1    -34.8     47.0
104.0623   104.0626     8    8    0    0    0    0     -2.8      5.0
           104.0581     7    7    1    0    0    0     40.2      5.0
           104.0660     5   12    0    0    0    1    -35.1      5.0
103.0551   103.0548     8    7    0    0    0    0      3.1      0.3
           103.0503     7    6    1    0    0    0     46.5      0.3
           103.0581     5   11    0    0    0    1    -29.6      0.3
102.0862   102.0919     5   12    0    1    1    0    -55.8      2.0
           102.0874     4   11    1    1    1    0    -12.0      2.0
102.0473   102.0469     8    6    0    0    0    0      3.4      1.9
           102.0425     7    5    1    0    0    0     47.2      1.9
           102.0503     5   10    0    0    0    1    -29.7      1.9
101.0840   101.0841     5   11    0    1    1    0     -0.3     25.2
           101.0796     4   10    1    1    1    0     43.9     25.2
101.0391   101.0391     8    5    0    0    0    0     -0.2      0.3
           101.0425     5    9    0    0    0    1    -33.6      0.3
100.1208   100.1252     7   16    0    0    0    0    -44.4      0.6
           100.1207     6   15    1    0    0    0      0.3      0.6
100.0766   100.0762     5   10    0    1    1    0      3.4      4.1
 99.1169    99.1174     7   15    0    0    0    0     -4.9      7.4
            99.1129     6   14    1    0    0    0     40.2      7.4
 99.0705    99.0684     5    9    0    1    1    0     21.2      0.1
 98.1097    98.1095     7   14    0    0    0    0      1.9      4.5
            98.1051     6   13    1    0    0    0     47.5      4.5
 98.0160    98.0156     8    2    0    0    0    0      3.3      0.3
            98.0190     5    6    0    0    0    1    -31.1      0.3
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CALCULATION OF HIGH RESOLUTION MASS SPECTRUM

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SPECTRUM REFERENCE NO.      4210
 RUN NO.       7

 FOUND       THEORY      C    H    *C    O    N    S    ERROR    AREA

 97.1017     97.1017     7   13    0     0    0    0     -0.4     0.6
 93.0619     93.0578     6    7    0     0    1    0     43.3     0.4
             93.0612     3   11    0     0    1    1      7.1     0.4
 92.0581     92.0626     7    8    0     0    0    0    -48.5    11.0
             92.0534     3   10    0     0    1    1     51.5    11.0
 91.0529     91.0548     7    7    0     0    0    0    -20.2   100.0
             91.0503     6    6    1     0    0    0     28.9   100.0
             91.0581     4   11    0     0    0    1    -57.2   100.0
 90.0469     90.0469     7    6    0     0    0    0     -1.0     1.0
             90.0425     6    5    1     0    0    0     48.6     1.0
             90.0503     4   10    0     0    0    1    -38.5     1.0
 89.0400     89.0391     7    5    0     0    0    0     10.0     2.5
             89.0425     4    9    0     0    0    1    -27.9     2.5
 87.0244     87.0235     7    3    0     0    0    0     10.8     0.5
             87.0268     4    7    0     0    0    1    -28.0     0.5
 86.1062     86.1095     6   14    0     0    0    0    -38.5     2.6
             86.1051     5   13    1     0    0    0     13.4     2.6
 86.0624     86.0606     4    8    0     1    1    0     21.4     0.2
 86.0168     86.0156     7    2    0     0    0    0     13.1     0.4
             86.0190     4    6    0     0    0    1    -26.1     0.4
 85.1026     85.1017     6   13    0     0    0    0      9.8    37.7
 84.0953     84.0939     6   12    0     0    0    0     16.4    10.1
 83.0871     83.0861     6   11    0     0    0    0     12.9     0.5
 82.0796     82.0782     6   10    0     0    0    0     16.0     0.2
 80.0593     80.0626     6    8    0     0    0    0    -41.5     0.6
 79.0556     79.0548     6    7    0     0    0    0     10.6     0.4
             79.0503     5    6    1     0    0    0     67.2     0.4
 78.0473     78.0469     6    6    0     0    0    0      4.3     7.6
             78.0503     3   10    0     0    0    1    -38.9     7.6
 77.0399     77.0391     6    5    0     0    0    0     10.6    10.5
             77.0347     5    4    1     0    0    0     68.6    10.5
             77.0425     3    9    0     0    0    1    -33.1    10.5
 76.0320     76.0313     6    4    0     0    0    0      8.9     1.2
             76.0347     3    8    0     0    0    1    -35.4     1.2
 75.0242     75.0235     6    3    0     0    0    0     10.3     1.2
             75.0268     3    7    0     0    0    1    -34.7     1.2
 74.0167     74.0156     6    2    0     0    0    0     14.5     1.6
             74.0190     3    6    0     0    0    1    -31.1     1.6
 72.0870     72.0939     5   12    0     0    0    0    -95.5     2.3
             72.0813     4   10    0     0    1    0     78.9     2.3
 71.0835     71.0861     5   11    0     0    0    0    -36.3    36.6
 70.0775     70.0782     5   10    0     0    0    0    -10.9    10.0
             70.0738     4    9    1     0    0    0     52.8    10.0
```

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        CALCULATION OF HIGH RESOLUTION MASS SPECTRUM

PECTRUM REFERENCE NO.       4218
 RUN NO.      7


 FOUND       THEORY     C    H   *C    O    N    S   ERROR    AREA

 69.0706     69.0704    5    9    0    0    0    0     3.0     3.2
             69.0668    4    8    1    0    0    0    67.7     3.2
 68.0625     68.0626    5    8    0    0    0    0    -1.2     0.3
             68.0581    4    7    1    0    0    0    64.5     0.3
 67.0547     67.0548    5    7    0    0    0    0    -0.9     0.8
 66.0457     66.0469    5    6    0    0    0    0   -18.6     1.3
             66.0425    4    5    1    0    0    0    49.1     1.3
 65.0392     65.0391    5    5    0    0    0    0     1.5     8.4
 65.0209     65.0265    4    3    0    0    1    0   -86.4     0.4
 64.0302     64.0313    5    4    0    0    0    0   -17.3     1.4
             64.0268    4    3    1    0    0    0    52.5     1.4
             64.0347    2    8    0    0    0    1   -69.9     1.4
 63.0233     63.0235    5    3    0    0    0    0    -2.3     6.4
             63.0190    4    2    1    0    0    0    68.6     6.4
             63.0268    2    7    0    0    0    1   -55.8     6.4
 62.0154     62.0156    5    2    0    0    0    0    -3.9     2.1
             62.0112    4    1    1    0    0    0    68.1     2.1
             62.0198    2    6    0    0    0    1   -58.3     2.1
 58.0729     58.0782    4   10    0    0    0    0   -92.8     4.3
             58.0738    3    9    1    0    0    0   -15.8     4.3
 58.0415     58.0419    3    6    0    1    0    0    -5.8     5.2
 57.0699     57.0704    4    9    0    0    0    0    -8.5    78.1
 56.0610     56.0626    4    8    0    0    0    0   -27.8    23.6
             56.0581    3    7    1    0    0    0    51.9    23.6
 55.0546     55.0548    4    7    0    0    0    0    -2.3    11.6
 55.0418     55.0422    3    5    0    0    1    0    -7.0     0.5
             55.0377    2    4    1    0    1    0    74.2     0.5
 54.0464     54.0469    4    6    0    0    0    0   -10.7     1.4
             54.0425    3    5    1    0    0    0    72.0     1.4
 54.0345     54.0344    3    4    0    0    1    0     2.3     0.6
 53.0392     53.0391    4    5    0    0    0    0     1.6     6.6
             53.0347    3    4    1    0    0    0    85.9     6.6
 52.0314     52.0313    4    4    0    0    0    0     2.3     8.5
             52.0268    3    3    1    0    0    0    88.2     8.5
 51.0237     51.0235    4    3    0    0    0    0     3.8    16.3
             51.0190    3    2    1    0    0    0    91.4    16.3
 50.0159     50.0156    4    2    0    0    0    0     4.2     5.9
             50.0112    3    1    1    0    0    0    93.6     5.9
             50.0190    1    6    0    0    0    1   -63.2     5.9
 45.0341     45.0340    2    5    0    1    0    0     0.9     0.9
```

CALCULATION OF HIGH RESOLUTION MASS SPECTRUM

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PECTRUM REFERENCE NO.      4218
 RUN NO.      8

  FOUND       THEORY     C    H   *C    O    N    S    ERROR     AREA

 129.1602    129.1643    9   21    0    0    0    0    -32.0      1.5
             129.1598    8   20    1    0    0    0      2.6      1.5
 128.1570    128.1565    9   20    0    0    0    0      4.2     14.2
 126.1414    126.1408    9   18    0    0    0    0      4.4      0.2
 108.0859    108.0850    6   10    2    0    0    0      8.6      0.3
             108.0813    7   10    0    0    1    0     42.3      0.3
 107.0826    107.0861    8   11    0    0    0    0    -32.9      9.4
             107.0816    7   10    1    0    0    0      8.9      9.4
             107.0769    4   13    0    0    1    1     53.1      9.4
 106.0775    106.0782    8   10    0    0    0    0     -7.4     83.5
             106.0738    7    9    1    0    0    0     34.7     83.5
             106.0816    5   14    0    0    0    1    -39.2     83.5
 105.0703    105.0704    8    9    0    0    0    0     -1.2     44.6
             105.0660    7    8    1    0    0    0     41.3     44.6
             105.0738    5   13    0    0    0    1    -33.3     44.6
 104.0620    104.0626    8    8    0    0    0    0     -5.8      4.5
             104.0581    7    7    1    0    0    0     37.1      4.5
             104.0660    5   12    0    0    0    1    -38.2      4.5
 103.0547    103.0548    8    7    0    0    0    0     -1.0      8.2
             103.0503    7    6    1    0    0    0     42.4      8.2
             103.0581    5   11    0    0    0    1    -33.7      8.2
 102.0865    102.0919    5   12    0    1    1    0    -52.3      2.3
             102.0874    4   11    1    1    1    0     -8.6      2.3
 102.0469    102.0469    8    6    0    0    0    0     -0.2      1.8
             102.0425    7    5    1    0    0    0     43.6      1.8
             102.0503    5   10    0    0    0    1    -33.2      1.8
 101.0836    101.0841    5   11    0    1    1    0     -4.4     30.8
             101.0796    4   10    1    1    1    0     39.8     30.8
 101.0392    101.0391    8    5    0    0    0    0      0.5      0.3
             101.0425    5    9    0    0    0    1    -32.9      0.3
 100.1209    100.1252    7   16    0    0    0    0    -42.6      0.5
             100.1207    6   15    1    0    0    0      2.1      0.5
 100.0761    100.0762    5   10    0    1    1    0     -1.5      5.4
             100.0718    4    9    1    1    1    0     43.1      5.4
  99.1169     99.1174    7   15    0    0    0    0     -4.3      6.9
              99.1129    6   14    1    0    0    0     40.8      6.9
  99.0677     99.0684    5    9    0    1    1    0     -6.7      0.3
  98.1095     98.1095    7   14    0    0    0    0     -0.5      4.3
              98.1051    6   13    1    0    0    0     45.0      4.3
  98.0160     98.0156    8    2    0    0    0    0      4.0      0.3
```

CALCULATION OF HIGH RESOLUTION MASS SPECTRUM

SPECTRUM REFERENCE NO. 4218
RUN NO. 8

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 FOUND      THEORY     C  .  H    *C     O     N     S    ERROR     AREA

            98.0190    5     6     0     0     0     1    -30.4       0.3
 97.1023    97.1017    7    13     0     0     0     0      5.7       0.6
 93.0616    93.0578    6     7     0     0     1     0     40.2       0.3
            93.0612    3    11     0     0     1     1      4.8       0.3
 92.0582    92.0626    7     8     0     0     0     0    -47.6      11.2
            92.0534    3    10     0     0     1     1     52.4      11.2
 91.0526    91.0548    7     7     0     0     0     0    -23.7     100.0
            91.0581    4    11     0     0     0     1    -60.7     100.0
 90.0460    90.0469    7     6     0     0     0     0    -10.4       0.9
            90.0425    6     5     1     0     0     0     39.3       0.9
            90.0503    4    10     0     0     0     1    -47.8       0.9
 89.0392    89.0391    7     5     0     0     0     0      1.2       2.8
            89.0425    4     9     0     0     0     1    -36.6       2.8
 87.0233    87.0235    7     3     0     0     0     0     -1.7       0.4
            87.0190    6     2     1     0     0     0     49.6       0.4
            87.0268    4     7     0     0     0     1    -40.5       0.4
 86.1053    86.1095    6    14     0     0     0     0    -48.7       2.4
            86.1051    5    13     1     0     0     0      3.2       2.4
 86.0605    86.0606    4     8     0     1     1     0     -0.5       0.2
 86.0156    86.0156    7     2     0     0     0     0     -0.5       0.4
            86.0190    4     6     0     0     0     1    -39.7       0.4
 85.1019    85.1017    6    13     0     0     0     0      2.0      36.2
            85.0972    5    12     1     0     0     0     54.5      36.2
 84.0938    84.0939    6    12     0     0     0     0     -1.0       9.6
            84.0894    5    11     1     0     0     0     52.1       9.6
 83.0863    83.0861    6    11     0     0     0     0      2.8       0.4
 80.0585    80.0626    6     8     0     0     0     0    -51.4       0.6
            80.0581    5     7     1     0     0     0      4.5       0.6
 79.0546    79.0548    6     7     0     0     0     0     -2.0       8.8
            79.0503    5     6     1     0     0     0     54.5       8.8
 78.0465    78.0469    6     6     0     0     0     0     -6.0       7.9
            78.0425    5     5     1     0     0     0     51.3       7.9
            78.0503    3    10     0     0     0     1    -49.2       7.9
 77.0396    77.0391    6     5     0     0     0     0      6.2      18.9
            77.0347    5     4     1     0     0     0     64.2      18.9
            77.0425    3     9     0     0     0     1    -37.5      18.9
 76.0316    76.0313    6     4     0     0     0     0      3.7       1.1
            76.0268    5     3     1     0     0     0     62.5       1.1
            76.0347    3     8     0     0     0     1    -40.6       1.1
 75.0237    75.0235    6     3     0     0     0     0      2.6       1.2
            75.0190    5     2     1     0     0     0     62.2       1.2
            75.0268    3     7     0     0     0     1    -42.3       1.2
 74.0161    74.0156    6     2     0     0     0     0      6.1       1.7
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         CALCULATION OF HIGH RESOLUTION MASS SPECTRUM

SPECTRUM REFERENCE NO.       4210
  RUN NO.    8


  FOUND       THEORY      C     H    *C     O     N     S     ERROR     AREA

             74.0190      3     6     0     0     0     1     -39.4      1.7
 72.0851     72.0813      4    10     0     0     1     0      52.8      2.4
 71.0815     71.0861      5    11     0     0     0     0     -64.5     38.9
 70.0765     70.0782      5    10     0     0     0     0     -24.3     20.1
             70.0738      4     9     1     0     0     0      39.5     20.1
 69.0704     69.0704      5     9     0     0     0     0      -0.4      3.1
             69.0660      4     8     1     0     0     0      64.3      3.1
 68.0625     68.0626      5     8     0     0     0     0      -1.6      0.3
             68.0581      4     7     1     0     0     0      64.1      0.3
 67.0549     67.0548      5     7     0     0     0     0       1.4      0.8
 66.0456     66.0469      5     6     0     0     0     0     -20.1      1.3
             66.0425      4     5     1     0     0     0      47.6      1.3
 65.0393     65.0391      5     5     0     0     0     0       2.8      8.2
             65.0347      4     4     1     0     0     0      71.5      8.2
 65.0207     65.0265      4     3     0     0     1     0     -90.1      0.4
 64.0311     64.0313      5     4     0     0     0     0      -3.3      1.4
             64.0347      2     8     0     0     0     1     -55.9      1.4
 63.0242     63.0235      5     3     0     0     0     0      11.1      6.7
             63.0268      2     7     0     0     0     1     -42.4      6.7
 62.0163     62.0156      5     2     0     0     0     0      10.2      2.4
             62.0190      2     6     0     0     0     1     -44.2      2.4
 59.0474     59.0497      3     7     0     1     0     0     -38.6      0.2
 58.0741     58.0782      4    10     0     0     0     0     -72.1      4.4
             58.0738      3     9     1     0     0     0       4.8      4.4
 58.0426     58.0419      3     6     0     1     0     0      13.1      5.7
 57.0707     57.0704      4     9     0     0     0     0       5.2     86.6
 57.0348     57.0340      3     5     0     1     0     0      12.5      0.2
 56.0608     56.0626      4     8     0     0     0     0     -31.6     24.5
             56.0581      3     7     1     0     0     0      48.1     24.5
 55.0551     55.0548      4     7     0     0     0     0       6.0     12.4
             55.0503      3     6     1     0     0     0      87.2     12.4
 55.0422     55.0422      3     5     0     0     1     0      -0.4      0.6
             55.0377      2     4     1     0     1     0      80.8      0.6
 54.0465     54.0469      4     6     0     0     0     0      -9.0      1.4
             54.0425      3     5     1     0     0     0      73.7      1.4
 54.0347     54.0344      3     4     0     0     1     0       5.6      0.9
 53.0390     53.0391      4     5     0     0     0     0      -2.4      6.8
             53.0347      3     4     1     0     0     0      81.9      6.8
 52.0311     52.0313      4     4     0     0     0     0      -4.6      9.7
             52.0268      3     3     1     0     0     0      81.3      9.7
 51.0233     51.0235      4     3     0     0     0     0      -3.4     17.9
             51.0190      3     2     1     0     0     0      84.2     17.9
 50.0154     50.0156      4     2     0     0     0     0      -5.8      5.8
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        CALCULATION OF HIGH RESOLUTION MASS SPECTRUM

PECTRUM REFERENCE NO.       4218
 RUN NO.     8


 FOUND       THEORY      C     H    *C     O     N     S    ERROR     AREA

             50.0112     3     1     1     0     0     0     83.6      5.0
             50.0190     1     6     0     0     0     1    -73.2      5.0
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        CALCULATION OF HIGH RESOLUTION MASS SPECTRUM

PECTRUM REFERENCE NO.      4218
 RUN NO.      9

 FOUND       THEORY       C    H    *C    O    N    S    ERROR     AREA

129.1596    129.1643     9   21    0    0    0    0    -36.2      1.5
            129.1598     8   20    1    0    0    0     -1.6      1.5
128.1565    128.1565     9   20    0    0    0    0     -0.3     14.9
108.0857    108.0813     7   10    0    0    1    0     40.2      0.3
107.0811    107.0861     8   11    0    0    0    0    -46.2      8.9
            107.0769     4   13    0    0    1    1     39.7      8.9
106.0761    106.0782     8   10    0    0    0    0    -20.4     78.7
            106.0738     7    9    1    0    0    0     21.7     78.7
            106.0816     5   14    0    0    0    1    -52.2     78.7
105.0704    105.0704     8    9    0    0    0    0     -0.3     49.0
            105.0660     7    8    1    0    0    0     42.2     49.0
            105.0738     5   13    0    0    0    1    -32.4     49.0
104.0616    104.0626     8    8    0    0    0    0     -9.3      4.5
            104.0581     7    7    1    0    0    0     33.7      4.5
            104.0660     5   12    0    0    0    1    -41.7      4.5
103.0547    103.0548     8    7    0    0    0    0     -0.4      7.9
            103.0503     7    6    1    0    0    0     43.0      7.9
            103.0581     5   11    0    0    0    1    -33.1      7.9
102.0867    102.0919     5   12    0    1    1    0    -51.1      2.8
            102.0874     4   11    1    1    1    0     -7.3      2.8
102.0471    102.0469     8    6    0    0    0    0      1.3      1.8
            102.0425     7    5    1    0    0    0     45.1      1.8
            102.0503     5   10    0    0    0    1    -31.7      1.8
101.0840    101.0841     5   11    0    1    1    0     -0.6     43.6
            101.0796     4   10    1    1    1    0     43.6     43.6
101.0393    101.0391     8    5    0    0    0    0      1.3      0.3
            101.0425     5    9    0    0    0    1    -32.1      0.3
100.1209    100.1252     7   16    0    0    0    0    -42.8      0.6
            100.1207     6   15    1    0    0    0      1.9      0.6
100.0764    100.0762     5   10    0    1    1    0      1.8      7.3
            100.0718     4    9    1    1    1    0     46.4      7.3
 99.1171     99.1174     7   15    0    0    0    0     -3.1      7.3
             99.1129     6   14    1    0    0    0     42.0      7.3
 99.0680     99.0684     5    9    0    1    1    0     -3.9      0.3
 98.1095     98.1095     7   14    0    0    0    0     -0.3      4.3
             98.1051     6   13    1    0    0    0     45.3      4.3
 98.0157     98.0156     8    2    0    0    0    0      0.9      0.3
             98.0190     5    6    0    0    0    1    -33.5      0.3
 97.1020     97.1017     7   13    0    0    0    0      3.2      0.6
```

CALCULATION OF HIGH RESOLUTION MASS SPECTRUM

PECTRUM REFERENCE NO. 4218
RUN NO. 9

FOUND	THEORY	C	H	*C	O	N	S	ERROR	AREA
93.0619	93.0578	6	7	0	0	1	0	43.6	0.4
	93.0612	3	11	0	0	1	1	7.4	0.4
92.0588	92.0625	7	8	0	0	0	0	-49.8	10.8
	92.0534	3	10	0	0	1	1	58.2	10.8
91.0525	91.0548	7	7	0	0	0	0	-25.4	100.0
	91.0581	4	11	0	0	0	1	-62.4	100.0
	91.0456	3	9	0	0	1	1	75.7	100.0
90.0455	90.0469	7	6	0	0	0	0	-15.6	0.9
	90.0503	4	10	0	0	0	1	-53.0	0.9
89.0378	89.0391	7	5	0	0	0	0	-14.4	2.4
	89.0425	4	9	0	0	0	1	-52.2	2.4
87.0214	87.0235	7	3	0	0	0	0	-23.4	0.4
	87.0268	4	7	0	0	0	1	-62.2	0.4
86.1029	86.1095	6	14	0	0	0	0	-76.9	2.2
	86.0970	5	12	0	0	1	0	69.1	2.2
86.0581	86.0606	4	8	0	1	1	0	-29.1	0.3
86.0130	86.0156	7	2	0	0	0	0	-31.1	0.4
	86.0190	4	6	0	0	0	1	-70.2	0.4
	86.0064	3	4	0	0	1	1	76.0	0.4
85.0987	85.1017	6	13	0	0	0	0	-35.8	34.0
84.0903	84.0939	6	12	0	0	0	0	-42.5	9.0
83.0821	83.0861	6	11	0	0	0	0	-48.2	0.4
80.0529	80.0500	5	6	0	0	1	0	35.7	0.6
79.0478	79.0422	5	5	0	0	1	0	70.5	7.3
	79.0456	2	9	0	0	1	1	27.8	7.3
78.0386	78.0344	5	4	0	0	1	0	53.9	7.3
	78.0377	2	8	0	0	1	1	10.7	7.3
77.0307	77.0265	5	3	0	0	1	0	54.0	16.5
	77.0299	2	7	0	0	1	1	10.2	16.5
	77.0254	1	6	1	0	1	1	68.3	16.5
76.0214	76.0187	5	2	0	0	1	0	34.7	1.1
	76.0221	2	6	0	0	1	1	-9.7	1.1
75.0123	75.0109	5	1	0	0	1	0	18.6	1.1
	75.0143	2	5	0	0	1	1	-26.4	1.1
68.0264	68.0262	4	4	0	1	0	0	3.0	0.1
66.0181	66.0139	1	6	0	1	0	1	62.8	1.1
65.0104	65.0061	1	5	0	1	0	1	66.2	7.3
58.0305	58.0293	2	4	0	1	1	0	21.3	3.9
57.0245	57.0215	2	3	0	1	1	0	52.6	72.0
56.0119	56.0136	2	2	0	1	1	0	-31.8	22.7

```
        CALCULATION OF HIGH RESOLUTION MASS SPECTRUM

PECTRUM REFERENCE NO.       4210
 RUN NO.     10


 FOUND       THEORY        C      H     *C      O      N      S     ERROR      AREA

129.1599    129.1643       9     21      0      0      0      0     -33.9       1.9
            129.1598       8     20      1      0      0      0       0.7       1.9
128.1569    128.1565       9     20      0      0      0      0       3.0      18.4
126.1415    126.1408       9     18      0      0      0      0       5.3       0.2
108.0632    108.0575       7      8      0      1      0      0      52.7       0.4
            108.0609       4     12      0      1      0      1      21.5       0.4
107.0572    107.0531       4     11      0      1      0      1      38.7      10.7
106.0497    106.0452       4     10      0      1      0      1      42.1     100.0
105.0387    105.0340       7      5      0      1      0      0      44.0      52.3
            105.0374       4      9      0      1      0      1      11.9      52.3
105.0199    105.0215       6      3      0      1      1      0     -15.0       0.2
            105.0248       3      7      0      1      1      1     -47.1       0.2
104.0266    104.0262       7      4      0      1      0      0       3.5       5.5
            104.0296       4      8      0      1      0      1     -28.9       5.5
103.0152    103.0184       7      3      0      1      0      0     -31.0       9.6
            103.0218       4      7      0      1      0      1     -63.8       9.6
            103.0092       3      5      0      1      1      1      58.3       9.6
102.0436    102.0469       8      6      0      0      0      0     -33.3       3.7
            102.0503       5     10      0      0      0      1     -66.3       3.7
            102.0377       4      8      0      0      1      1      56.9       3.7
101.0356    101.0391       8      5      0      0      0      0     -34.7      49.3
            101.0425       5      9      0      0      0      1     -68.0      49.3
            101.0299       4      7      0      0      1      1      56.4      49.3
100.0226    100.0187       7      2      0      0      1      0      38.6       8.8
            100.0221       4      6      0      0      1      1       4.9       8.8
 53.0396     53.0391       4      5      0      0      0      0       8.5       1.4
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Organic Mass Spectrometry

in press

The Analysis of some Heterocyclic Compounds

by

R. Borhani and R. I. Reed

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