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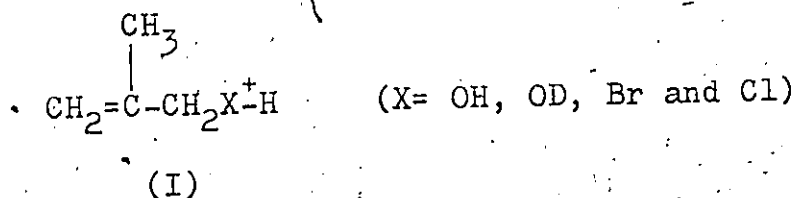
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ABSTRACTPART I: THE MASS SPECTRA OF SOME ORGANIC COMPOUNDSThe mass spectra of some neopentyl compounds

The mass spectra of neopentyl alcohol, bromide and chloride and some ^{13}C and ^2H labelled analogues have been studied. Most fragmentations of the molecular ions of these molecules occur by simple bond cleavages and do not involve rearrangement before fragmentations. The neopentyl cation, observed only in the mass spectrum of the bromide, fragments mainly by loss of an ethylene molecule containing randomly selected hydrogen and carbon atoms. The C_4H_7^+ ion also was observed to undergo complete atom scrambling.

Isomerization and decomposition reactions of $\text{C}_4\text{H}_8\text{X}^+$ ions

Isomeric $\text{C}_4\text{H}_8\text{X}^+$ ions ($\text{X} = \text{OH}, \text{OD}, \text{Br}$ and Cl) have been generated in the mass spectrometer from various sources. Extensive ^2H -labelling has been used to investigate the structures of the decomposing ions, and the mechanisms of decomposition. For the formation of $(\text{C}_4\text{H}_8\text{X}-\text{CH}_4)$, $(\text{C}_4\text{H}_8\text{X}-\text{C}_2\text{H}_4)$ and $(\text{C}_4\text{H}_8\text{X}-\text{HX})$ ions in the decomposition reactions of $(\text{CH}_3)_2\text{C}^+-\text{CH}_2\text{X}$, the common structure (I):



is the best representation of the decomposing ions. There is no evidence that the isomeric $\text{CH}_3\text{C}^+\text{HCH}_2\text{CH}_2\text{X}$ ions rearrange to

ions of structure (I).

The mass spectra of some chlorohydrins and some chloroacids.

The mass spectra of the homologous series of chlorohydrins $\text{HOH}_2\text{C}(\text{CH}_2)_n\text{CH}_2\text{Cl}$ from $n=0$ to 4, and $\text{ClCH}_2\text{C}(\text{CH}_3)_2\text{CH}_2\text{OH}$ have been studied together with certain deuterium labelled members. The fragmentation mechanisms of the lower homologues and $\text{ClCH}_2\text{C}(\text{CH}_3)_2\text{CH}_2\text{OH}$ are discussed in some detail. The losses of HCl and H_2O from the molecular ions arise from chlorine-hydroxyl and hydroxyl-methylene interaction respectively. The mass spectra of some chloroacids were also briefly investigated.

The mass spectra of some isomeric cyclic hydrocarbons

The mass spectra of methylcyclopentene and cyclohexene and 4-methylcyclohexene and cycloheptene and deuterium labelled derivatives thereof have been studied. Fragmentations of each pair of these isomers for the most part proceed via common intermediates in which hydrogen atoms have lost their positional identity. The loss of a methyl radical from methylcyclopentene and 4-methylcyclohexene molecular ions involve to a great extent, simple direct bond cleavage.

PART II: THE PYROLYSIS OF 2- and 3-CHLOROPENTANE

1. The decompositions of 3-chloropentane and 2-chloropentane were studied in a reaction vessel coated with carbon produced from cis-but-2-ene pyrolysis.
2. A temperature range of $293-376^\circ\text{C}$ was used for the pyrolyses.
3. The n-pentenes produced in the reactions were analyzed by

gas-liquid chromatography. The individual rate constants for their production and the corresponding Arrhenius parameters were calculated.

4. It was found that the trans- to cis-pent-2-ene product ratio from both pyrolyses indicates that coplanarity is a requirement of the transition state in these elimination reactions. That is, the trans-product predominated over the cis-form.

PART I

MASS SPECTROMETRY OF SOME ORGANIC COMPOUNDS

CHAPTER 1INTRODUCTIONGeneral Theory of Mass Spectrometry

The use of mass spectrometry for the identification of organic compounds is becoming extremely attractive to the organic chemist. The identification of structural features solely from mass spectral data is, however, no simple task. Although a sample molecule yields a characteristic mass spectrum, the exact behaviour of most organic compounds within the mass spectrometer is still largely unpredictable. While analysis is based on the assumption that the ground state geometry will be reflected in the fragmentation sequence, many examples are known wherein extensive, unpredictable rearrangements have occurred^{1a}. For example, hydrogen and even skeletal atoms have participated in the generation of the tropylium ion from numerous isomeric C_7H_8 compounds^{2-3, 16}, in the production of $C_2H_5^+$ in neopentane^{1(c), 4-6} and the loss of $^{13}C_2H_2$ from 1,3,5- $^{13}C_3$ -benzene⁷.

Such observations discourage one from the unequivocal assignment of definite structures to fragment ions, and even to molecular ions. Usually, many isomeric forms of a species can conceivably fragment according to the sequence registered in the mass spectrum. For molecular ions, it is assumed that the ground state geometry is retained, unless there is strong evidence to the contrary. This assumption will be made throughout this work. In fragmentation schemes, structures are shown to illustrate a possible dissociation sequence. These structures are justified by the observation of appropriate metastable

transitions and by analogy with neutral molecule chemistry (e.g. McLafferty rearrangement^{1b}). Another useful technique is high resolution mass spectrometry. For example, loss of C_2H_4 or CO of the same nominal mass from an ion can be distinguished. This difficulty in structural assignment, however, need not necessarily impair analysis of a mass spectrum, because knowledge of the exact structure of a fragment ion, while important, may not be essential. Indeed, whether the benzene molecular ion is linear or cyclic is of relatively little consequence. The important feature is the behaviour of the ion. For example, the fact it fragments mainly by loss of acetylene⁷ contributes more to the structural identification of this ion than the question of its exact shape.

At present, many compounds apparently fragment in a fashion peculiar to themselves. Thus it is difficult to extract general rules from the mass spectra of a series of related compounds. For this reason, the prediction of fragmentation sequences is hazardous. The description of adequate fragmentation mechanisms for compounds of known structure requires extensive investigation. It is hoped that when the behaviour of each functional group in a variety of environments has been described, its presence within a molecule will be more easily detected, and the identification of structural features in unknown molecules will become more feasible.

The Mass Spectrum

The production of a mass spectrum using a double focusing mass spectrometer of Nier-Johnson geometry will now be reviewed⁸. It should be noted that the instrument is operated

at low ambient pressure in order to avoid collision induced reactions between the various species present. Sample pressures in the range of 10^{-7} to 10^{-6} mm mercury, in the ion source, are sufficient to produce an intense spectrum.

Two inlet systems (a) (Fig. 1) are available for sample insertion. The direct inlet system may be used for relatively involatile samples. The all-glass heated inlet system is used for samples of high volatility. In the ion source, the sample molecules interact with a beam of high energy electrons (b) (the electrons suffer a potential drop of 70 volts), become energized, and produce molecular ions by ejection of an electron. These ions may then dissociate in a variety of ways.

When the sample molecules enter the ion source, they move with random velocity due to their thermal kinetic energy. This random velocity, when summed with that due to the acceleration potential (described below), produces a small energy distribution amongst the ions.

Upon formation, the ions experience an acceleration due to the potential difference between the walls of the ion source (V_{acc} volts) and the exit slit (0 volt). This acceleration directs the ions from the source towards the electrostatic sector (d) via the first field-free region (e). The potential across the electrostatic sector, E_{sector} is such that,

$$r_e = 2V_{acc}/E_{sector} \dots\dots\dots(1)$$

where r_e is the radius of curvature of ion path in the electrostatic sector and V_{acc} is the acceleration potential. Since r_e and E_{sector} are kept constant, only ions with acceleration potential

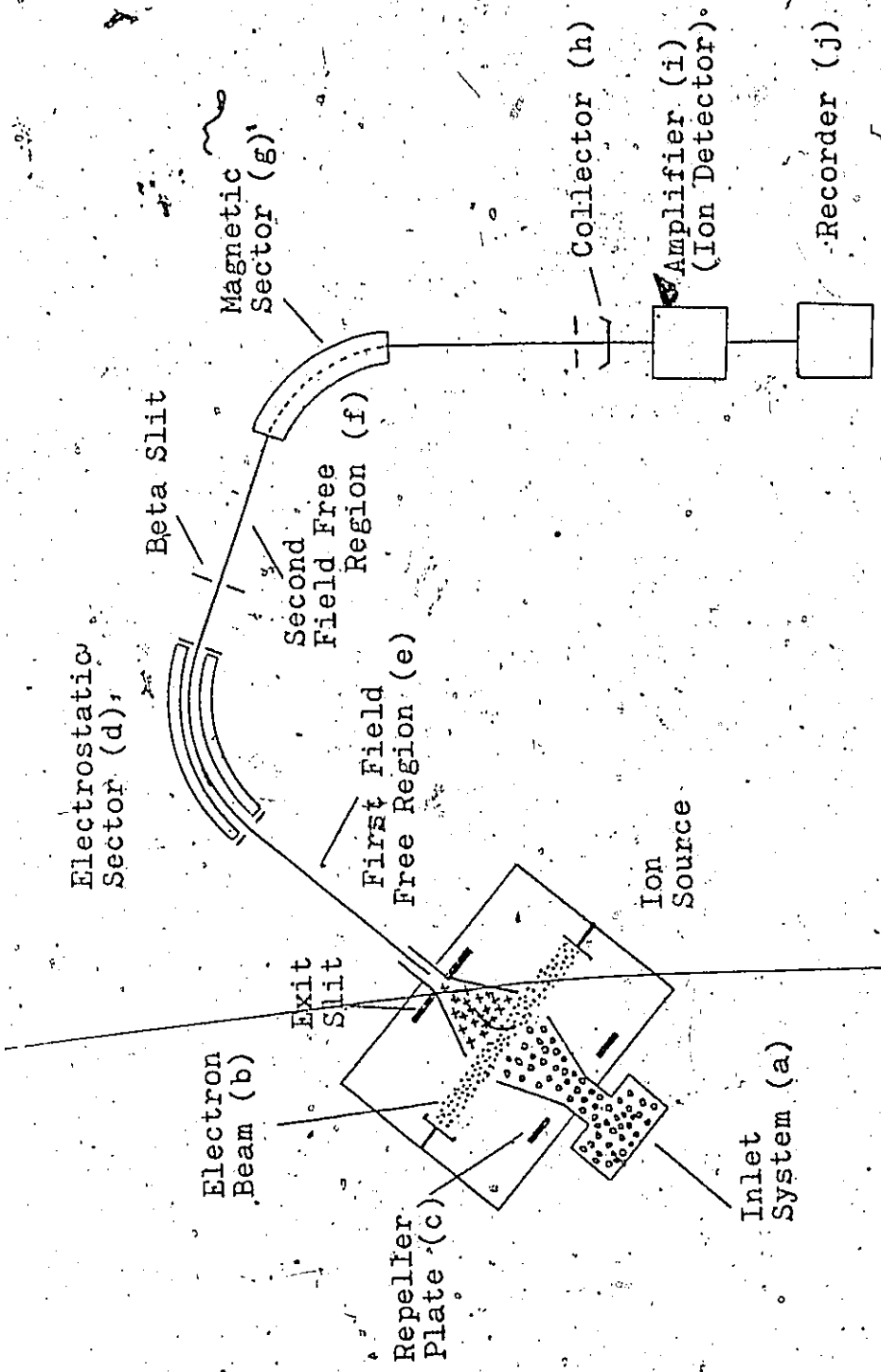


Fig. 1. Schematic diagram of a double-focusing mass spectrometer of Nier-Johnson geometry.

V_{acc} (that is, ions in a very narrow energy range) pass through the exit slit of the sector. The beam of transmitted ions then passes through the second field-free region (f) into the magnetic sector (g). Under the influence of the magnetic field, the ions will suffer a deflection through an angle that is proportional to their mass.

The motion of the ions thus far described may be represented by the following equations. If the acceleration potential is V_{acc} , the kinetic energy imparted to the ions will be

$$eV_{acc} = \frac{1}{2} mv^2 \dots\dots\dots (2)$$

where e = electronic charge

m = mass of the ion

v = velocity of the ion

In the magnetic sector, the centripetal force, Hev , due to the magnetic field is balanced by the centrifugal force, mv^2/r ,

$$Hev = mv^2/r \dots\dots\dots (3)$$

where H = magnetic field

r = radius of curvature of ion path

Eliminating v between (2) and (3) yields that,

$$m/e = H^2 r^2 / 2V_{acc} \dots\dots\dots (4)$$

Thus by using a combination of an electrostatic field and a magnetic field, one achieves velocity focusing (the focusing of an ion beam containing ions of the same mass travelling in the same direction, but with different energy), and direction

7-

focusing (the focusing of ions of all masses into individual beams containing only ions of one mass/charge ratio). This combination is called double-focusing.

The motion of the ion throughout its flight can be controlled by varying any of three parameters H , V_{acc} and r . It is obviously convenient to retain r constant. Two modes of scanning are then available in order to allow an ion of mass to charge ratio m/e to describe a path whose radius of curvature is r . Most instruments used magnetic scanning devices in conjunction with a fixed (but variable) acceleration potential. Ions of successive m/e values may then be focused to strike the collector plate (h). The induced current flowing from the collector may then be amplified (i) by one of the three methods, (A) Faraday cup, (B) electron multiplier, and (C) photomultiplier; and then recorded (j) conveniently by using a visicorder, i.e. recording on ultraviolet light sensitive paper.

For simple presentation, the intensity of the strongest peak (base peak) in the mass spectrum is arbitrarily equated to 100 units. Other peaks may then be measured relative to the base peak and plotted as a bar graph. This process yields the mass spectra shown throughout this work.

Ion Detectors

As mentioned above, the AEI MS 902S double-focusing mass spectrometer used in the present study is equipped with three types of ion detectors, namely, Faraday cup, electron multiplier and scintillator-photomultiplier.

(A) Faraday Cup

The small metal electrode that the positive ions intercept is mounted in a Faraday cup which has the form of an open-ended, reflecting cup. The metal surface is inclined with respect to the ion trajectory so that reflected ions or ejected secondary electrons cannot escape from the cup. Thus the measured and amplified ion current is directly proportional to the number of ions and number of charge per ion.

(B) Electron Multiplier

The electron multiplier utilizes the principle of secondary electron emission to effect amplification. In the mass spectrometer, the positive ions focused on the collector slit bombard the conversion dynode which emits electrons. These secondary electrons are accelerated and focused onto the second dynode. Amplification is accomplished through a "cascading effect" of secondary electrons from dynode to dynode because the number of electrons ejected from each dynode surface is greater than the number of electrons impinging upon it. Each dynode is connected to a successively higher potential by a voltage divider and the final collector is connected to a conventional amplifier.

(C) Scintillator-Photomultiplier -- the Daly Detector

The Daly detector, based on a scintillator/photomultiplier system, provides an excellent conventional detector with many desirable properties in addition to the metastable enhancement feature. The principle of operation is described below.

A schematic diagram of the Daly detector is shown as Fig. 2. Positive ions enter the detector through the mass

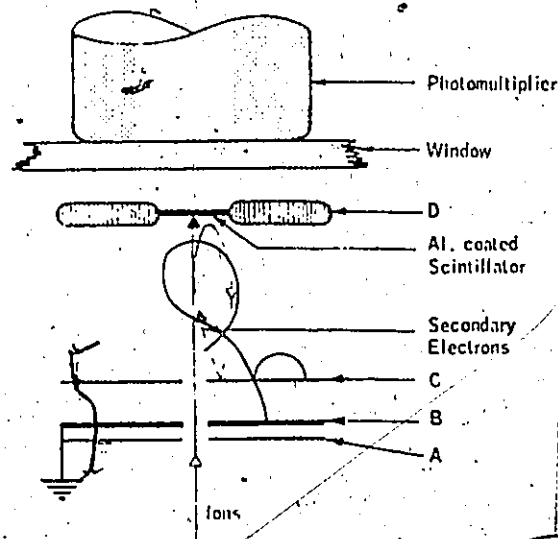


Fig. 2. Schematic diagram of a Daly detector

spectrometer resolving slit A and pass through another earthed slit B. The ions are then accelerated by the negative potential on C and pass through a slit in C. They are then retarded by the positive potential on the scintillator electrode D.

To detect normal peaks in addition to metastable peaks, D is at source potential or higher, and the ions are turned back and strike the surface of C. To ensure that ions travelling between C and D are turned away from the normal and thus do not travel back through the slit in C, C is asymmetric. Secondary electrons are emitted from C which accelerate to D, pass through the aluminium coating, and penetrate the scintillator. Electrons entering the scintillator cause light emission which passes through the glass window onto the photocathode of a photomultiplier. The output of the photomultiplier is then equivalent to a conventional mass spectrum.

When the potential of D is reduced below source voltage all the ions with source energy are lost to the scintillator aluminium coating. Thus only ions of lower energy are turned back and detected. In this case, only ions resulting from metastable transitions, in which kinetic energy has been lost, are recorded. Since normal peaks have been suppressed, higher gain can be used. Thus an enhanced metastable spectrum can be recorded.

Metastable Ions

(A) Second Field-free Region Generated Metastable Ions

Equation (4), above, is only valid for those ions that are formed within the ion source, and thus possess kinetic energy

eV_{acc} . If, however, an ion (m_1) fragments in the second field-free region, between the electrostatic sector and the magnetic sector of a double-focusing mass spectrometer, it will produce an ion (m^*) that has a mass (m_2), characteristic of its own chemical composition, but a velocity (v_1) characteristic of its precursor ion (m_1). Such ions (m^*) are energetically different from those ions of mass m_2 that are formed in the ion source. The latter ions, m_2 , will appear in the spectrum at m_2/e . The former, m^* , however, will appear as a broad diffuse peak²², centered at m_2^2/m_1 . These ions, m^* , are called metastable ions owing to the instability of their precursor ions. The presence of a metastable ion in a mass spectrum may be regarded as conclusive evidence for the transition that give rise to it. Caution must, however, be exercised, as more than one transition may yield a specific second field-free metastable ion. An example of this was found in the mass spectrum of o-Nitrobenzaldehyde⁹. A metastable ion was observed at 71.5 ± 0.2 . Two possible transitions (m/e 151 $\rightarrow$ m/e 104, $m^* = 71.6$; and m/e 121 $\rightarrow$ m/e 93, $m^* = 71.5$) could yield such a second field-free metastable ion. It is not immediately obvious which transition does so. However, the molecular ion (m/e 151) was very weak (~1% of base peak). Thus the second possibility is more likely. In the fragmentation schemes, where a dissociation is supported by a metastable ion peak, the transition is labelled by an asterisk.

(B) First Field-free Region Generated Metastable Ions¹⁰

Due to the energy focusing effect of the electrostatic field, it is not possible for both the main ion beam and the

metastable ions (formed in the first field-free region between the ion source and the electrostatic sector) to pass through the electrostatic unit at the same applied potential. This is because the metastable ions are energetically different from the main ion beam. The first field-free metastable ions for the metastable transition, $m_1^+ \rightarrow m_2^+$, can be observed uniquely either by increasing the ion accelerating potential by a factor m_1/m_2 (keeping the electrostatic sector voltage constant), or by reducing the electrostatic sector voltage by a factor m_2/m_1 (keeping the ion accelerating potential constant). In either case, the main beam of stable ions is then not transmitted.

Whichever method is used to study the metastable ion peaks in a mass spectrum, the position, shape and size of the peaks can be used to obtain useful structural information about the decomposing ions. These will be discussed further in a later section.

Analysis of a Mass Spectrum and Approaches to the Determination of Ion Structure

Having obtained the mass spectrum of the compound under investigation, various approaches are possible. The simplest is to record the relative intensities of the peaks, such compilations exist as the "Dow Uncertified Mass Spectra Data, 1963"; "Mass Spectrometry Data Centre, A.W.R.E., Aldermaston, Berks"; and "Compilation of Mass Spectra Data" (and its two supplements) by A. Cornu and R. Massot (Heyden and Son Ltd., 1966, 1967 and 1971). Only the ten most intense peaks are presented in the last compilations. This information, with the

molecular weight, then allows the organic chemist to identify his material by comparing its spectrum with those in the compilations. This process is greatly aided by computer methods. However, useful this approach may be to the organic chemist, it requires little or no understanding of the fragmentation mechanisms. If one is to identify "unidentified original compounds" that do not appear in such compilations, it will be necessary to have some understanding of fragmentation mechanisms. For this purpose, knowledge of the identity of the major peaks is needed. Of greater importance, perhaps, is the origin of each peak and its structure. Throughout this work, we are interested in the determination of ion structures and the fragmentation mechanisms for their formation.

By the structure of an ion, we mean "the arrangement of atoms at any one instant". The structure given to an ion will therefore depend on the experimental conditions.

During the last few years, it has been realized that there is far more information about ion structures and decomposition mechanisms to be gleaned from a mass spectrum than is obtainable merely from the normal ion abundances in the 70eV spectrum. Some of this extra information is easily obtainable from isotopic labelling experiments, from studies of metastable ions and from measurements of the heats of formation of ions. These will be discussed briefly.

(A) Isotopic Labelling Experiments

Isotopic labelling, combined with the assumption of minimum structure change and cyclic structures which are intuitively reasonable by analogy with ground state chemistry,

has been used to adduce the structures of ions. The labels, most commonly used, are ^2H , ^{13}C and ^{18}O .

In this method, we can only really propose transition-state structures because we study the movements of isotopic labels placed in known positions in a ground state molecule, and study their distribution among the various fragment ions.

There are two types of observations in an isotopic labelling experiments that are simple to interpret:

(1) Results showing either 0 or 100% incorporation of a label (or labels) into a fragment ion peak are easy to interpret. For example, in the mass spectra of some neopentyl compounds¹¹, $(\text{CH}_3)_3\text{-CCH}_2\text{-X}$ ($\text{X} = \text{OH}$, OD , Br and Cl), the 1,1-d₂ dideuterated neopentyl molecular ions give fragment ions C_4H_8^+ and C_4H_9^+ , and $\text{C}_4\text{H}_6\text{D}_2\text{X}^+$ and CD_2X^+ respectively. The results show complete loss of the labels for the former two fragments, but complete retention of labels for the latter. These indicate that molecular ions have fragmented by simple bond cleavage only. There is no rearrangement or atom scrambling before or during fragmentation (Chapter 2).

(2) Specific atom participation. Labelling shows which atom from the original molecule takes part in a particular fragmentation process. Information of this type is most useful. For example, we found that the molecular ions of a series of chlorohydrins, $\text{ClCH}_2(\text{CH}_2)_n\text{CH}_2\text{OH}$ ($n = 1$ to 4), fragment by hydrochloric acid loss. Deuterium labelling of the compounds in the hydroxyl position has shown that the hydrogen in the hydrochloric acid molecule originates mainly from the hydroxyl group (Chapter 4).

Apart from the above two types of observations, there

are inherent difficulties in the method. The interpretation of results have not always been correct because of scrambling of labels, isotope effects and interference by secondary fragmentations (Chapter 5).

(B) Studies of Metastable Ions

There are several reasons for the utility of metastable transitions in the investigation of mass spectral processes.

(i) Unlike reactions occurring in the ion source, metastable transitions occur from a narrow range of ion energies corresponding to rate constants for decomposition of 10^4 - 10^6 sec⁻¹. (ii)

The occurrence, absence or relative abundance of metastable transitions for different processes give valuable information on relative activation energies. (iii) Information about

rearrangement reactions may be obtained by appropriate comparison of metastable and normal ion abundances. (iv) Competing meta-

stable abundance ratios are a valuable criterion for the identity or non-identity of ion structures. (v) Since metastable

transitions uniquely define a reaction, it is much simpler (and often the only way) to study scrambling reactions. (vi) The

metastable defocusing technique has enabled metastable ions to be uniquely and sensitively identified. (vii) Shapes of meta-

stable ion peaks provide another criterion for the non-identity of ion structures where shapes are different. (viii) Isotope

effects are largest in metastable transitions. Throughout this work, extensive use of metastable transitions in the study of mass spectral processes has been attempted.

Recently, Yeo and Williams¹² proposed that if a given ion undergoes two or more competing metastable decompositions;

the rates for the two or more processes must be similar. Further, if two ions of the same elemental composition undergo the same metastable decompositions in the same or similar ratios, this is an excellent criterion that the two ions are decomposing from the same structure (or structures). This was justified by Yeo and Williams¹² who showed theoretically and experimentally that the ratio of metastable abundances for two competing reactions at any given internal energy is a function of the internal energy of the ion generating the metastable ions. Therefore, ions with the same structure but different internal energies can give rise to significantly different metastable abundance ratios. It follows that ions decomposing in the first field-free region can also give rise to metastable abundance ratios significantly different from those decomposing in the second field-free region.

This criterion has been used to establish that isomeric $C_2H_5O^+$ ions decompose from two distinct structures¹³⁻¹⁵ and that n-, sec-, iso- and tert-butyl bromide provide $C_4H_9^+$ ions which decompose from the same structure (or structures)^{17, 30}.

Evidently, the activation energies required for interconversion of the various butyl ions are less than that required for unimolecular decomposition. In general, it appears that the presence of heteroatoms O, N, Br and Cl in organic ions increases the barriers for internal rearrangements, relative to those for unimolecular decompositions (Chapter 3).

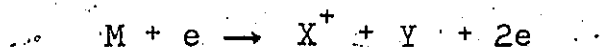
To summarize: the metastable ion abundance ratios criterion for ion structure determination compares ion structures from different sources at energies just above the lowest activation

energy for decomposition. The applicability of the method is limited by the requirement for two or more competing reactions.

The shapes of metastable ion peaks provide another criterion for the non-identity of ion structures where shapes are different. For example, we have established that for the (M-CH₃) processes in the mass spectra of cyclohexene and methylcyclopentene; and cycloheptene and 4-methylcyclohexene, the molecular ions of each pair of compounds (dissociating within the first field-free region) have at least two (or more) distinguishable structures and /or electronic excited states (Chapter 5).

(C) Measurements of Heats of Formation of Ions

The comparison of heats of formation of organic ions in the mass spectrometer is the most widely used criterion for the identity or non-identity of ion structures. For the reaction,



the appearance potential, AP(X⁺), of X⁺ may be expressed as shown in equation 5:

$$AP(X^+) = \Delta H_f(X^+) + \Delta H_f(Y) - \Delta H_f(M) + E_1 \dots \dots \dots (5)$$

the term ΔH_f is the heat of formation of the species. E_1 is included to allow for possible formation of either X⁺ and/or Y with excess energy at the threshold for the reaction.

The measured appearance potential is not necessarily equal to the minimum energy that must be imparted to the neutral molecule M in order to form M⁺. The excess energy (above the minimum energy for reaction) required to achieve a rate constant

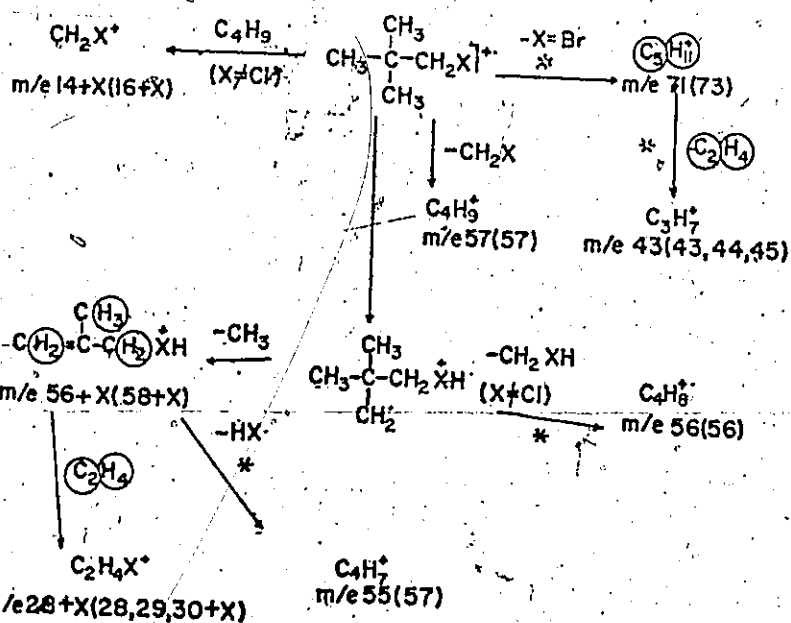
such that the ion is generated in the ion source is termed the "kinetic shift"¹⁸. The consequence of the kinetic shift is that appearance potential measurements for daughter ions, produced in the ion source (and hence their heats of formation) will be too high. Appearance potential values, however, obtained by electron-impact by using an electron monochromator combined with a quadrupole mass filter¹⁹ were lower than those obtained using a conventional mass spectrometric ion source²⁰. Those former values were free of any appreciable error due to kinetic shift because the ion withdrawal potential and the acceleration potential were very low (~ 50 mv). Such error, may, however, be present in values obtained with conventional mass spectrometers. Another factor should be recognized which may compromise appearance potential (and/or ionization potential) measurements. McLafferty and his co-workers²¹ noted the occurrence of the "competitive shift" which may arise where two k vs E curves cross, k represents the rate constant at total energy E of a reaction. The reaction which has the higher appearance potential may need to proceed at a rate considerably faster than 10^6 s^{-1} to compete with the other reaction sufficiently to be observed in the ion source.

It is generally accepted that if the heats of formation of an ion X^+ produced from different sources are identical, then the structure of the ion is the same. Lossing²³, for example, generated $C_3H_5^+$ and $C_4H_7^+$ from five isomeric C_4H_8 molecules using mono-energetic electrons¹⁹. The heats of formation of all $C_3H_5^+$ and $C_4H_7^+$ were found to be 226 ± 2 kcal/mole and 206 kcal/mole respectively. Ionization potentials have been measured for

C_3H_5 allyl radicals (8.07 v)²⁴ and C_4H_7 methallyl radicals (7.54 v), produced pyrolytically. Corresponding heats of formation for $C_3H_5^+$, the allyl ion and $C_4H_7^+$, the methallyl ion were 226 ± 2 kcal/mole²³⁻²⁴ and 204 ± 3 kcal/mole²⁴ respectively. Thus the precursor ions $C_4H_8^+$ have isomerized to a common intermediate before dissociation to produce $C_3H_5^+$ (the allyl ion), and $C_4H_7^+$ (the methallyl ion) at the threshold (Chapter 2).

CHAPTER 2THE MASS SPECTRA OF SOMENEOPENTYL COMPOUNDS

The mass spectra of some neopentyl esters²⁵, neopentane and neopentane-2-¹³C 1(c), 4-6 have previously been studied. In the case of the neopentyl esters²⁵, transfer of two H atoms from the methyl groups to the ester function took place. H atoms at C-1, however, were not displaced in any fragmentations of the molecular ions. The previously proposed migration of a methyl group from C-2 to ester oxygen was ruled out²⁶. The observations on neopentane were interpreted with respect to extensive rearrangement of the t-butyl cation leading to a methylated cyclopropane ion, before the loss of ethylene. The ability of the halogens and hydroxyl to direct fragmentation in competition with other groups in multi-functional compounds has been the subject of some discussion^{1(d)}. In the present work, the mass spectra of neopentyl alcohol, bromide and chloride and some ¹³C and deuterium labelled analogues were studied¹¹, to appreciate the fragmentation-directing capabilities of isolated functional groups in a molecule. The fragmentation scheme is speculative except insofar as (i) the appropriate metastable peaks were observed and, (ii) the structures shown are compatible with the results of the labelling experiments. In Scheme 1 and text, masses in parentheses are for the 1,1-d₂ labelled compounds. For the alcohols, the exchange deuterated hydroxyl compound (-OD) and the 1,1-d₂ derivative are appropriately



SCHEME 1. Fragmentation mechanism for neopentyl compounds. (X = OH, OD, Br, Cl unless otherwise indicated).

indicated. Enclosure of atoms by a circle indicates their randomization (or loss of positional identity) in the appropriate fragmentations.

Neopentyl Alcohol

The mass spectrum of this compound is shown as Fig. 1a. It agrees well with previously tabulated data²⁷. The mass spectra of the -OD and 1,1-d₂ alcohols are shown as Figs. 1b and c respectively. The base peak is m/e 57, C₄H₉⁺, the t-butyl cation. It arises from simple cleavage of the C-1 - C-2 bond without rearrangement of the molecular ion (no label retention by this ion in either 1b or 1c). The peak m/e 56 C₄H₈⁺ arises (at least in part) from the molecular ion by the same cleavage following H atom transfer from a methyl group to the heteroatom. Its origin is confirmed by the presence of appropriate metastable ion peaks. The formation of (M-CH₃)⁺ and (M-C₄H₉)⁺ from the molecular ions also involve simple bond cleavage and the absence of hydrogen rearrangement. The ion m/e 73 (C₄H₉O)⁺ (74-OD, 75-d₂) loses a water molecule to yield m/e 55 (55-OD, 57-d₂). An appropriate metastable was observed in each case. This process therefore involves loss of the hydroxyl group plus a methyl H atom. The same ion (C₄H₉O)⁺ loses ethylene to produce m/e 45 (46-OD, 45, 46, 47-d₂). The ion m/e 43 consists of C₃H₇⁺ and C₂H₃O⁺ in approximately equal proportions. A metastable ion peak (m/e 25.3) indicated that one (or both) of these ions could arise from m/e 73, C₄H₉O⁺, by loss of CH₂O and C₂H₆, respectively.

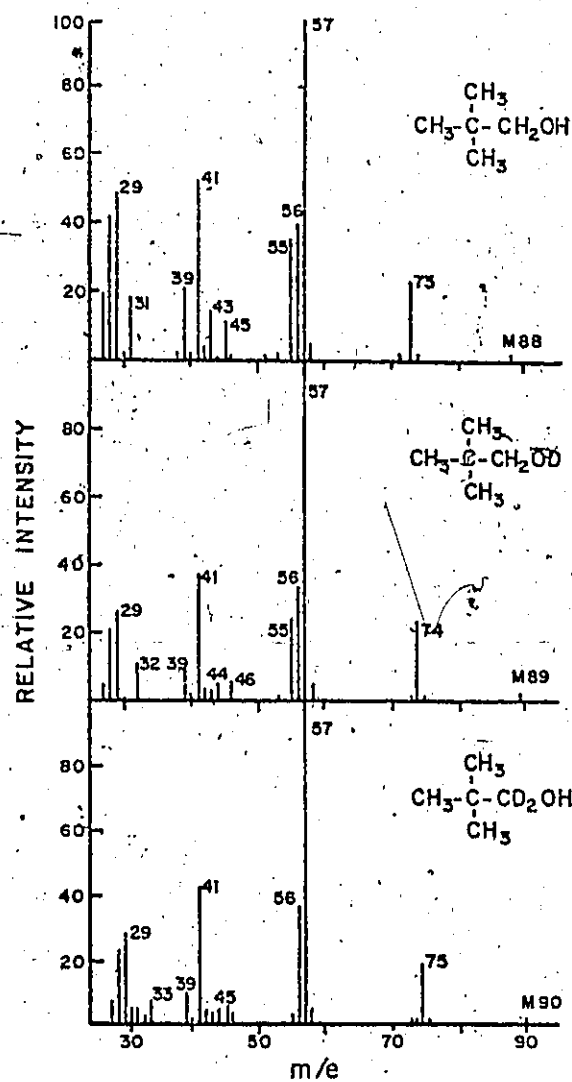


FIG. 1. The mass spectra of (a) neopentyl alcohol; (b) neopentyl alcohol-OD; (c) 1,1-d₂ neopentyl alcohol.

Neopentyl Bromide

The mass spectra of this compound and its 1,1-d₂ analogue are shown in Figs. 2a and 2b respectively. With the exception of the neopentyl cation, C₅H₁₁⁺, m/e 71 (73-d₂) (absent in the mass spectra of the alcohol and chloride) the mass spectra of these compounds closely parallel that of the alcohol.

Neopentyl Chloride

The mass spectra of this compound and its 1,1-d₂ analogue are shown as Fig. 3a and 3b respectively. It can be seen that these mass spectra are also closely similar to those of the corresponding alcohols and bromides. Thus the discussion below applies to all three neopentyl compounds.

Discussion

I. Hydrocarbon Ions

These form the most abundant species in the mass spectra.

(A) The t-butyl cation

This cation, the base peak, is known to undergo extensive rearrangement before fragmentation. Metastable ion peaks were observed here for the dissociation of C₄H₉⁺ ion by loss of methane, ethylene, ethyl and ethane. The structures of C₄H₉⁺ cations were previously studied intensively^{1(c), 4-6, 17, 25, 28-39}. In the gas phase, it appeared that C₄H₉⁺ cations, at the instant of production by electron impact from structures containing isomeric C₄H₉ units, retained their original structures. For example, electron impact data³¹⁻³² gave heats of formation in

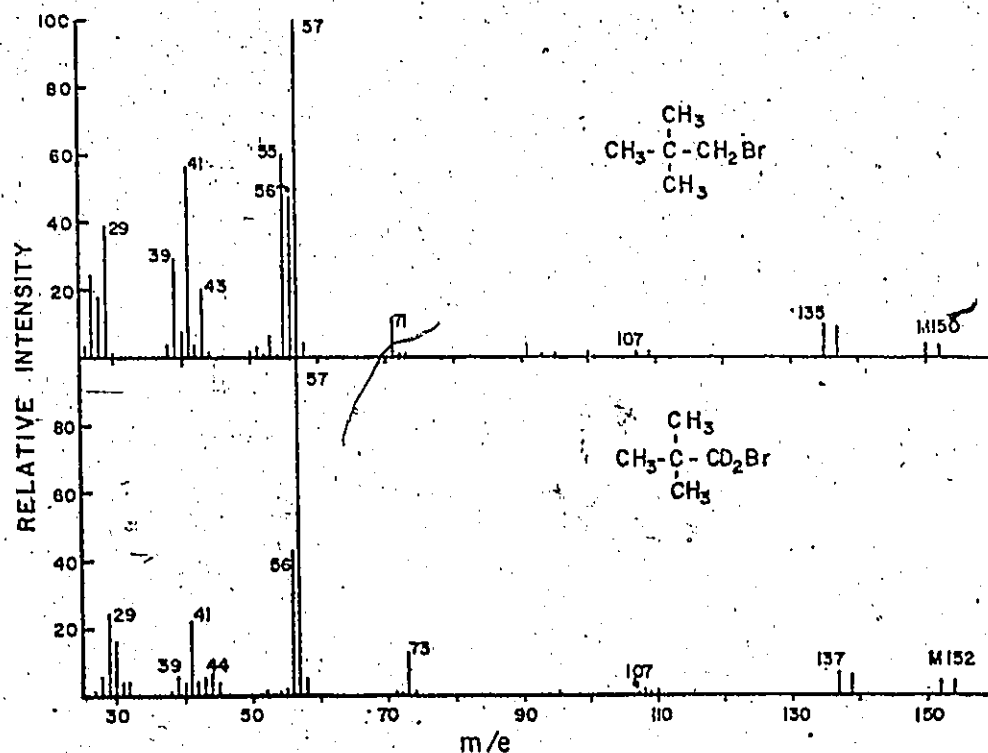


FIG. 2. The mass spectra of (a) neopentyl bromide and (b) 1,1-d₂ neopentyl bromide.

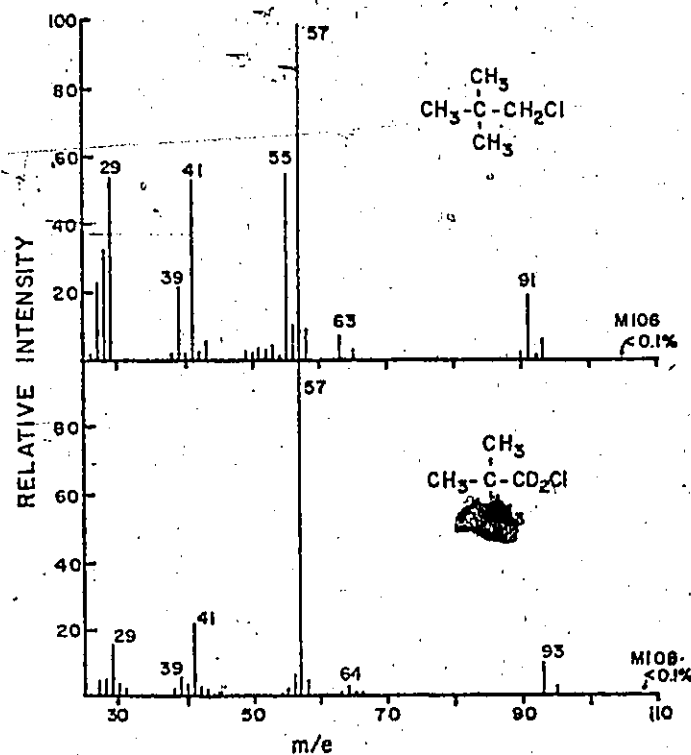
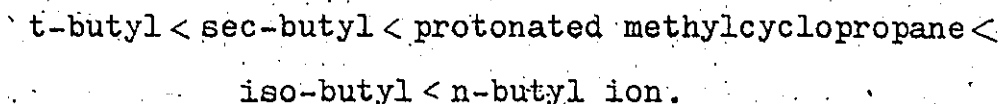


FIG. 3. The mass spectra of (a) neopentyl chloride; and (b) 1,1-d₂ neopentyl chloride.

the increasing order:



This indicated that the t-butyl cation was the most stable isomer. In addition, Munson³³ showed that butyl ions produced by chemical ionization from n-butane and iso-butane had different reactivities and, it was inferred, different structures. Ausloos and his co-workers²⁸ observed by ⁶⁰Co γ-ray-radiation that the sec-butyl ion isomerized to the t-butyl ion, increasing in importance with increasing internal energy content of the ion. Also, the protonated cyclobutane ion²⁸, formed by proton transfer to cyclobutane, isomerized mainly to the sec-butyl structure. This is in agreement with heats of formation data³¹⁻³².

The mass spectrum of ¹³C-labelled neopentane was interpreted^{1(c)}, 4-6 with respect to extensive carbon scrambling of the t-butyl cation leading to a methylated cyclopropane ion, before the loss of ethylene. Williams and his co-workers³⁰ reported that the C₄H₉⁺ ions generated from n-, iso-, sec- and t-butyl structures have isomerized completely to the same structure (or mixtures of structures) prior to methane and ethylene loss in the first field-free region. It was proposed that the competing losses of methane and ethylene from C₄H₉⁺ ions might occur from different, but rapidly equilibrating structures. For example, ethylene might be lost from a methylated cyclopropane and/or the sec-butyl ion. Methane might be lost from the t-butyl cation. More recently, Liardon

and Gäumann¹⁷ studied the loss of methane and ethylene from $C_4H_9^+$ produced from precursor molecules having the n- and t-butyl structures. They observed complete carbon and hydrogen randomization in the n-butyl ion in the metastable ion peaks for methane and ethylene loss. In the case of the t-butyl ion, the loss of methane without rearrangement was found as a minor process. A protonated cyclobutane structure was introduced as a possible intermediate in the fragmentation of the $C_4H_9^+$ ions.

In solution, the four isomeric butyl fluorides³⁴ or butyl alcohols³⁵ under the influence of SbF_5 and $SbF_5-HSO_3F-SO_2$ respectively, furnished the corresponding cations, and these then isomerized to the t-butyl ion.

Although deaminations of butylamines might be carried out without extensive isomerization or deuterium scrambling³⁶⁻³⁷, it appeared that the t-butyl ion was the most stable form of $C_4H_9^+$. This, however, may be formed not only via 1,2-hydrogen or 1,2-alkyl shifts in the n-, iso- and sec-butyl ions, but also via edge-protonated methylcyclopropanes^{29, 37-39}.

In any case, rapid equilibration among the above mentioned structures would lead to scrambling of both carbons and hydrogens of $C_4H_9^+$ ions.

(B) The odd electron ion, $C_4H_8^+$

No metastable ion peaks were observed for the fragmentation of the odd electron ion, $C_4H_8^+$. We suggest that this ion formed in the source is probably a terminal ion. It does not undergo any appreciable further fragmentation. This ion was absent in the spectrum of neopentyl chloride. With the assumption that no skeletal rearrangement occurs prior to the

formation of the $C_4H_8^+$ ions in the source, the proposed structure of the ions at threshold is iso- $C_4H_8^+$. Evidence in favour of representation in Scheme 1 for the formation of iso- $C_4H_8^+$ has been obtained from the mass spectra of neopentyl alcohol-OD, 1,1-d₂-neopentyl alcohol and 1,1-d₂-neopentyl bromide (Figs. 1 and 2). The loss of a molecule CH_2X-H from the molecular ion involves the methylene group. The third hydrogen (which comes from a methyl group) is probably associated with the heteroatom (Scheme 1). The mechanisms, kinetics and energetics of fragmentation of isomeric $C_4H_8^+$ ions generated from various sources were previously studied^{29-30, 40-44}. Lossing, for example, generated $C_3H_5^+$ and $C_4H_7^+$ ions from five isomeric C_4H_8 molecules²³ using mono-energetic electrons¹⁹. The heats of formation of all $C_3H_5^+$ and $C_4H_7^+$ were 226 ± 2 kcal/mole and 206 ± 2 kcal/mole respectively. Thus, the precursor ions $C_4H_8^+$ have isomerized to a common structure before dissociation to produce $C_3H_5^+$, the allyl ion and $C_4H_7^+$, the methallyl cation at the threshold. Williams and Smith⁴¹ reached the same conclusions by studying competing metastable transitions (i.e. CH_3 , CH_4 , H_2 , and C_2H_4 loss) from $C_4H_8^+$ ions generated in the mass spectrometer from six C_4H_8 molecules and compounds of the form $n-C_4H_9X$ ($X = OH, F, SH$ and OAc). These conclusions were in accord with the findings that both the hydrogens⁴⁵ and carbons⁴⁶ of but-1-ene were randomized before methyl radical loss. Also these $C_4H_8^+$ odd-electron ions generated from compounds n -butyl- X underwent hydrogen scrambling before methyl radical loss metastable transitions³⁰. However, photoionization of the acyclic and

cyclic C_4H_8 isomers at 10 ev yielded only parent ions without rearrangement (the appearance potentials of the possible fragment ions were higher than 11 ev)⁴⁸. Thus, Ausloos and his co-workers reported recently that at 10.6 ev, various butene isomers and methylcyclopropane and cyclobutane remained as parent ions after ionization^{42,44}. At 11.6 ev or higher energy, most of the cyclic and acyclic $C_4H_8^+$ ions isomerized to the iso- $C_4H_8^+$, 2- $C_4H_8^+$ and 1- $C_4H_8^+$ structures^{42-44, 47, 49}. Partial retention of the cyclic structure because of an activation energy requirement for ring opening might account for the higher relative stability of the methylcyclopropane and cyclobutane ions.

(C) The $C_4H_7^+$ ions

For the ion $C_4H_7^+$, metastable ion peaks were observed for the loss of a hydrogen molecule, methane, acetylene and ethylene. Metastable ion peak intensities were measured for the loss of $^{13}CH_4$ and CH_4 from $^{13}CC_3H_7^+$ ions. The observed intensity ratio ($1.2 \pm 0.3 : 3.2 \pm 0.3$) is in good agreement with the ratio calculated on the basis of complete carbon atom scrambling (1:3). For the $^{13}CC_3H_5D_2^+$ ions, metastable ion peak intensities were measured for the loss of acetylene. The observed ratios for loss of C_2H_2 , ($C_2HD + ^{13}CCH_2$), and ($C_2D_2 + ^{13}CCHD$) were $6 \pm 1 : 10 \pm 1 : 5 \pm 1$. Complete carbon and hydrogen atom scrambling requires 5: 10 : 5.5. The metastable ion peak for loss of $^{13}CCD_2$ was too weak for accurate measurement. The calculated relative intensity is 0.5. These results indicate considerable rearrangement and/or scrambling of both hydrogen⁴⁵ and carbon atoms in these species.

It was recently proposed⁵⁰ that $C_4H_7^+$ ions generated from different precursors isomerized fully to a common intermediate (or mixture of intermediates) before they dissociated by the pathways listed above. This conclusion was based on the observation that relative abundances of metastable ion peaks for the given fragmentations were similar for $C_4H_7^+$ ions generated from different precursors. For example, in the work quoted, the abundance ratios for the processes $C_4H_7^+ \rightarrow CH_4 + C_3H_3^+$; $C_4H_7^+ \rightarrow C_2H_2 + C_2H_5^+$ were from 0.6 to 0.9. In this work, the corresponding ratio is 1.0.

It has been discussed in Chapter 1 and the previous section that by heat of formation measurement, the precursor ions $C_nH_{2n}^+$ ($n=4$ and 5) have isomerized to a common intermediate before dissociation to produce $C_4H_7^+$ at the threshold²³. Williams's experiments⁵⁰ on the other hand, showed that at some undefined stage before metastable fragmentation the $C_4H_7^+$ ions isomerized to a common intermediate (or set of intermediates). We infer from all the above observations that $C_4H_7^+$ ions which fragment via a common intermediate are energy rich methyl allyl cations.

(D) The neopentyl cation

This ion, $C_5H_{11}^+$, m/e 71 ($73-d_2$), was only observed in the mass spectrum of the bromide (12% of base peak). It does not fragment by methyl loss because there is no increase in abundance of m/e 58 in the $1,1-d_2$ bromide. Its chief fragmentation appears to be by ethylene loss to yield m/e 43 (m/e 43, 44, $45-d_2$). The metastable ion peaks for loss of C_2H_4 , C_2H_3D and $C_2H_2D_2$ from $C_5H_9D_2^+$ were independent of electron energy and were of relative abundance $20.4 \pm 0.6 : 27.7 \pm 0.6 : 6.0 \pm 0.6$.

respectively. The calculated ratios for complete hydrogen-deuterium scrambling are 21:28:6. In the neopentyl-1-¹³C-bromide, the metastable ion peaks for loss of ¹³CCH₃ and C₂H₅ from the ¹³CC₄H₁₁⁺ ion were of relative abundance 6±0.6 : 8.7±0.3, respectively. Complete carbon atom scrambling requires a ratio of 2:3. We therefore conclude that complete carbon and hydrogen scrambling occurs in the neopentyl cation prior to its fragmentation by loss of ethylene.

In conclusion, isomerization of the above studied hydrocarbon ions to a common structures (or structures) will occur before or during fragmentation, given a sufficient lifetime and internal energy.

II. Hetero-atom-containing Ions

(A) The molecular ions

The molecular ions yield the major peaks in the mass spectra of these compounds by simple bond cleavages. This is clearly seen from the spectra of the labelled compounds.

Besides simple bond cleavages, a second fragmentation which is characteristic of hydroxyl compounds and halides (chlorides and bromides) of most types is the loss of water and hydrogen halide from the molecular ion^{1(d)}. This is not observed in our present study.

* It has been established that loss of water from acyclic^{1(d)}, 41, 52-55, 57 and cyclic 1(d), 52, 58, 62, 66

alcohols occurs as a 1,3- and 1,4-elimination, with a low frequency factor^{55, 58, 62}. A low activation energy for a

mass spectrometric elimination often requires concerted bond formation and cleavage and hence a cyclic transition state⁶³. This explains the 1,4-elimination mechanism. The low frequency factor arises from the low probability of the cyclic molecular ion taking up a cyclic conformation in which interaction between OH and the C-4-H can occur.

Loss of hydrogen halide (HCl and HBr) from halogen compounds occurs as a 1,3-elimination in acyclic^{1(d)}, 30, 41, 64-65 compounds and as 1,3- or 1,4-process in cyclic compounds^{1(d)}, 52, 56.

To investigate the lack of water and hydrogen halide loss from the molecular ions of neopentyl alcohol and neopentyl halides (bromide and chloride), the relative rates of (M⁺HX) (X=OH, Br and Cl) elimination from the appropriate molecular ions $\text{CH}_3^+-\text{R}_1-\text{C}-\text{R}_2-\text{CH}_2\text{X}$ of the form $\text{CH}_3\text{CH}_2\text{CH}_2\text{X}$ ($\text{R}_1 = \text{R}_2 = \text{H}$), $(\text{CH}_3)_2-\text{C}(\text{H})-\text{CH}_2\text{X}$ ($\text{R}_1 = \text{CH}_3$, $\text{R}_2 = \text{H}$) and $(\text{CH}_3)_3-\text{C}-\text{CH}_2\text{X}^+$ ($\text{R}_1 = \text{R}_2 = \text{CH}_3$) are compared. The rates of production of (M-CH₂X) was assumed to be the same. The results are as shown in Table 1.

It is clear from Table 1 that the relative rate of elimination of HX from molecular ions of the form $\text{CH}_3-\text{R}_1-\text{C}-\text{R}_2-\text{CH}_2\text{X}$ decreases drastically as R₁ and R₂ groups are replaced progressively by bulky CH₃ groups instead of hydrogens. These observations are expected if we consider the elimination of HX to involve a transfer of hydrogen from C-3 via a five-membered cyclic transition state. The bulky cyclic transition state of neopentyl compounds, $(\text{CH}_3)_3-\text{C}-\text{CH}_2\text{X}$, would be thermodynamically least favorable. These findings are in accord with the mass spectra of the rigid exo-2-norbornyl chloride molecule. No (M-HCl) ion was observed⁶⁸. In the case of cyclohexyl chloride, on the other hand, trans- and

Table 1.

Relative rates of (M-HX) elimination from M^{+}
of the form $CH_3-(R_1)-C-(R_2)-CH_2X$ (X=OH, Br or Cl)

Compound	Relative rates of (M-HX) elimination from the molecular ion		
	X= OH ^{a,c}	X= Br ^{b,c}	X= Cl ^{b,c}
$CH_3CH_2CH_2X$	100	100	100
$(CH_3)_2CH-CH_2X$	8	7.5	2.8
$(CH_3)_3C-CH_2X$	0	0	0

*The rate of production of (M-CH₂X) production was assumed to be the same.

a. Reference 27.

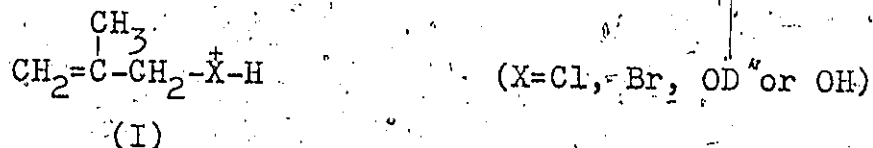
b. Reference 67.

c. Present studies.

cis-1,3- and cis-1,4-eliminations were operative due to the geometry of the molecular ions⁵⁶.

(B) The (M-CH₃), C₄H₈X⁺ ions

We propose that these ions, C₄H₈X⁺, have the common structure I shown below:



We have generated C₄H₈X⁺ ions from various other precursors. For ease of comparison, the behaviour of these C₄H₈X⁺ ions will be discussed collectively in Chapter 3.

(C) The CH₂X⁺ ions (X=OH, OD, Br and Cl)

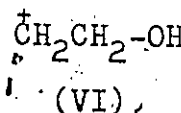
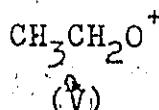
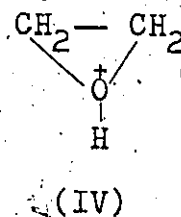
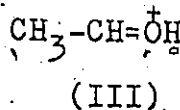
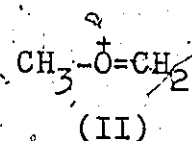
The CH₂X⁺ ions were produced by simple α-bond cleavage from the molecular ions without rearrangement. It has the well-known common structures of CH₂=X⁺ (X=OH, OD, Br and Cl)^{1(d)}.

Here, the positive charge resides on the heteroatoms.

(D) The C₂H₄X⁺ ions (X=OH, OD, Br and Cl)

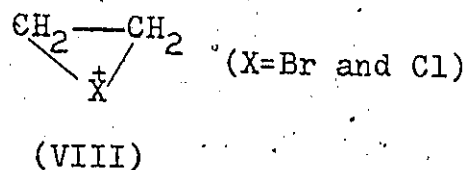
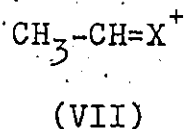
The C₂H₄X⁺ ions (X=OH, OD, Br and Cl) and its labelled analogues were produced randomly from the common ion (I) as will be discussed in Chapter 3. Since the fragmentations of the C₂H₄X⁺ ions have not been studied in the present work, their structures cannot be established. However, various techniques have been employed in an attempt to identify the structural isomers of C₂H₅O⁺. These included thermochemical studies⁶⁹⁻⁷⁵, a detailed analysis of metastable ion characteristics¹³⁻¹⁵, collision induced decompositions¹⁵ and ion cyclotron resonance

spectroscopic studies⁷⁶. Of the five isomers of $C_2H_5O^+$ ion represented by structures (II) to (VI):



it was concluded that only the first three commonly occurred to a significant extent. This was shown in heat of formation data⁷⁶: (II), ~ 170 kcal/mole; (III), ~ 143 kcal/mole; (IV), ~ 170 kcal/mole; (V), ~ 211 kcal/mole and (VI), ~ 211 kcal/mole. Structure (III) was the most stable, with (II) and (IV) being comparable and somewhat higher in energy. On the basis of metastable ion characteristics¹³⁻¹⁴ and isotopic labelling studies⁷¹⁻⁷², the protonated oxirane structure (IV), rather than the expected structure (III), was postulated as the favored structure. However, evidence derived from studies of the mass spectrum⁷² of 2-propanol-2-¹³C, and collision-induced metastable ion peaks¹⁵ indicated that the fraction of the higher energy (IV) relative to (III) decreased with increasing electron energy. On the basis of the above evidence and the result that hydroxyl-hydrogen remains intact in structure (I), (X=OH or OD) prior to the ejection of ethylene, the $C_2H_5O^+$ ions produced probably are a mixture of structures (III) and (IV). The production of ions with structure (II), $\text{CH}_3-\overset{+}{\text{O}}=\text{CH}_2$, is very unlikely. This species is generally acknowledged to be

generated from neutrals which possess the structure $\text{CH}_3\text{-O-CH}_2\text{-R}^{15, 76}$. By analogy with the structure of $\text{C}_2\text{H}_5\text{O}^+$ ion, the $\text{C}_2\text{H}_4\text{Br}^+$ and $\text{C}_2\text{H}_4\text{Cl}^+$ ions produced in the present studies probably have a mixture of common structures of the forms (VII) and (VIII):



CHAPTER 3

ISOMERIZATION AND DECOMPOSITIONREACTIONS OF $C_4H_8X^+$ IONS

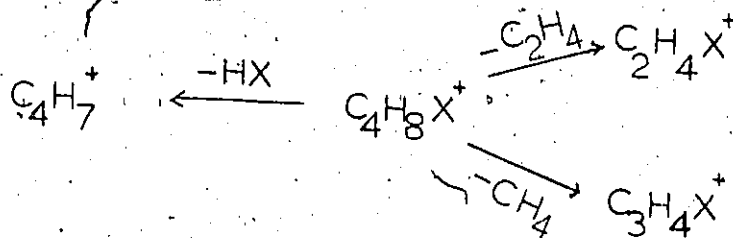
One of the major uses of mass spectrometry in recent years has been in the study of the unimolecular decomposition of gaseous organic ions, and especially in investigating the structures of the decomposing ions and the extent of atom scrambling and isomerization reactions that precede decomposition. For example, it has been shown that $(C_nH_{2n+1})^+$ ($n=4, 6, 8$) ions generated from different sources upon electron impact isomerized completely to the same structures prior to decomposition^{30,78-79,17} in the metastable drift regions. In addition, complete scrambling of carbon and hydrogen for the isomeric $C_4H_9^+$ ions prior to fragmentation was observed^{30, 17}. Decomposition from common structures also occurred in unsaturated hydrocarbon ions such as $(C_nH_{2n})^{++}$ ($n=4, 6$)⁴¹, $(C_nH_{2n-1})^+$ ($n=4, 5, 6$)⁵⁰, $(C_5H_8)^{++}$ ⁸⁰, $(C_nH_{2n-3})^+$ ($n=5, 6, 7, 8$)^{50, 81} and $(C_nH_{2n-4})^{++}$ ($n=7, 8$)⁸¹. Appearance potential measurements support this conclusion in the case of $(C_4H_8)^{++}$ ^{23, 40} and $(C_5H_8)^{++}$ ⁸⁰ isomers. It should be mentioned that at least two types of structurally distinct $(C_3H_6)^{++}$ isomers have been detected in the ion cyclotron resonance cell⁸². Similar studies of organic ions containing heteroatoms have been made. By studies of metastable transitions, $C_3H_8N^+$ ⁸³, benzenoid $C_9H_{11}^+$ ions⁸⁴, $C_2H_5O^+$ ¹³, the unsaturated ions $C_3H_5O^+$ ⁸⁵, $C_3H_5O_2^+$ ⁸⁵, $C_4H_7O_2^+$ ⁸⁵, $C_8H_{10}O^{++}$ ⁸¹ and $C_8H_{12}O^{++}$ ⁸¹.

and the saturated ions $C_3H_6O^{+}$ ⁸⁶, $C_3H_7O_2^{+}$ ⁸⁵, $C_4H_8O^{+}$ ⁸⁷ and $C_4H_9O^{+}$ ⁸⁸ generated from a variety of precursors, have been classified into distinct groups. Ion cyclotron resonance has been used in investigation of the $C_2H_5O^{+}$ ⁷⁶ and $C_3H_6O^{+}$ ^{89,90} radical ions. It has become apparent that in ions containing a heteroatom (O, N), isomerization reactions are generally less prevalent than in hydrocarbon ions. This is because the activation energies for decomposition paths are frequently lower than the corresponding energies for internal rearrangement (relative to the hydrocarbon cases). In order to determine the ability of oxygen, bromine, and chlorine atoms to limit isomerization and scrambling reactions in aliphatic organic ions, we have generated $C_4H_8X^{+}$ ions (X= OH, Br and Cl) from a variety of sources. 2H and ^{13}C labelling was used to yield information on the extent of scrambling, on breakdown mechanisms, on isotope effects, and on the structures of the $C_4H_8X^{+}$ ions themselves. All the investigations are carried out on normal ion peak measurement and on metastable transition in the first and second drift regions of a double-focusing mass spectrometer. The criterion of similar first field-free region metastable ion peak shapes is used to identify common structures.

Results and Discussion

Two isomeric dideuterated $C_4H_6D_2X^{+}$ ions of structures $(CH_3)_2^+C-CD_2X$ (X= OH, Br and Cl) and $CH_3CH_2CH^+CD_2X$ (X= OH and Cl) were generated by electron bombardment of various alcohols, chlorides and bromides. Three fragmentations of $C_4H_8X^{+}$ were

observed (Scheme 1), the major transition being (C_4H_8X-HX).



Scheme 1. Fragmentation scheme for the decomposition of $C_4H_8X^+$ ions ($X= OH, Br$ and Cl)

(A) Isomeric $(CH_3)_2\dot{C}CD_2X$ ions

Compounds 1-8 which were used as sources of the isomeric $(CH_3)_2\dot{C}CD_2X$ ions are given in Table 1. The relative abundances of daughter and first field-free metastable ion peaks for the $((CH_3)_2CCH_2X-HX)$ process are also included. It was assumed that the $(CH_3)_2\dot{C}CD_2X$ ions listed in Table 1 were initially generated without skeletal reorganization. The assumption seems reasonable, since the $C_4H_6D_2X^+$ ions were formed by direct bond cleavage. Moreover, all these $C_4H_6D_2X^+$ ions show complete retention of the two deuterium atoms.

We have shown that (a) peak ratios indicate that the dideuterated $(CH_3)_2\dot{C}CD_2X$ ions ($X= OH, OD, Br$ and Cl), generated from neopentyl derivatives, dissociate by loss of HX , i.e. hydrogen from C-1 is not involved. We proposed that these high energy ions have the structure (I):

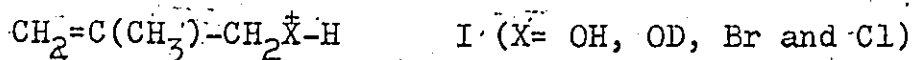


Table 1.

Relative abundances of daughter and metastable ion peaks^a for the
(C₄H₈X-HX) fragmentation of the labelled (CH₃)₂-¹³C-CD₂X ions (70ev)

Origin	Ratios					
	Peaks			m/e		
	57	56	55	57	56	55
(CH ₃) ₂ -C(Br)-CD ₂ Cl ⁺ → (CH ₃) ₂ - ¹³ C-CD ₂ Cl (1)	7.0	1.0	-	7.2	1.0	-
(CH ₃) ₃ -C-CD ₂ Cl ⁺ → (CH ₃) ₂ - ¹³ C-CD ₂ Cl (2)	1.0	0	-	6.4	1.0	-
(CH ₃) ₂ C(CH ₂ Cl)CD ₂ Cl ⁺ → (CH ₃) ₂ - ¹³ C-CD ₂ Cl (3)	6.0	0	-	4.9	1.0	-
(CH ₃) ₃ CCD ₂ Br ⁺ → (CH ₃) ₂ - ¹³ C-CD ₂ Cl (4)	1	0	-	6.5	1.0	-
(CH ₃) ₂ C(CH ₂ Cl)CD ₂ Br ⁺ → (CH ₃) ₂ - ¹³ C-CD ₂ Br (5)	-	-	^b	4.7	1.0	-
(CH ₃) ₃ CCD ₂ OH ⁺ → (CH ₃) ₂ - ¹³ C-CD ₂ OH (6)	1.0	0	0	14.5	1.0	0
(CH ₃) ₂ CCCH ₂ OD ⁺ → (CH ₃) ₂ - ¹³ C-CH ₂ OD (7)	0	0	1.0	-	-	^c
(CH ₃) ₂ C(CH ₂ Cl)CD ₂ OH ⁺ → (CH ₃) ₂ - ¹³ C-CD ₂ OH (8)	-	-	^b	12.4	1.0	0
				(1.0	0	0) ^d

a. First field-free metastable ion peaks measured by the method of Jennings.¹⁰

b. Not measured, due to contribution from some other processes.

c. Not measured.

d. Second field-free metastable ion peaks.

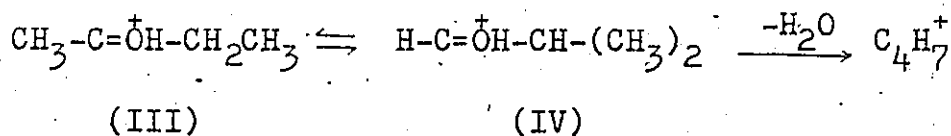
(b) For metastable ion abundances for the process, H_2O loss from $C_4H_6D_2OH^+$ is favored over DHO loss, with ratios from 7.9:1.0 to 14.5:1.0 (D_2O loss being negligible). The relative $(C_4H_6D_2Br-HBr)/(C_4H_6D_2Br-DBr)$ and $(C_4H_6D_2Cl-HCl)/(C_4H_6D_2Cl-DCl)$ losses from $C_4H_6D_2Br^+$ and $C_4H_6D_2Cl^+$, respectively, however, vary from 4.7 to 7.2. Random loss of HX ($X=OH, OD, Br$ and Cl) requires a ratio of 3:1. From these results, three conclusions are evident. First, water loss involves a substantially intact OH bond. Scrambling among the hydroxyl-hydrogen and the hydrogens of the methyl groups is not significant. Secondly, for most of the $C_4H_8X^+$ ions, either scrambling of all eight hydrogen atoms has occurred (especially for the low energy, metastable generating species) with or without an isotope effect. Or, complete hydrogen scrambling in these species before the hydrogen (which comes from a methyl group) associated with the heteroatom is transferred to form structure (I). This would imply an isotope effect of 1.6 to 2.4 for $C_4H_6D_2X^+$ ($X=Br$ and Cl). It is interesting to note that the magnitude of isotope effect 1.6 to 2.4 (assuming complete hydrogen randomization) is compatible with the isotope effect 1.4 to 2.7 of gas phase pyrolytic elimination of halogen acid, from cyclic and acyclic bromides and chlorides⁹¹⁻⁹⁵. A small isotope effect of 1.4 and 1.6 respectively was observed in the mass spectra of n-hexanol⁵⁵ and the $C_4H_8OH^+$ ion of structure $CH_3-C=OH-CH_2-CH_3$ ⁸⁸. The isotope effect for electron impact induced elimination of HX from acyclic and cyclic halides was usually very small⁵⁶. Thus the differences in the ratios for the loss of HX and DX cannot be satisfactorily explained by an isotope effect alone. The elimination of HX is most likely

preceded by incomplete hydrogen atom scrambling in these more slowly dissociating, low energy ions (with or without a small isotope effect). The differences in metastable ion peak ratio for the process may reflect the differences in energy content for the dissociating species. Thirdly, assuming a similar isotope effect, the oxygen atom must be more powerful than bromine and chlorine atoms in limiting scrambling in the low energy $(CH_3)_2\dot{C}CH_2X$ ions.

It has been emphasized that most hydrocarbon ions will isomerize and scramble to a common structure (or structures) prior to fragmentation, given a sufficient lifetime and internal energy. In view of the known properties of heteroatoms in "directing" the mass spectral decompositions of aliphatic organic ions, it might be anticipated that isomerization and scrambling reactions in such ions would be less prevalent. This is because the activation energies for decompositions of these heteroatom-containing organic ions are relatively lower. This is in accord with the $CH_2=C(CH_3)-CH_2\dot{X}-H$ structure postulated here, at least in the case of fragment ion abundances in neopentyl compounds.

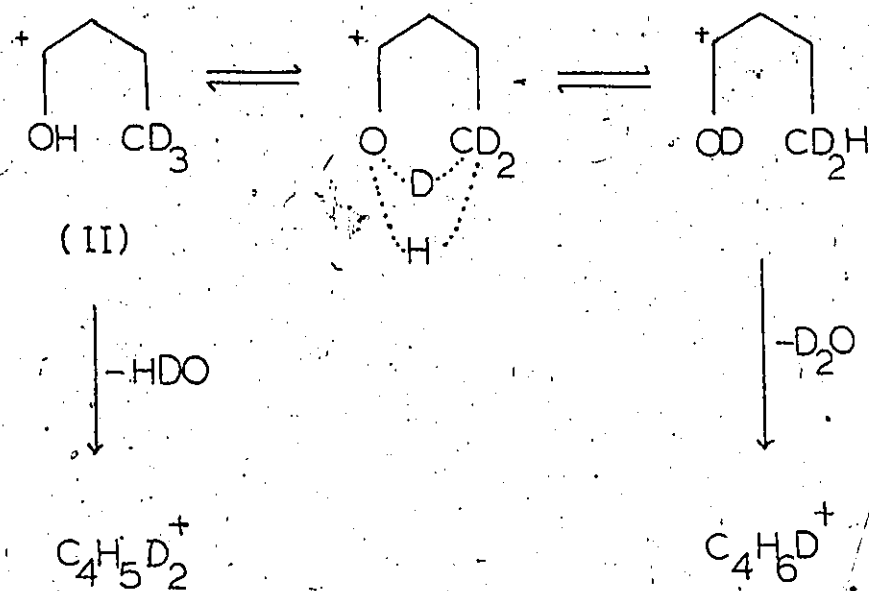
Williams and his co-worker⁸⁸ has recently produced ions $CH_3CH_2CH_2CH=\dot{O}H$ (II), $CH_3-C=\dot{O}H-CH_2CH_3$ (III), and $(CH_3)_2CH-CH=\dot{O}H$ (IV) from various secondary alcohols, with extensive deuterium labelling. From metastable ion peak results, three conclusions were drawn. Firstly, although water loss involved a substantially intact OH bond, there was appreciable scrambling among the hydroxyl-hydrogen and the hydrogens of the alkyl chain for ions of structure (II). Considerably less scrambling was seen for ions of structure (III) and (IV) and (I). Secondly, water

loss involved mainly or exclusively the hydroxyl-hydrogen and the hydrogens of the terminal methyl groups. Thirdly, in ions of structure (II), scrambling occurred initially between the hydroxyl-hydrogen and the hydrogens of the terminal methyl groups (or groups). It was suggested that water loss from structure (II) may be an 1,4-elimination (six-membered transition state), as shown in Scheme 2. It was proposed that water loss has an activation energy comparable to that for the scrambling reactions. Similar observations were reported by Holmes and Benoit for the mass spectra of 1,2-cyclohexanediol⁹⁶. It was shown that the predominant mode of water loss from the molecular ion involved "scrambling" of six hydrogen atoms, those in the 4- and 5-methylene group and the hydroxyl pair. In the case of cyclohexanol, some hydrogen atom scrambling between hydroxyl-hydrogen and C-4 hydrogen could occur before or during 1,4-elimination of water from the molecular ion⁹⁷. This explanation however is not favored by more recent studies⁶⁶. Two fragmentation mechanisms for water losses from structures (III) and (IV) were suggested⁸⁸. (a). Structure (IV) rearranged to (III) and followed by a 1,3-elimination of water (five-membered transition state). (b). structure (III) rearranged to (IV) and then followed by competitive 1,2- and 1,3-eliminations (Scheme 3):



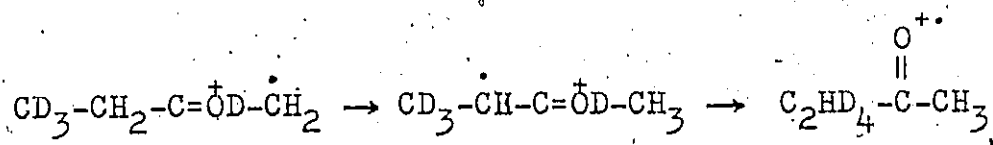
Scheme 3. Fragmentation mechanisms for water loss from

$\text{C}_4\text{H}_8\text{OH}^+$ ions of structures (III) and (IV).



Scheme 2. Fragmentation mechanism for the loss of water from ion of structure (II).

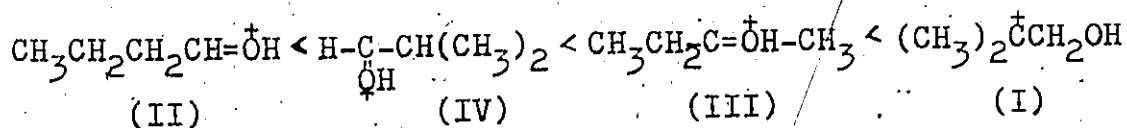
There seems to be sufficient evidence to support the idea that for scrambling among the hydroxyl-hydrogen and the hydrogens of the alkyl chain to be effective, one (or both) of the following two conditions must be met. The concerted exchange of hydroxyl-hydrogen and hydrogens in the C-4 position, via a six-membered ring transition state, as shown in Scheme 2^{55, 88}. Or, the stepwise rearrangement of H of an enolic ion to a radical site. This is shown in Scheme 4, for the enolic $C_4H_8O^{+}$ ion⁸⁷:



Scheme 4. Stepwise rearrangement of H of an enolic ion to a radical site.

A similar mechanism was proposed for the $C_3H_6O^{+}$ ions¹⁶. This is consistent with our observations and those of Williams and his co-worker⁸⁸. Scrambling of ions with structure (II) among the hydroxyl-hydrogen and the hydrogens of the alkyl chain via a six-membered ring transition state (Scheme 2) is possible. There is no scrambling of the same type for the isomeric ions (I), (III) and (IV). Here six-membered ring transition state cannot be formed.

Our results are also compatible with Williams and his co-worker's work⁸⁸ if we consider that the stability of ion structures (I) to (IV) increases as follows:



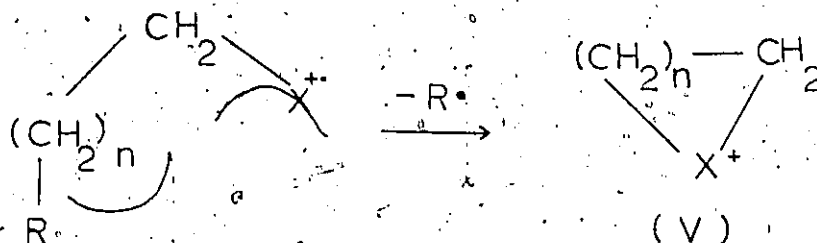
This is by analogy with the stability of isomeric butyl ions³². Scrambling between the hydroxyl-hydrogen and the methyl group hydrogens in ions of structure (I) (which is the most stable ion) would then be negligible.

It is interesting to note that similar to the hydroxyl group, N-H bonds of ions $\dot{\text{C}}\text{H}_2\text{-NH-CH}_2\text{CH}_3$, $(\text{CH}_3)_2\dot{\text{C}}\text{-NH}_2$, $\text{CH}_3\text{CH}_2\text{-}\dot{\text{C}}\text{H-NH}_2$ and $\text{CH}_3\text{-}\dot{\text{C}}\text{H-NH-CH}_3$ remained structurally distinct throughout all electron-impact induced reactions⁸³.

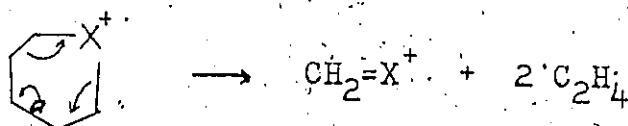
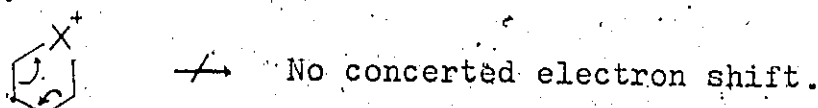
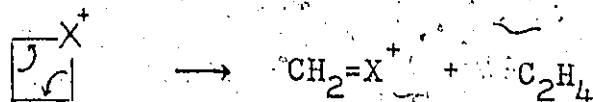
More recently, the loss of water from ions of structure $\text{C}_6\text{H}_5\text{-(CH}_3\text{)-}\dot{\text{C}}\text{-CH}_2\text{-OH}$ generated from 2-methyl-2-phenyl-propane-1,3-diols⁹⁸ has been examined. Second field-free metastable ion abundance ratios indicated that the ion eliminated water with participation of all hydrogen atoms, but not in a completely random manner. Scrambling of hydroxyl-hydrogen and ortho-ring hydrogen was, however, predominant. This may involve a six-membered transition state. Scrambling of hydroxyl-hydrogen and hydrogens in the methyl group (via a five-membered transition state) however, seems to be unimportant. The apparent complexity of this mechanism may arise as a result of the metastable ion peaks being composite, and, perhaps, can be resolved into at least two Gaussian components (see Chapter 5) for each of the composite peaks. For example, if the $\text{C}_6\text{H}_5\text{-}\dot{\text{C}}(\text{CD}_3)\text{-CH}_2\text{OH}$ ion lost D_2O , DHO and H_2O to give three first field-free metastable ion peaks, each of which can be resolved into two Gaussian components A and B, then there would be at least two distinguishable structures and/or electronic excited states for the precursor ion, dissociating within the first field-free region. From the overall relative metastable peak abundances for the

losses of D_2O , HDO and H_2O from the precursor ion, the relative abundances of each structure (A and B) can be determined. This result may, hopefully, provide information as to the structure (or structures) of the $C_6H_5-\dot{C}(CH_3)-CH_2-OH$ ion prior to water loss. We have employed this technique to study the $(M-CH_3)$ process in the mass spectra of methylcyclopentene and cyclohexene, and 4-methylcyclohexene and cycloheptene (Chapter 5).

The structure of $C_{n+1}H_{2n+2}X^+$ ions ($n=1$ to 4, $X=OH$, Br and Cl) in the spectra of alcohols and halides has been postulated^{1e, 67} to be of the cyclic form (V);

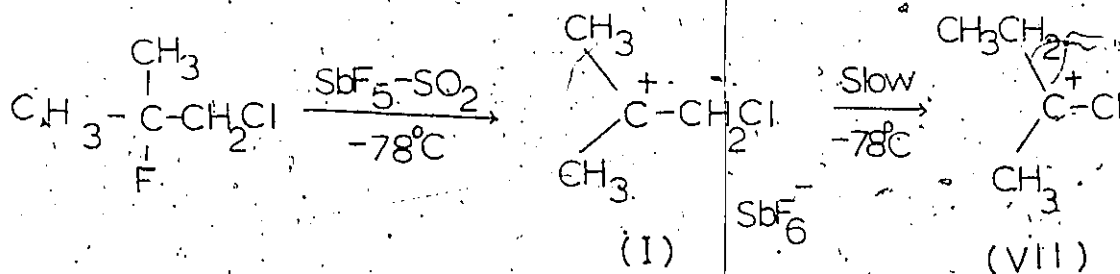
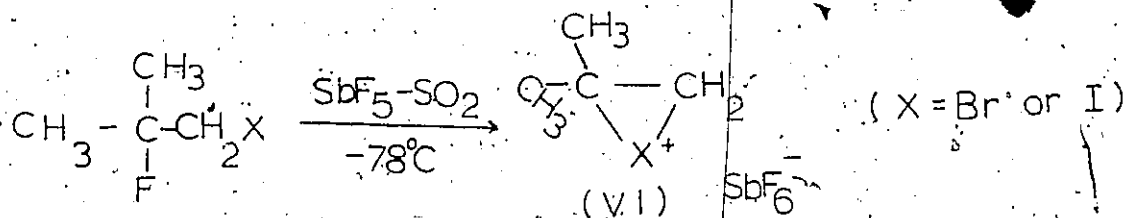


Of the homologous ions, five-membered cyclic ions of the formulas $C_4H_8X^+$ (V, $n=3$) gave rise to intense peaks. $C_5H_{10}X^+$ (V, $n=4$) was much less abundant and $C_3H_6X^+$ (V, $n=2$) was negligibly small. From steric considerations alone, the six-membered ring, $C_5H_{10}X^+$ should be more stable than the four-membered ring, $C_3H_6X^+$ ion and should be roughly equivalent to the $C_4H_8X^+$ ion. This seems not to be the case. In fact it has been postulated that rearrangements tended to proceed through four- or six-membered ring transition states instead of five-membered⁶⁷. It was also thought that a concerted effect was a significant part of the driving force of the reaction. Here the five-membered ring was in the product ion, not the transition



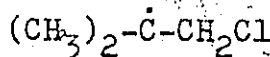
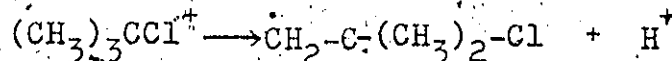
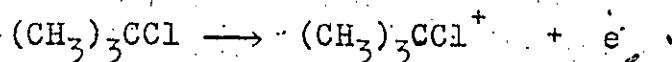
state. Thus just the opposite was desired- i.e. stability rather than tendency to decompose. Therefore, it is likely that the ion structure (I) we propose is the decomposing ion for the loss of HX and ethylene. The five-membered ring ion, however, is the product ion, which does not fragment.

In the liquid phase, the ion⁹⁹ produced from 2-fluoro-3-halo-2-methylbutanes (i.e. $(\text{CH}_3)_2\text{C}(\text{F})\text{CH}_2\text{X}$, X= Br, Cl and I) under the influence of $\text{SbF}_5\text{-SO}_2$, furnished ions with structure (I). This then isomerized to dimethylethylenehalonium ions, (VI) (X=Br and I) and structure (VII) (X=Cl):

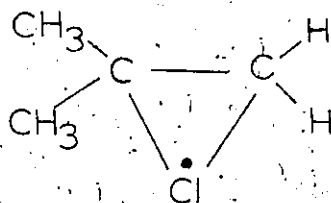


It should be noted that some of the ions still remained as structure (I) when $X = Cl$. Thus at least in solution, ions of structures (I), (VI) and (VII) seem to be stable.

It is interesting to compare the above results with some recent observations by Symons¹⁰⁰ on the $(C_4H_8Cl)^\cdot$ radical produced in the ^{60}Co γ -ray-radiation of t-butyl chloride. The mechanism for the formation of the radical was as follows:



Thus the $CH_2-C-(CH_3)_2-Cl$ radical isomerized to $(CH_3)_2-\dot{C}-CH_2Cl$ radical. The previously proposed cyclic radical of the form



was ruled out.

In conclusion, the common structure (I) we propose for the $(CH_3)_2-\dot{C}-CH_2-X$ ions is a reasonable representation of the decomposing ions which lose HX .

(B) Isomeric $CH_3-\dot{C}H-CH_2CH_2X$ ions ($X=OH$ and Cl)

To determine the extent of scrambling and isomerization reactions of the $CH_3-\dot{C}H-CH_2CH_2X$ ions preceding decomposition,

labelled isomeric $\text{CH}_3\text{-}\overset{+}{\text{CH}}\text{-CH}_2\text{CD}_2\text{OH}$ and $\text{CH}_3\text{-}\overset{+}{\text{CH}}\text{-CH}_2\text{CD}_2\text{Cl}$ ions generated from 3-bromo-1,1-d₂-butanol and 1-chloro-1,1-d₂-3-bromo-butane respectively were studied. It was assumed that the ions are initially generated without skeletal reorganization. This assumption seems reasonable, because in these cases the ions are formed in reactions of low activation energy, through loss of a labile bromine atom. Observations on $\text{CH}_3\text{-}\overset{+}{\text{CH}}\text{-CH}_2\text{CD}_2\text{X}$ ions for the $(\text{C}_4\text{H}_8\text{X-HX})$ fragmentation are summarized in Table 2. Two conclusions can be drawn. First, in the fast decomposing $\text{CH}_3\text{-}\overset{+}{\text{CH}}\text{-CH}_2\text{CD}_2\text{OH}$ ion, there is little scrambling. This is consistent with the results obtained for the isomeric ion $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}=\overset{+}{\text{OH}}$, described in the preceding section⁸⁸. Secondly, the first field-free region metastable ion peak ratios $(\text{C}_4\text{H}_6\text{D}_2\text{X-HX})^+ : (\text{C}_4\text{H}_6\text{D}_2\text{X-DX})^+$ are 7.9 and 5.1 for $\text{CH}_3\text{-}\overset{+}{\text{CH}}\text{-CH}_2\text{CD}_2\text{OH}$ and $\text{CH}_3\text{-}\overset{+}{\text{CH}}\text{-CH}_2\text{CD}_2\text{Cl}$ ions respectively. These are similar to those obtained from their isomeric $(\text{CH}_3)_2\text{-}\overset{+}{\text{C}}\text{-CD}_2\text{X}$ ions. This result ; however, does not necessarily mean that the $\text{CH}_3\text{-}\overset{+}{\text{CH}}\text{-CH}_2\text{CD}_2\text{X}$ ions isomerize to the more stable isomeric ions, $(\text{CH}_3)_2\text{-}\overset{+}{\text{C}}\text{-CD}_2\text{X}$ prior to fragmentation. Hydrogen scrambling followed by 1,3- (X= Cl) and 1,4- (X= OH) elimination of HX and DX for the ions may occur.

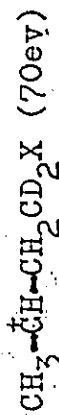
(C) Ion structures of isomeric $\text{C}_4\text{H}_8\text{Cl}^+$ ions

It has been discussed earlier that although metastable ion peak ratios $(\text{C}_4\text{H}_6\text{D}_2\text{Cl-HCl})^+ : (\text{C}_4\text{H}_6\text{D}_2\text{Cl-DCl})^+$ are very similar (varying from 4.9 to 7.2) for isomeric ions $(\text{CH}_3)_2\text{-}\overset{+}{\text{C}}\text{-CD}_2\text{Cl}$ and $\text{CH}_3\text{-}\overset{+}{\text{CH}}\text{-CH}_2\text{CD}_2\text{Cl}$, they do not necessarily decompose via a common ion structure (or mixtures of structures). First field-

Table 2.

Relative abundances of daughter^a and metastable ion peaks^b

for the (C₄H₈X-HX) fragmentation of the labelled ions



origin		Ratios			
		m/e 57	Peaks 56	m/e 57 [*]	m/e 56
CH ₃ -CH(Br)-CH ₂ CD ₂ OH	$\xrightarrow[\text{-e}]{\text{-Br}}$	17.6	1	0	0
				7.9	1.0
				(6.1)	(1.0)
				0.03	0
CH ₃ CH(Br)-CH ₂ CD ₂ Cl	$\xrightarrow[\text{-e}]{\text{-Br}}$	-	-	- ^d	-
				5.1	1.0
				-	-

- After ¹³C and unlabelled corrections.
- First field-free metastable peaks separated by the method of Jennings.¹⁹
- Second field-free metastable ion peaks.
- Not measured, due to contribution from the (M-Cl, HBr) process.

free metastable ion peaks for the $(C_4H_8Cl-HCl)$ process are of Gaussian shape. An attempt to identify different $C_4H_8Cl^+$ structures was studied and their metastable ion peak shapes were compared. The results are shown in Table 3. In the table, a represents the half-height width of the metastable ion peak $(C_4H_8^{35}Cl-H^{35}Cl)$ and b represents the distance between the tops of the isotopic metastable ion peaks $(C_4H_8^{35}Cl-H^{35}Cl)$ and $(C_4H_8^{37}Cl-H^{37}Cl)$. From the table, it is clear that the three isomeric $C_4H_8Cl^+$ ions, $(CH_3)_2-\dot{C}-CH_2Cl$, $(CH_3)_2-C-Cl-CH_2^+$ and $CH_3-\dot{C}H-CH_2CH_2Cl$ are indistinguishable according to the criterion of metastable ion peak shapes.

(D) Rapid dissociations of the $C_4H_8X^+$ ions

Like the $C_4H_9^+$ hydrocarbon ions¹⁷, the $C_4H_8X^+$ ions ($X=Br, Cl, OH$ and OD) dissociate by ethylene and methane losses to produce $C_2H_4X^+$ and $C_3H_4X^+$ fragments (Scheme 1). There are no metastable ion peaks corresponding to their formation from the $C_4H_8X^+$ ions. Thus it is concluded that losses of ethylene and methane from the species take place rapidly in the ion source.

(1) $(CH_3)_2-\dot{C}-CH_2X$ ions ($X=Br, Cl, OH$ and OD)

The loss of ethylene from the $(CH_3)_2-\dot{C}-CH_2X$ ions generated from neopentyl compounds ($X=Br, Cl, OH$ and OD) was studied in detail¹¹. This process is not accompanied by appropriate metastable ion peaks and formally therefore, $C_2H_4X^+$ could arise directly from the molecular ions by $C_3H_7\cdot$ loss (again no metastable ion peaks observed). The relative abundances of the peaks $C_2H_4X^+$, $C_2H_3DX^+$ and $C_2H_2D_2X^+$ for the 1,1-d₂ compounds were carefully measured over a range of electron

Table 3.

First field-free metastable ion peak^c shapes
for the (C₄H₈Cl-HCl) process

Origin	b/a [*]
$(\text{CH}_3)_2\text{-C}(\text{CH}_2\text{Cl})_2 \xrightarrow[-e]{-\text{CH}_2\text{Cl}} (\text{CH}_3)_2\text{-}\overset{+}{\text{C}}\text{-CH}_2\text{Cl}$	2.68
$(\text{CH}_3)_2\text{-C}(\text{Br})\text{-CH}_2\text{Cl} \xrightarrow[-e]{-\text{Br}} (\text{CH}_3)_2\text{-}\overset{+}{\text{C}}\text{-CH}_2\text{Cl}$	2.73
$(\text{CH}_3)_2\text{-C}(\text{Cl})\text{-CH}_2\text{-Br} \xrightarrow[-e]{-\text{Br}} (\text{CH}_3)_2\text{-C}(\text{Cl})\text{-CH}_2^+$	2.65
$\text{CH}_3\text{-CH}(\text{Br})\text{-CH}_2\text{CH}_2\text{Cl} \xrightarrow[-e]{-\text{Br}} \text{CH}_3\text{-}\overset{+}{\text{CH}}\text{-CH}_2\text{CH}_2\text{Cl}$	2.70

c. First field-free metastable ions by the technique of Jennings.¹⁰

* a represents the half height width of the metastable ion peak (C₄H₈³⁵Cl-H³⁵Cl), and b represents the distance between the tops of the isotopic metastable ion peaks (C₄H₈³⁵Cl-H³⁵Cl) and (C₄H₈³⁷Cl-H³⁷Cl).

energies. The results are shown in Table 4. For the chloride and bromide, the relative peak intensities are independent of electron energy (indicating a common precursor). They are compatible with those for randomly selected hydrogen and deuterium atoms in ethylene expelled from the $C_4H_8X^+$ ion (involving 5H and 2D- see structure I for this species). The alternative routes, $C_3H_7^+$ radical expelled from the molecular ion (involving 8H and 2D atoms in a structure similar to I) or $C_3H_7^+$ loss from a completely "scrambled" molecular ion, would yield fragment ions in a ratio $C_2H_4X:C_2H_3DX:C_2H_2D_2X = 7:7:1$ or $3.5:4.7:1$, respectively. The relative intensities of the peaks $C_2H_4X^+$ and $^{13}CCH_4X^+$ for the 1- ^{13}C bromide are also compatible with random selection of carbon atoms in ethylene lost from the bromo-t-butyl cation. These again are not compatible with their originating from a completely scrambled molecular ion. Thus these ions very probably originate from the $C_4H_8X^+$ species for the halogen compounds. We propose that this precursor ion has a hydrogen atom from a methyl group bonded to halogen and unavailable for scrambling. For the alcohol, similar results are complicated by the presence of an overlapping peak at m/e 45. However, this ion was shown (by high resolution) to consist of approximately equal parts of $C_3H_5D^+$ and $C_2H_4OH^+$. Thus the results for the alcohol and the halides are in good agreement. Non-participation by one H atom in the otherwise completely scrambled fragmentation of an ion has not been previously observed.

Table 5 lists the normal peak abundances for the loss of methane and its deuterated analogs for the $((CH_3)_2C-CH_2X-CH_3)$

TABLE 4. Relative intensities of the peaks $[C_5H_5X]^+$, $[C_5H_4DX]^+$ and $[C_5H_3D_2X]^+$ at various electron energies for 1,1-d, neopentyl compounds

Electron energy (eV)		Relative intensities ^a				Calculated for random loss		
		70	20	15	10	6H, 2D	5H, 2D	4H, 2D
Ion	m/e							
C_5H_5OH	45	2.3	2.3	2.2	2.2 ^b	3	2	6
C_5H_4DOH	46	4.6	4.6	4.2	3.8	8	4	8
$C_5H_3D_2OH$	47	1.0	1.0	1.0	1.0	3	1	1
$C_5H_4^{81}Br$	109	2.2	2.2	0	2.2	3	2	6
$C_5H_3D^{81}Br$	110	3.9	3.8	—	3.9	8	4	8
$C_5H_2D_2^{81}Br$	111	1.0	1.0	—	1.0	3	1	1
$C_5H_4^{35}Cl$	63	2.3	2.3	2.3	2.3	3	2	6
$C_5H_3D^{35}Cl$	64	4.2	4.1	4.2	4.1	8	4	8
$C_5H_2D_2^{35}Cl$	65	1.0	1.0	1.0	1.0	3	1	1

^a The observed relative intensities are corrected for incomplete labelling and appropriate contributions from ^{13}C , ^{37}Cl and ^{79}Br .

^b Corrected for ~50% contribution from $C_5H_5D_2$ (see text).

Table 5.

Relative intensities of the peaks^a $C_3H_2D_2X^+$,
 $C_3H_3DX^+$ and $C_3H_4X^+$ from the $(C_4H_8X-CH_4)$
 process for 1,1-d₂ neopentyl alcohol
 and chloride (70ev)

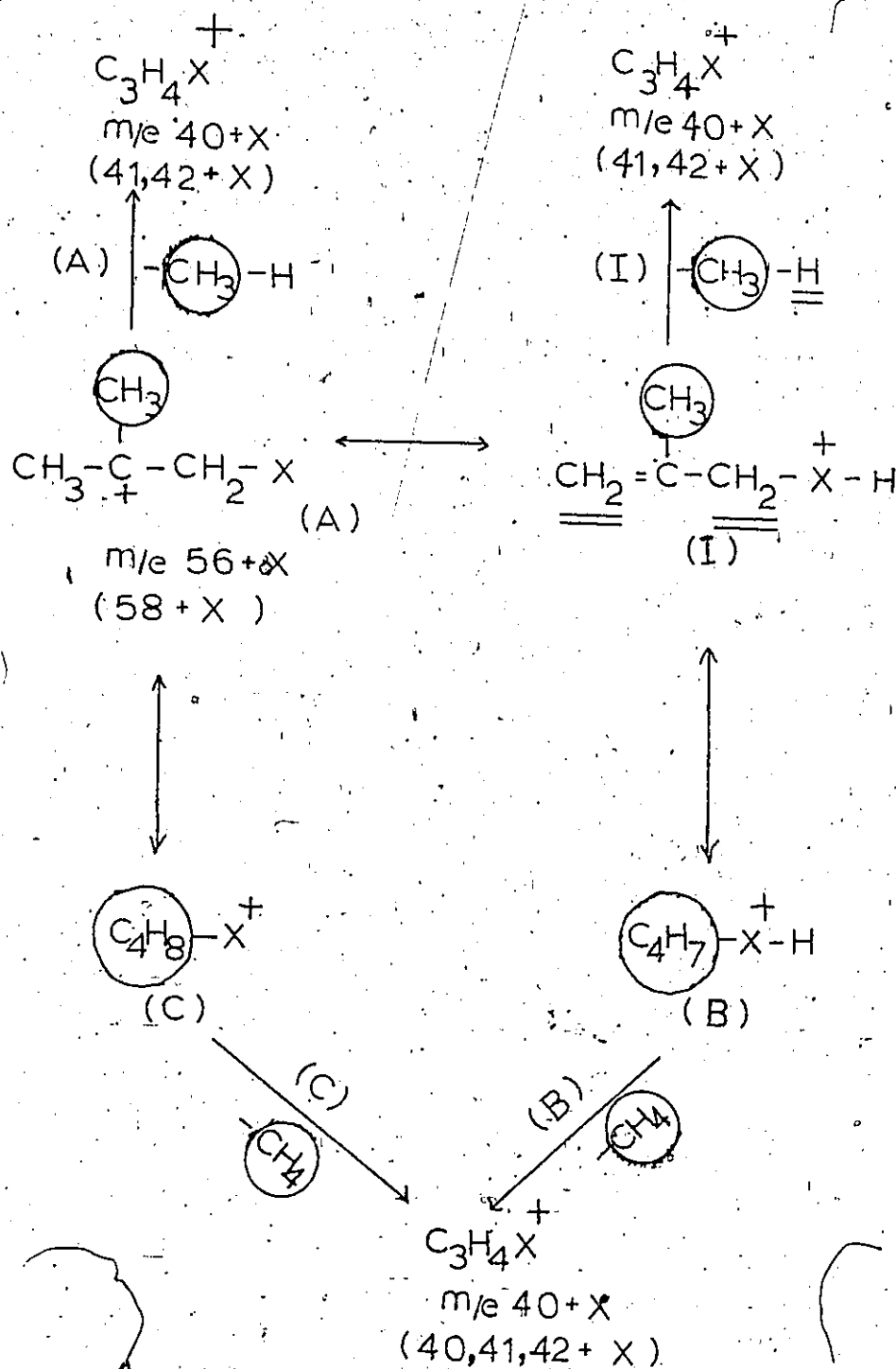
Ion	m/e	Relative ^a intensities	Calculated for random loss	
			6H,2D	5H,2D
^b $C_3H_2D_2OH^+$	59	16.8	1	1
$C_3H_3DOH^+$	58	2.67	2.67	4
$C_3H_4OH^+$	57	~ 0.0	1	2
$C_3H_2D_2^{35}Cl^+$	77	14.2	1	1
$C_3H_3D^{35}Cl^+$	76	5.5	2.67	4
$C_3H_4^{35}Cl^+$	75	< 1.0	1	2

a. The observed relative intensities are corrected for incomplete
 labelling and appropriate contribution from ^{13}C and ^{37}Cl .

b. High resolution measurement.

process from three representative sources. They were very weak in intensity. There are four possible mechanisms for the loss of methane from the $(\text{CH}_3)_2\text{-}\dot{\text{C}}\text{-CD}_2\text{X}$ ions. These are shown as Scheme 5.

In mechanism (A), methane loss originates from direct 1,2-elimination. One of the methyl group picks a hydrogen atom either from another methyl group or from the methylene group (structure (A)). Predicted value from structure (A) is 1.5:1. There are two possible fragmentation mechanisms arising from structure (I), ^{see p.39} proposed previously for the $((\text{CH}_3)_2\text{-C-CH}_2\text{X-HX})$ process. First, all the hydrogens (except the one which has migrated to the heteroatom) are completely scrambled prior to methane loss (structure (B)). The random value is 1:4:2 for $\text{C}_3\text{H}_2\text{D}_2\text{X}^+ : \text{C}_3\text{H}_3\text{DX}^+ : \text{C}_3\text{H}_4\text{X}^+$. Another possibility is that methane loss originates from the "intact" methyl group and a hydrogen atom from either one of the two methylene groups (direct 1,2-elimination). Predicted $(\text{C}_4\text{H}_6\text{D}_2\text{X-CH}_4)^+ : (\text{C}_4\text{H}_6\text{D}_2\text{X-CH}_3\text{D})^+$ ratio is 1:1 (mechanism (I)). The fourth mechanism (mechanism (C)) (structure (C) in Scheme 5) is that complete scrambling of all eight hydrogens prior to methane loss. Random value for methane loss, $\text{C}_3\text{H}_2\text{D}_2\text{X}^+ : \text{C}_3\text{H}_3\text{DX}^+ : \text{C}_3\text{H}_4\text{X}^+$ is then 1:2.7:1. Daughter ion abundance results (Table 5) indicate that the observed values are compatible with direct cleavage mechanism (mechanisms (A) and (I)). They are not compatible with random selection of hydrogens (mechanisms (B) and (C)). Mechanism (I) is, however, preferred to mechanism (A). It is likely that hydrogen atoms in the CH_2X group, due to the influence of the heteroatom X, are



Scheme 5. Four possible fragmentation mechanisms for the elimination of methane from the $(\text{CH}_3)_2\text{C}^+-\text{CH}_2\text{X}$ species ($\text{X} = \text{OH}, \text{OD}, \text{Br}, \text{Cl}$).

more strongly bonded to carbon. The relative intensities of peaks $^{13}\text{CC}_2\text{H}_4\text{Br}^+$ and $\text{C}_3\text{H}_4\text{Br}^+$ of 1.0:0.0 for the neopentyl- ^{13}C -bromide are also compatible with the specific selection of carbon atoms (from CH_3 group only) in methane from bromo-*t*-butyl cation. The random value for $^{13}\text{CC}_2\text{H}_4\text{Br}^+ : \text{C}_3\text{H}_4\text{Br}^+$ is 3:1. This agrees with the results obtained from the 1,1- d_2 chloride and alcohol (Table 5). Thus from these two sets of results, we propose that methane is lost from the unrearranged and unscrambled $(\text{CH}_3)_2-\dot{\text{C}}-\text{CH}_2\text{X}$ ions.

We have stressed (see Chapter 2) that the hydrocarbon analog $\text{t-C}_4\text{H}_9^+$ of the $(\text{CH}_3)_2-\dot{\text{C}}-\text{CH}_2\text{X}$ ions ($\text{X}=\text{Br}, \text{Cl}, \text{OH}$ and OD) lost ethylene in a completely random manner^{17,30}. The loss of methane, however, involved a combination of 1,2-direct bond elimination as well as a complete scrambling of carbon and hydrogen atoms¹⁷. This is in direct contrast to the fragmentation mechanism of $(\text{CH}_3)_2-\dot{\text{C}}-\text{CH}_2\text{X}$ for ethylene and methane loss. Ethylene loss involves random selection of hydrogens from the $\text{CH}_2=(\text{CH}_3)-\text{C}-\text{CH}_2\text{X}^+-\text{H}$ ion (involving 5H and 2D atoms, see structure (I) for this species). CH_4 loss, however, is a specific 1,2-elimination. These clearly demonstrate that the presence of the heteroatoms increases the barrier for internal rearrangement relative to their hydrocarbon ion analogs. Recently, Williams and Uccella studied⁸⁸ $\text{C}_6\text{H}_5-\text{C}_3\text{H}_6^+$ ions of structures $\text{C}_6\text{H}_5-(\text{CH}_3)_2\text{C}^+$, $\text{C}_6\text{H}_5-\text{CH}(\text{CH}_3)\text{CH}_2^+$, $\text{C}_6\text{H}_5-\text{CH}_2\text{CH}_2\text{CH}_2^+$, $\text{C}_6\text{H}_5-\text{CH}_2-\dot{\text{C}}\text{H}-\text{CH}_3$ and $\text{C}_6\text{H}_5-\text{CH}-\text{CH}_2\text{CH}_3$. It was found that in these ions only the six hydrogens of the C_3 side chain became equivalent before unimolecular decomposition via loss of C_2H_4 , C_3H_4 and C_6H_6 .

In contrast, CH_4 loss from the C_3 chain was specific 1,2-elimination without any rearrangement. They concluded that the latter reaction occurred from an excited state in which 1,2-shifts were forbidden. These observations are consistent with our own studies.

(2) $\text{CH}_3-\dot{\text{C}}\text{H}-\text{CH}_2\text{CH}_2\text{X}$ ions ($\text{X}=\text{OH}$ and Cl)

The $\text{CH}_3-\dot{\text{C}}\text{H}-\text{CH}_2\text{CH}_2\text{X}$ ions also dissociated by losing ethylene and methane to yield $\text{C}_2\text{H}_4\text{X}^+$ and $\text{C}_3\text{H}_4\text{X}^+$ fragments respectively (Scheme 1). However, the measurement of the former fragment is complicated by the presence of some competing contribution from the $(\text{M}-\text{CH}_3\text{CHBr})$ process by direct bond cleavage. On the other hand, the $\text{C}_3\text{H}_4\text{X}^+$ ion from both $\text{CH}_3-\dot{\text{C}}\text{H}-\text{CH}_2\text{CH}_2\text{X}$ ions were too weak in intensity to be measured accurately. Thus speculation on their mechanisms of formation is unjustified.

Conclusion

We have shown that for the formation of $((\text{CH}_3)_2\text{CCH}_2\text{X}-\text{HX})$, $((\text{CH}_3)_2-\text{C}-\text{CH}_2\text{X}-\text{C}_2\text{H}_4)$ and $((\text{CH}_3)_2-\text{C}-\text{CH}_2\text{X}-\text{CH}_4)$ ions in the decomposition reactions of $(\text{CH}_3)_2-\dot{\text{C}}\text{H}-\text{CH}_2\text{X}$ ions, the common structure (I) ^{see p.39} is the best representation of the decomposing ions. There is no evidence that the $\text{CH}_3-\dot{\text{C}}\text{HCH}_2\text{CH}_2\text{X}$ isomeric ions isomerize to ions of structure (I). It is therefore apparent that the presence of an oxygen atom, or bromine and chlorine atoms severely limits scrambling and isomerization reactions compared with hydrocarbon ions.

CHAPTER 4INTRAMOLECULAR AND INTERMOLECULAR FUNCTIONALGROUP INTERACTION IN THE MASS SPECTRA OFSOME CHLOROHYDRINS AND SOME CHLOROACIDS

Recent years have seen much effort devoted to understanding the role that various functional groups play in directing electron impact induced fragmentation processes.

This has been essential for the facile application of mass spectrometry to problems of structure elucidation. Naturally occurring molecules however, often contain an array of functional groups. Thus it is not only important to appreciate the fragmentation-directing capabilities of isolated functionalities in a molecule, it is also of primary significance to determine the extent to which functional centers within a molecule interact with each other after ionization^{96, 101-114}.

In considering this problem with respect to a molecule containing functional groups A and B, two questions arise. (1) Are the individual fragmentation pathways associated with A and B retained in the spectrum of the bifunctional compound? (2) Do new decomposition routes characteristic of neither A nor B individually appear? In answering, it is important to note the effect of varying the distance separating the A and B centers. Of the cases studied thus far^{96, 101-121}, the latter possibility seems to be more prevalent. Direct interaction of the functional groups^{96, 101-114}, migration of electron rich groups to carbonium

ion centers¹¹⁵⁻¹¹⁶, and anchimeric assistance¹¹⁷⁻¹²¹ were the reasons cited to explain the unusual fragmentation patterns in these instances.

Numerous recent studies suggest that the electron-impact induced fragmentation of organic compounds can be influenced by interaction between remote functional groups. Such interactions are demonstrated most unambiguously when they result in direct bond formation between the functional groups. For example, the mass spectra of a series of trimethylsilyl *o*-phenoxyalkanoates¹⁰¹ exhibited prominent fragmentations which depended upon the interaction of the phenyl ether and silyl ester groups. The mass spectra of some phenyl, benzaloxy and alkoxy analogs, as well as some methyl ester analogs illustrated the necessity of the presence of a heteroatom in both of the functional groups at the ends of the polymethylene chain in order to observe the appropriate interactions. Thus in open-chain bifunctional molecules these interactions appeared to be essentially independent of the distance between the functionalities, and charge transfer with coiling of the carbon chain has been invoked. In the case of dicarboxylic acids of the form $\text{HOOC}-(\text{CH}_2)_n-\text{COOH}$ ($n=0$ to 12), studied by Holmes and St. Jean¹⁰², it was found that 27% to 35% of the water loss from the molecular ion of succinic acid to pimelic acid ($n=2$ to 5) came from carboxyl-carboxyl interaction. From suberic acid to dodecane dicarboxylic acids ($n=6$ to 12), ions $(\text{M}-\text{H}_2\text{O})^+$ resulting from carboxyl-carboxyl interaction were very few or absent. However, the significant observation in the series was that $(\text{M}-\text{H}_2\text{O})^+$

intensities fell sharply in 10 to 15 membered rings ($n = 5$ to 10) from 8% to ~1% and then rose to an approximately constant yield of 3% from 16 membered rings onward ($n \geq 11$). More recently, Fenselau and her co-workers¹⁰⁴ used some steroid molecules such as dihydroxy-5-cholestane and dihydroxy-4-androsten-3-one as rigid templates to determine how far apart two functional groups can be moved before detectable interaction ceases. A number of steroidal diols, with the hydroxyl groups deuterated, were examined for loss of D_2O on electron impact induced fragmentation. Three conclusions were drawn according to the observation. Firstly, neither intermolecular deuterium transfer nor indiscriminate intramolecular scrambling of hydrogen and deuterium was a significant process. Secondly those compounds in their study which lost D_2O on electron impact were all 1,2- or 1,3-diols. Thirdly these diols all showed strong intramolecular hydrogen bonding in solution. The range of O-D....O-D distances within which D_2O loss occurred was thus the range within which intramolecular hydrogen bonding occurred. In conclusion, the results seemed to offer direct evidence that electron impact induced intramolecular interactions of functional groups would result in bond formation only when the atoms involved could be brought to within approximately normal bonding distances. Thus the works of Holmes and his co-worker¹⁰², and Fenselau and her co-workers¹⁰⁴ should allow assessment of the role played by chain coiling¹⁰¹ and ring opening shown by acyclic and cyclic systems respectively. Recently, Horvath and Kuszmann¹⁰⁵ observed an intense ion, m/e 85, in the mass spectrum of hexane-2,5-diol

($M^{+} 118$). This ion might arise either from the ($M-H_2O-CH_3$) or the ($M-CH_3-H_2O$) process, or both. It was unfortunate that appropriate metastable ion peaks for the above two processes were not reported. If the ion, m/e 85, was partly produced from the latter process, it might indicate that two functional groups (hydroxyl groups in this case) could become more proximate following a ($M-CH_3$) cleavage, which favored water loss.

Water elimination involving direct hydroxyl-hydroxyl interaction from molecular ion has been most intensively studied. Thus electron impact studies on α, β diols¹⁰⁵, and cyclohexane-1,4-diol¹⁰⁶; cyclohexane-1,3-diol¹⁰⁶; cyclohexane-1,2-diol^{96,106-108} and cyclopentane-1,2-diol¹⁰⁹ were shown to lose water involving direct hydroxyl-hydroxyl interaction for molecular ion via seven-, six- or five-membered ring transition states respectively. It is interesting to note that, as discussed in Chapter 2, similar mono-hydroxyl aliphatic and cyclic compounds lost water from the molecular ion via five- and six-membered transition states; with the latter ring size more favorable.

In the present study, the mass spectrum of 3-chloro-2,2-dimethyl-propanol was investigated. The results show that elimination of hydrochloric acid from the molecular ion arises from two sources. These are direct interaction of chlorine and hydroxyl at the ends of the open-chain bifunctional molecule ($\sim 95\%$), and chlorine- β -methylene and chlorine- β -methyl interaction ($\sim 5\%$). To determine how far apart these two functional groups (OH and Cl) can be before detectable interaction ceases, the

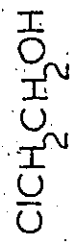
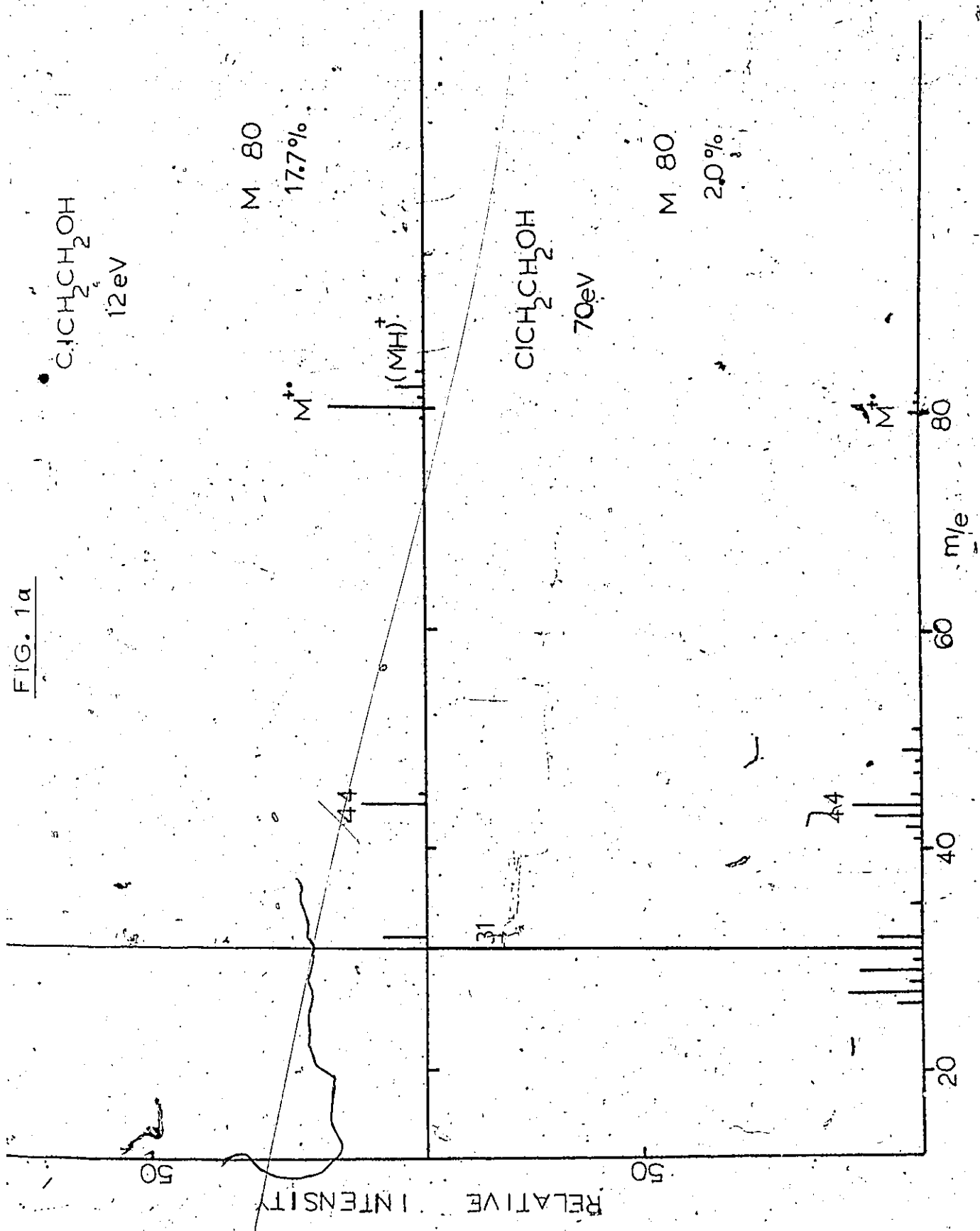
mass spectra and fragmentation mechanisms for the homologous chlorohydrins $\text{ClCH}_2-(\text{CH}_2)_n-\text{CH}_2\text{OH}$ from $n=0$ to 4 were studied. Moreover, the mass spectra and fragmentation mechanisms of three chloroacids, chloroacetic acid, 3-chloropropanoic and 3-chloro-2,2-dimethyl-propanoic acid were also examined briefly to determine if there is any direct chlorine-carboxyl interaction. None of these compounds has received previous attention. It was also hoped that through these studies, more information regarding direct functional group interaction could be discovered. The mass spectra of the chlorohydrin series are described first.

THE MASS SPECTRA OF SOME CHLOROHYDRINS

(A) 2-chloroethanol

The mass spectra of 2-chloroethanol and 2-chloro-1,1-d₂-ethanol are shown as Figs. 1a and b. Examination of the molecular ion region of the mass spectra shows that besides M^+ , $(M-H)^+$ and $(M+H)^+$ (m/e 79, 81; 80, 82; and 81, 83) for 2-chloroethanol and $(M-D)^+$ and $(M+H)^+$ (m/e 78, 80; 82, 84 and 83, 85) for 2-chloro-1,1-d₂-ethanol are present. These are confirmed by high resolution measurements using the double-focusing A.E.I. MS 902-S instrument. At low ev, $(M-H)^+$ and $(M-D)^+$ are absent for 2-chloroethanol and 2-chloro-1,1-d₂-ethanol respectively. The $(M+H)^+$ ion formation is independent of electron energy (10 ev. to 70 ev) and sample pressure in the ion source (varied from 0.8×10^{-7} mm to 6.0×10^{-6} mm Hg pressure). Thus "ion-molecule reactions" for the formation of $(M+H)^+$ ion are very unlikely. The $(M-H)^+-d_0$, $(M-D)^+-d_2$; and $(M+H)^+-d_0$ and $-d_2$ ions lose Cl

FIG. 1a



70eV

M 80

20%

44

$\text{M}^{+\bullet}$

80

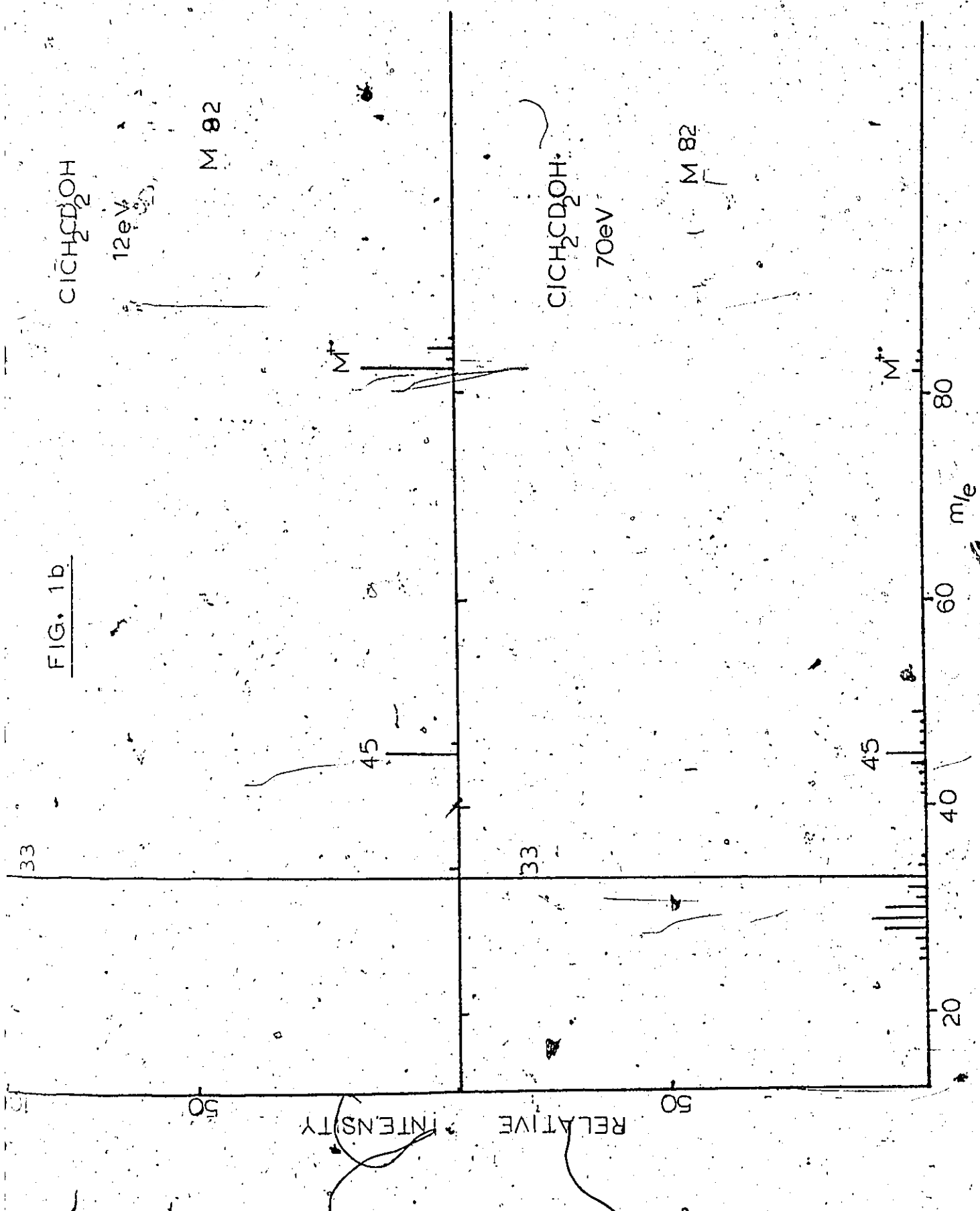
m/e

40

20

RELATIVE INTENSITY

FIG. 1b



and H_2Cl (HDCl-d_2) respectively to give fragment ions at m/e 44 ($45-d_2$). These two processes are confirmed by the observation of the appropriate metastable ion peaks in both the first and second field-free region, and the presence of H_2Cl^+ and HDCl^+ ($-d_2$) ions from high resolution measurement. The proposed fragmentation mechanism for the formation and dissociation of $(\text{M}+\text{H})^+$, and $(\text{M}-\text{H})^+$ and M^{++} is shown in Schemes 1 and 2 respectively.

We show the formation of the stable $\text{ClCH}_2\text{CH}=\text{OH}^+$, m/e 79, 81 ($80, 82\text{-OD}, 80, 82\text{-d}_2$) as resulting from loss of the hydrogen atom attached to the carbinol carbon atom followed by chlorine loss to give m/e 44, $\cdot\text{CH}_2\text{CH}=\text{OH}^+$ (m/e $45\text{-OD}, -d_2$).

The ionization of the hydrogen bonded dimer $(\text{ClCH}_2\text{CH}_2\text{-OH})_2$ (chlorine-hydroxyl intermolecular hydrogen bonding) splits during or after ionization into $\text{C}_2\text{H}_4\text{OCl}$ and $\text{HCl-CH}_2\text{-CH}_2\text{-OH}$, m/e 81, 83 (m/e 83, 85-d_2). The protonated 2-chloroethanol ion $\text{HCl-CH}_2\text{CH}_2\text{OH}^+$

then fragments by loss of H_2Cl (HDCl-d_2) to give a stable radical ion $\cdot\text{CH}_2\text{-CH}=\text{OH}^+$, m/e 44 (45-d_2). It is to be noted that the ion

$\text{HCl-CH}_2\text{CH}_2\text{OH}$ indeed originates from the dimeric molecular ion.

This is evident from the mass spectrum of 2-chloroethanol-OD

which shows no $(\text{M}+\text{H})^+$ or $(\text{M}+\text{D})^+$ ions. This observation is

consistent with the property of intermolecular hydrogen bonding,

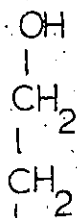
i.e. at high dilution (solvent deuterium oxide used for deuteration)

intermolecular hydrogen bonding is unimportant. "Terminal" chlorine-

hydroxyl interaction via a five-membered ring intermediate is

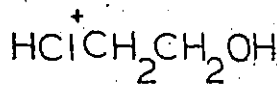
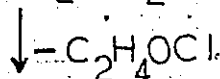
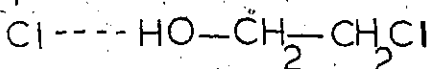
also of no importance for 2-chloroethanol. This is supported by

the low electron energy (12 eV) mass spectrum of 2-chloroethanol-OD.



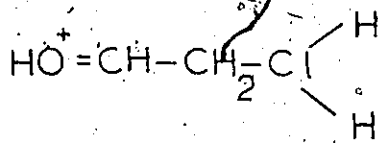
m/e 160, 162

(164, 166-d₂)



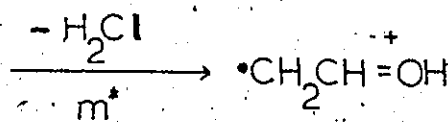
m/e 81, 83

(83, 85-d₂)



m/e 81, 83

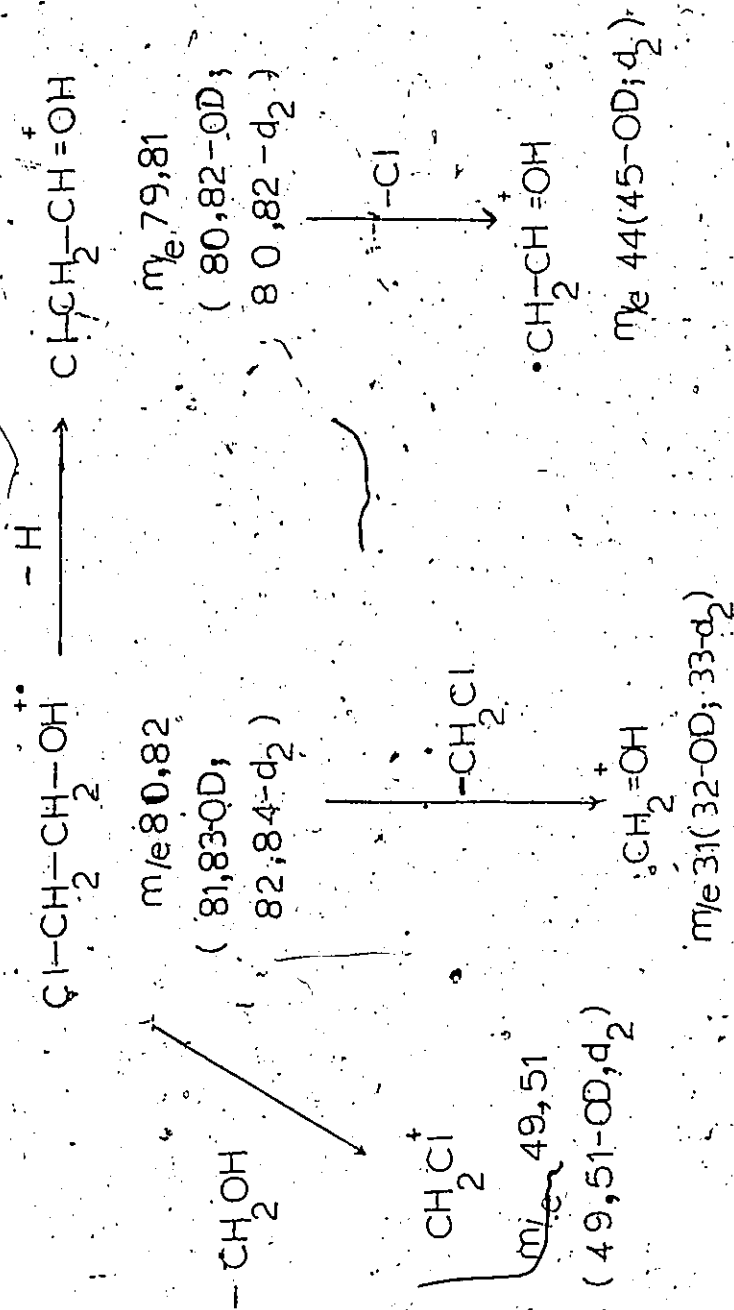
(83, 85-d₂)



m/e 44

(45-d₂)

Scheme 1. Fragmentation mechanism for 2-chloroethanol-chlorine-hydroxyl intermolecular interaction.



Scheme 2. Fragmentation mechanism for 2-chloroethanol- unrearranged molecular ion.

Here, the ion $(M-DCl)^+$, m/e 44, is relatively small compared to the ion $(M-H, -Cl)^+$, m/e 45. This parallels the behaviour of oxalic acid¹⁰². "Terminal" water loss from the molecular ion following H to COOH transfer via a five-membered cyclic intermediate was a very minor process (0.3% of the base peak).

(B) 3-chloropropanol

The mass spectra of 3-chloropropanol, 3-chloropropanol-OD and 3-chloro-1,1-d₂-propanol are shown as Figs. 2a, 2b and 2c. With the exception of $(M-1)^+$ species, the mass spectrum of this compound is different from that of 2-chloroethanol. First field-free metastable ion measurements indicate that for 3-chloro-1,1-d₂-propanol, processes $(M-HCl)$, $(M-DCl)$, $(M-D, -HCl)$ and $(M-HD, -Cl)$ to give ions m/e 60, 59, 58 and 58 respectively, all take place. Comparing Fig. 2a, b and c and the first field-free metastable ion data for 3-chloro-1,1-d₂-propanol, the fragmentation mechanism for 3-chloropropanol is proposed as shown in Schemes 3-6. These account for the most abundant ions in each of Figs. 2a, b and c.

The relative abundance of ions $(M-HCl)^+$, $(M-DCl)^+$ and their generating first field-free metastable ion peaks from the molecular ions of 3-chloropropanol-OD and 3-chloro-1,1-d₂-propanol are shown, as Table 1 (after ¹³C correction). Chlorine-hydroxyl interaction leading to hydrochloric acid expulsion from the molecular ion involves a six-membered ring transition state (Table 1 and Scheme 3). This is more favorable than chlorine- β -methylene interaction in this compound involving a five-membered, geometrically less favorable, ring intermediate

FIG. 2a

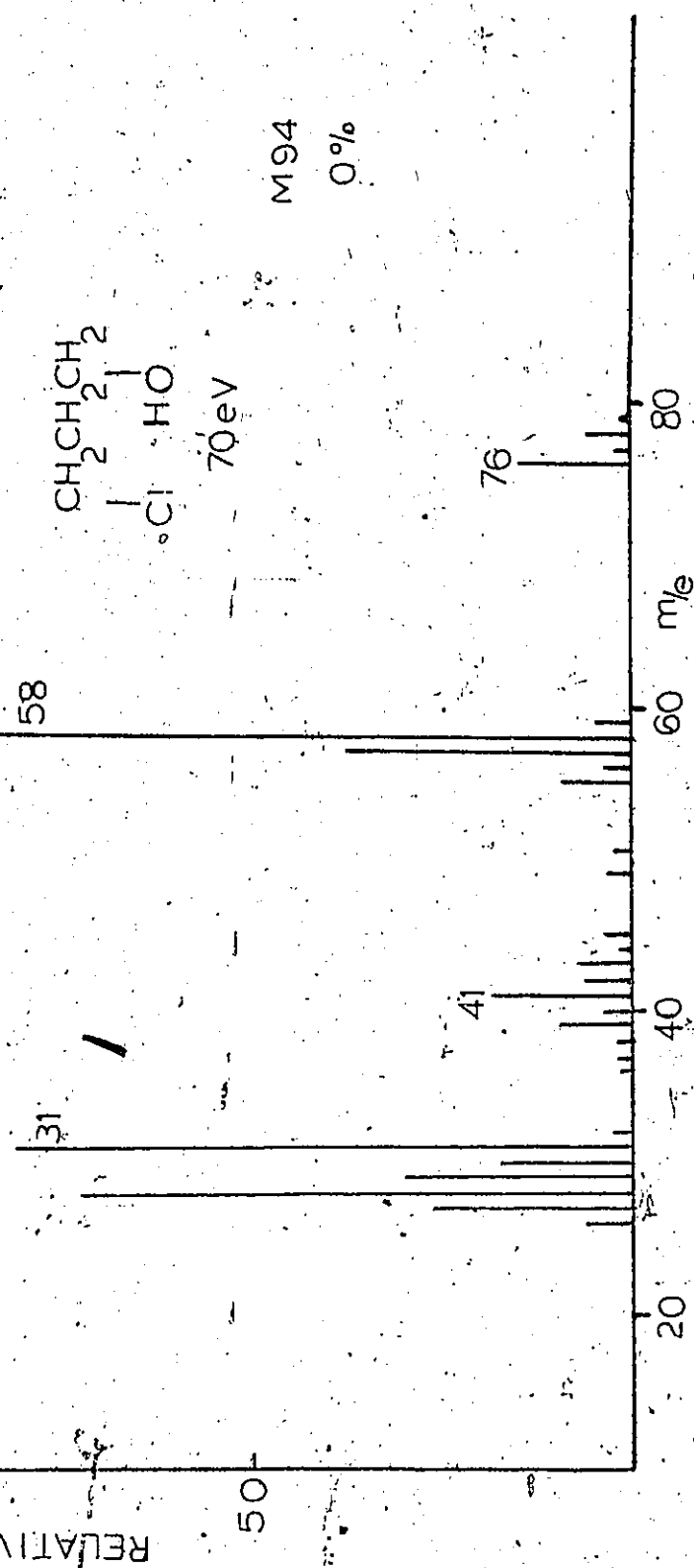
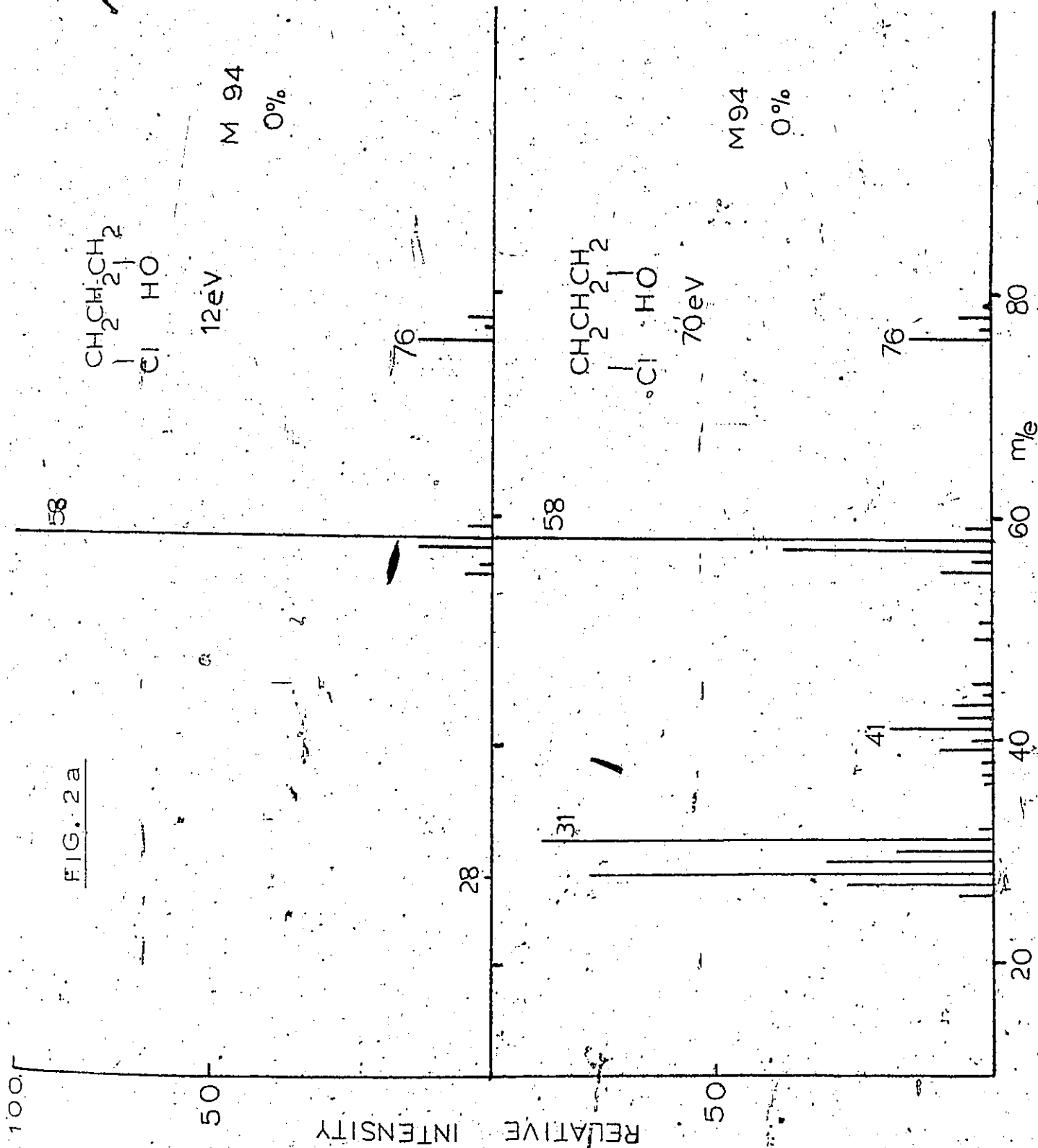
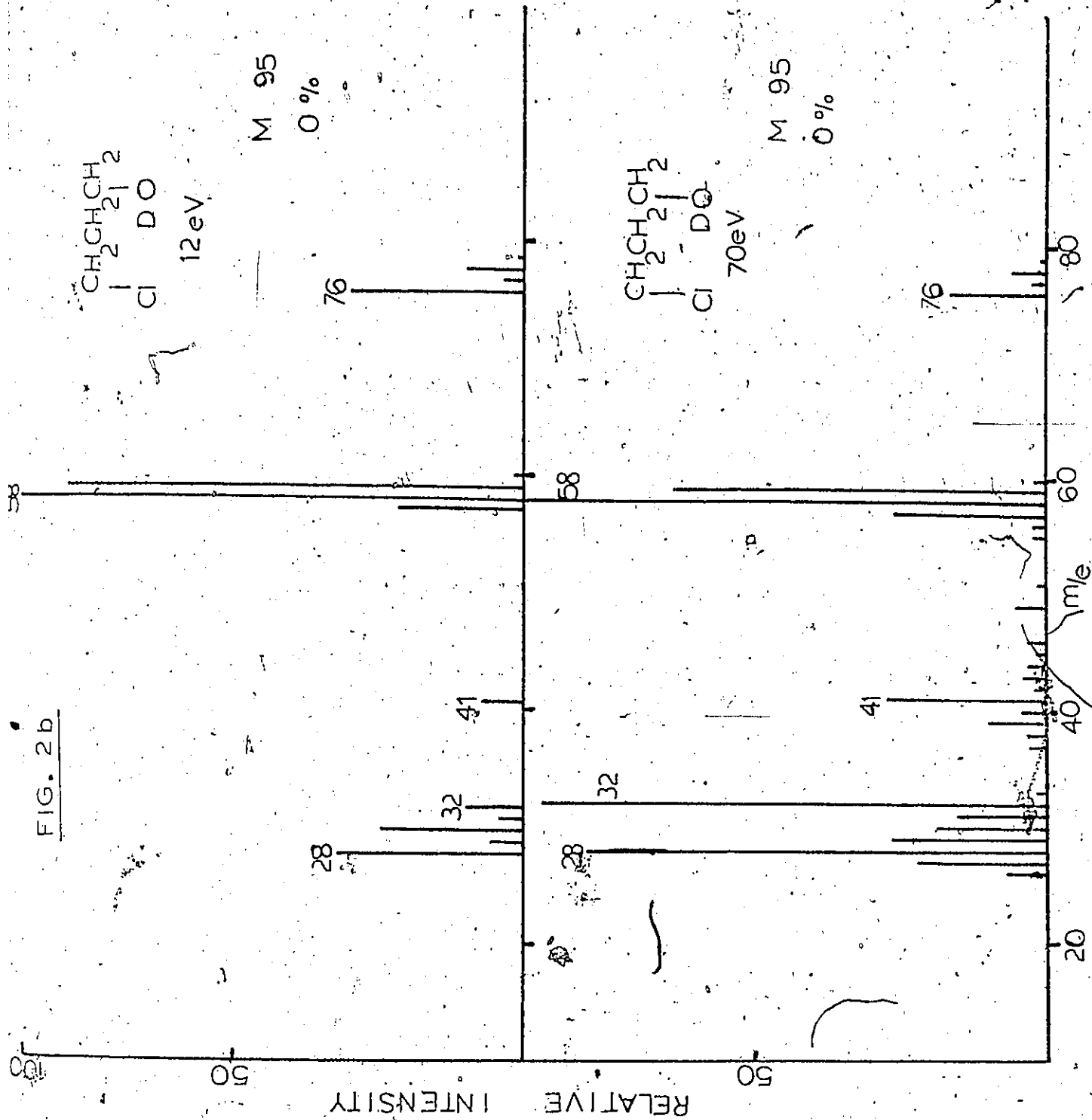


FIG. 2b



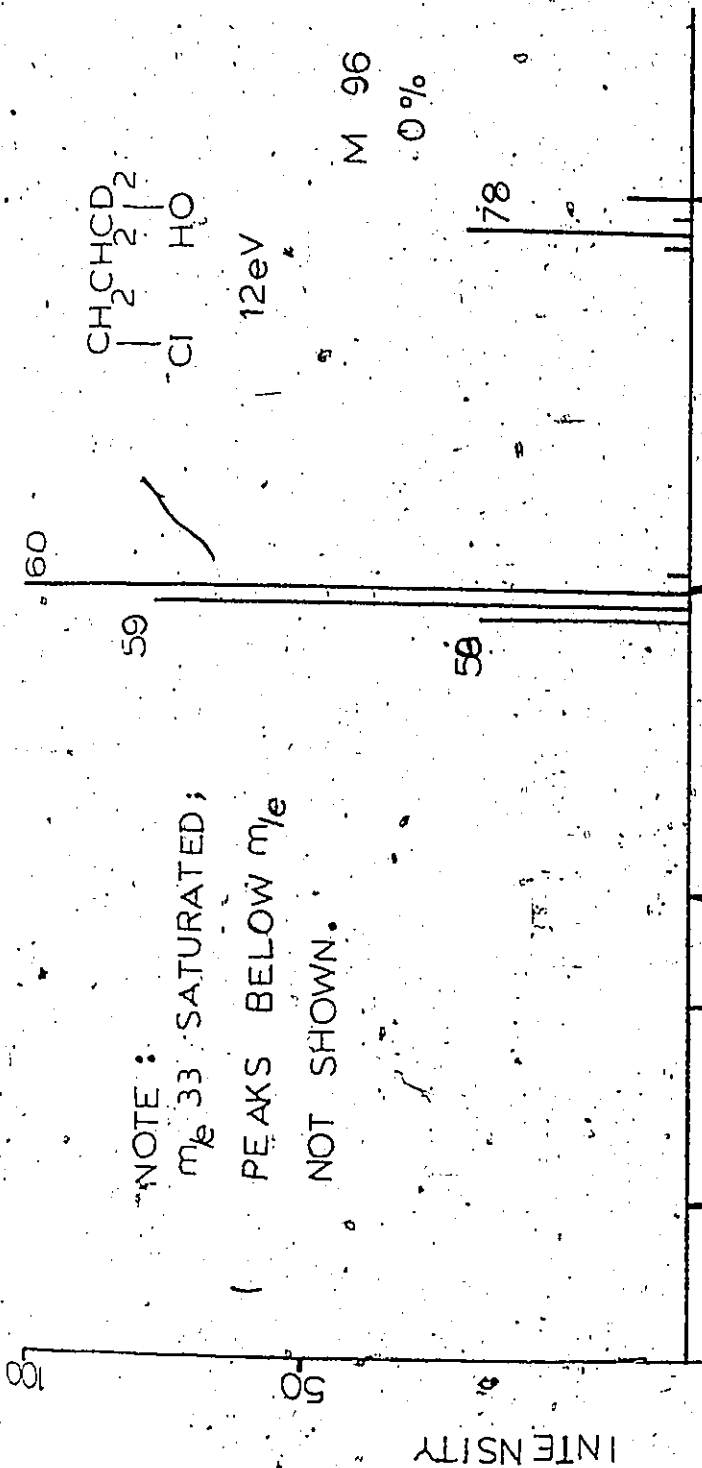
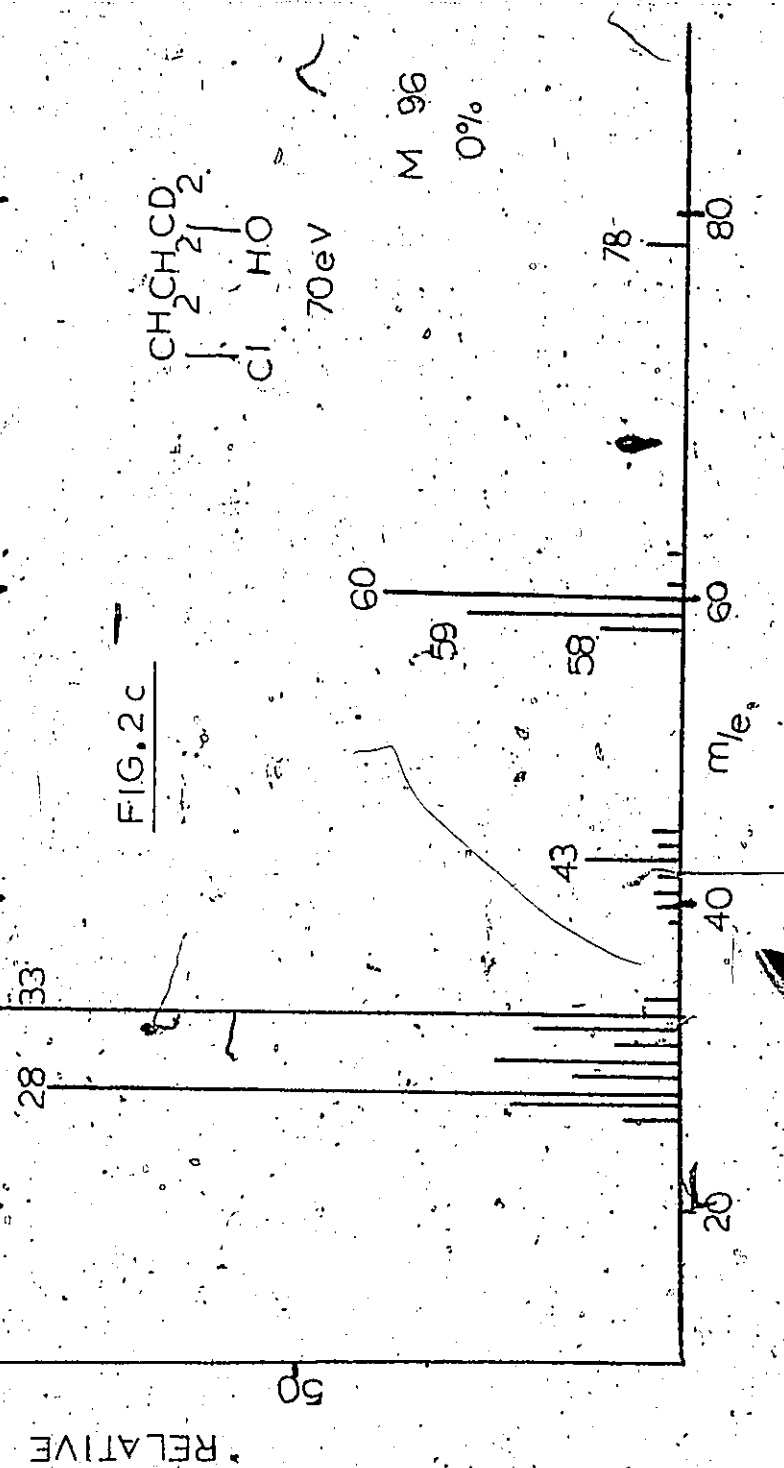
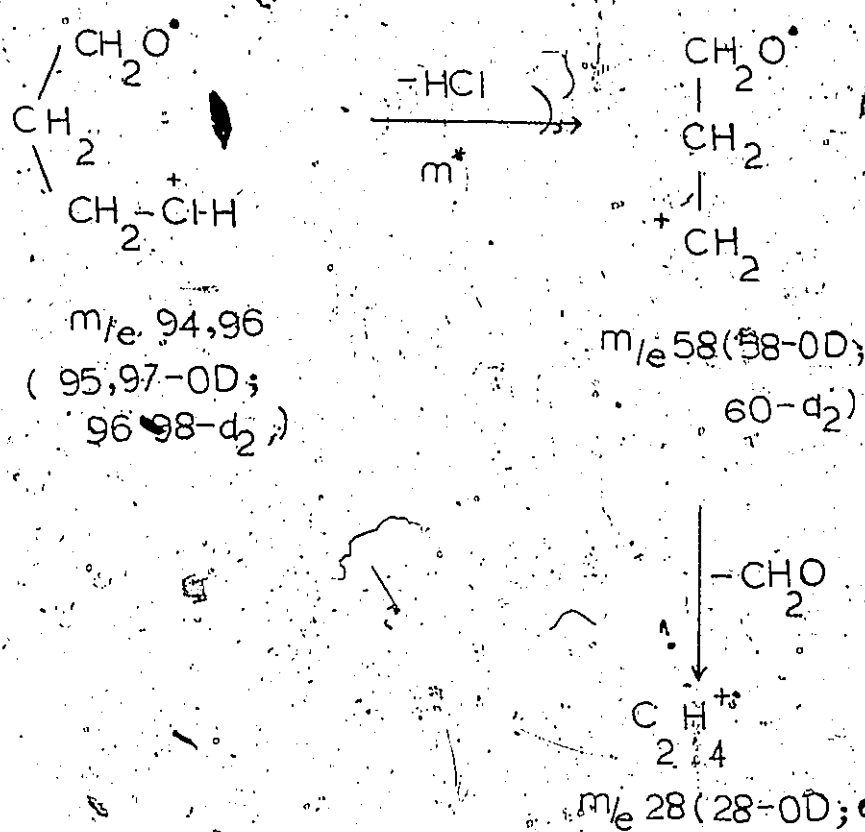
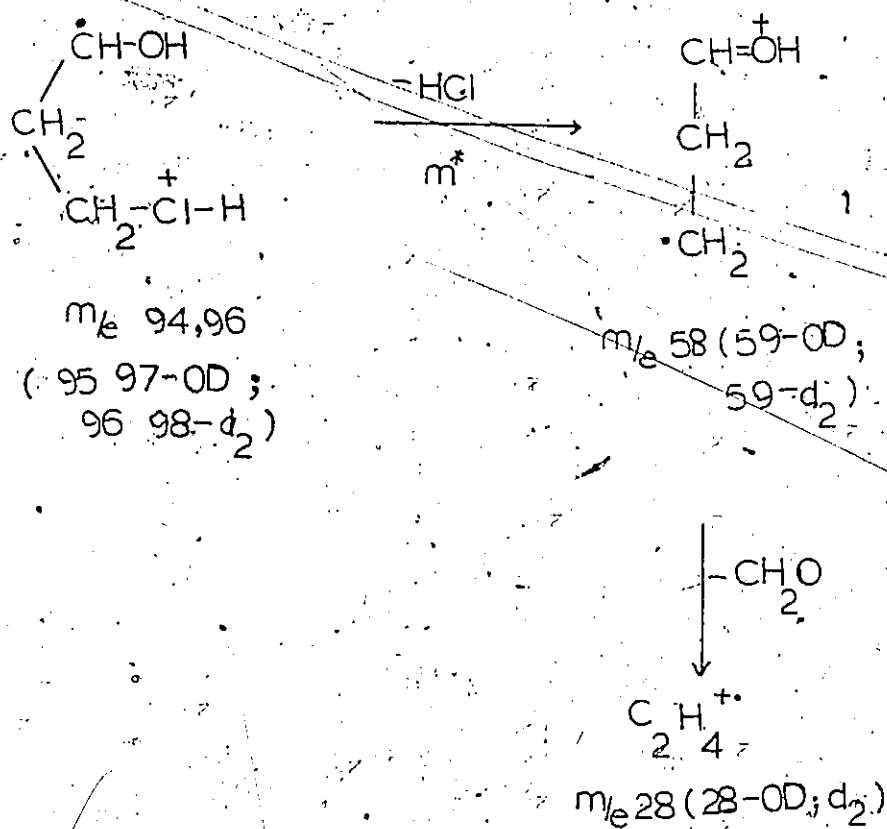


FIG. 2c

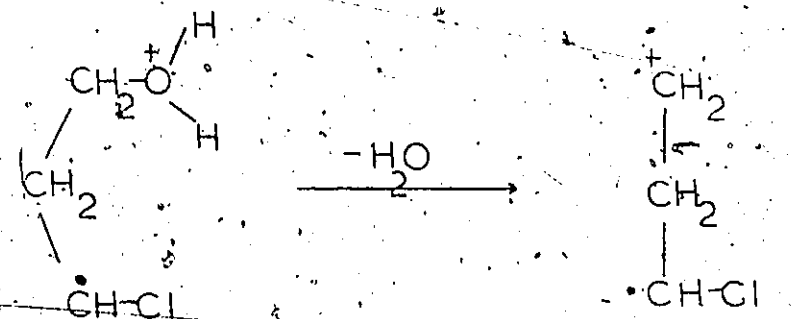




Scheme 3. Fragmentation mechanism for 3-chloropropanol-chlorine-hydroxyl interaction.



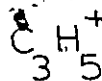
Scheme 4. Fragmentation mechanism for 3-chloropropanol-chlorine- β -methylene interaction.



m/e 94, 96
(95, 97-OD;
96, 98-d₂)

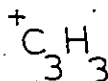
m/e 76, 78
(76, 78-OD;
78, 80-d₂)

-Cl



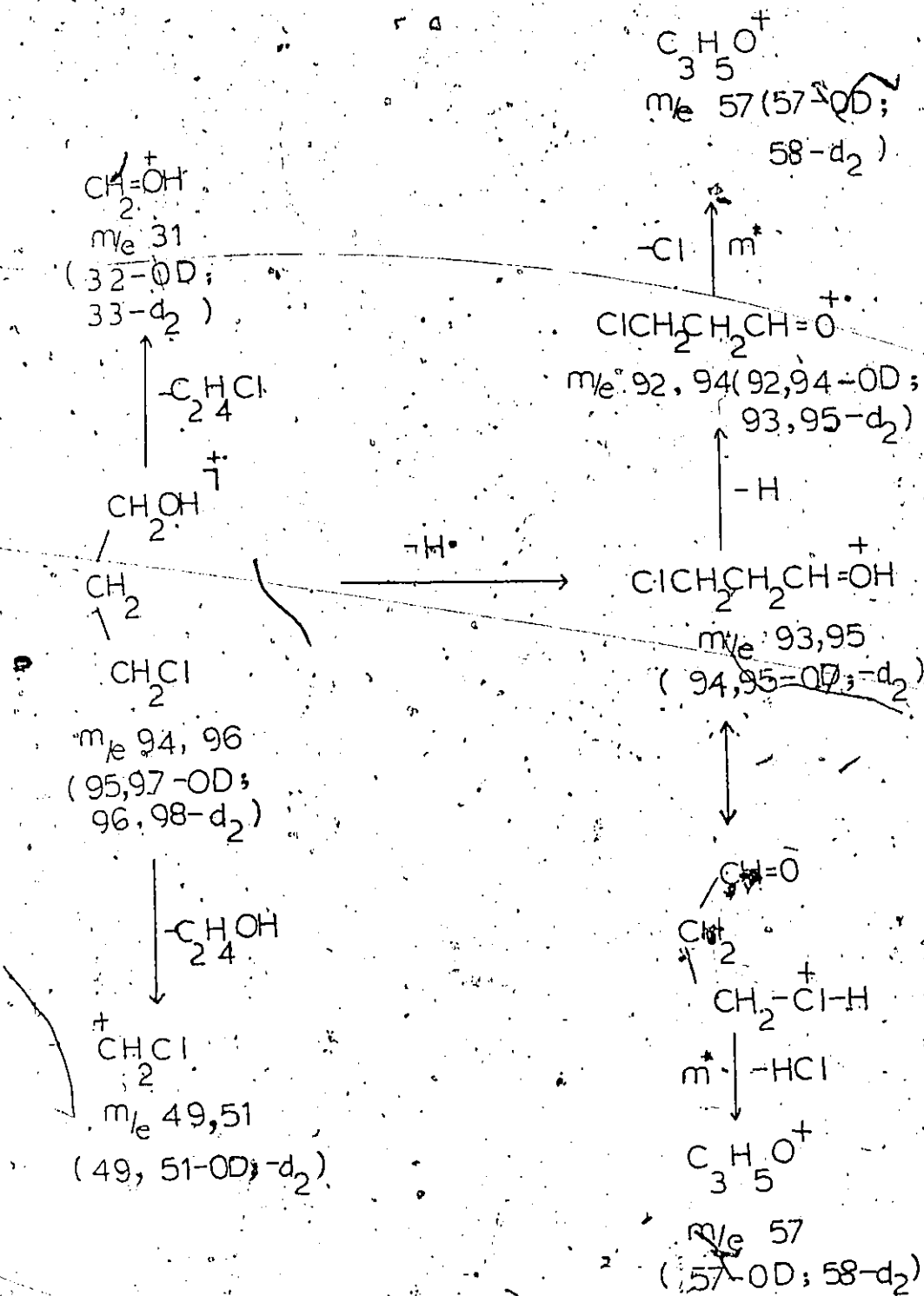
m/e 41 (41-OD;
43-d₂)

m -H₂



m/e 39 (39-OD;
39, 40, 41-d₂)

Scheme 5. Fragmentation mechanism for 3-chloropropanol-hydroxyl- β -methylene interaction.



Scheme 6. Fragmentation mechanism for 3-chloropropanol-unrearranged molecular ion.

-79-

Table 1.

Relative abundances of ions(M-HCl) and
(M-DCI) and their generating first
field-free metastable ion peaks^a
labelled
from 3-chloro-propanol

	3-chloro-propanol-OD		3-chloro-1,1-d ₂ -propanol		
m/e	<u>Peak</u> 70ev	15ev	<u>Peak</u> 70ev	15ev	m* (70ev)
58	100	100	-	-	-
59	65	82	81	78	1.0
60	-	-	100	100	5.2

(a) Metastables separated by the method of Jennings.

(Table 1 and Scheme 4). We also show the hydroxyl- β -methylene interaction leading to water loss from the molecular ion as involving a five-membered ring transition state (Scheme 5).

(C) 3-Chloro-2,2-dimethylpropanol

The mass spectra of this compound and its -OD and 1,1-d₂ analogs are shown as Figs. 3a, b and c respectively. Comparing Figs. 3a, b and c, it can be shown that about 95% of the loss of hydrochloric acid from the molecular ion arises from chlorine-hydroxyl interaction, to give (M-HCl)⁺ at m/e 86 (86-OD and 88-d₂). The proposed mechanism which accounts for the formation of most of the abundant peaks is shown as Scheme 7 and 8. We shown the chlorine-hydroxyl interaction which leads to hydrochloric acid expulsion from the molecular ion as involving a six-membered ring transition state. Chlorine- β -methyl group and chlorine- β -methylene group interactions in this compound involve a bulky five-membered ring transition state. This is not favorable, contributing only to about 5% of the total (M-HCl) loss. This is in accord with the observations on 3-chloropropanol, where chlorine- β -methylene interaction does not involve such a bulky five-membered as in the present compound, and so is more favorable.

(D) Higher homologues, ClCH₂(CH₂)_nCH₂OH (n=2 to 4), and

general discussion

The mass spectra of 4-chlorobutanol, 5-chloropentanol and 6-chlorohexanol are shown in Figs. 4-6 respectively. The most prominent ions in this group are hydrocarbon ions. Heteroatom containing ions of interest are (M-HCl)⁺, (M-H₂O)⁺ and

FIG. 3b

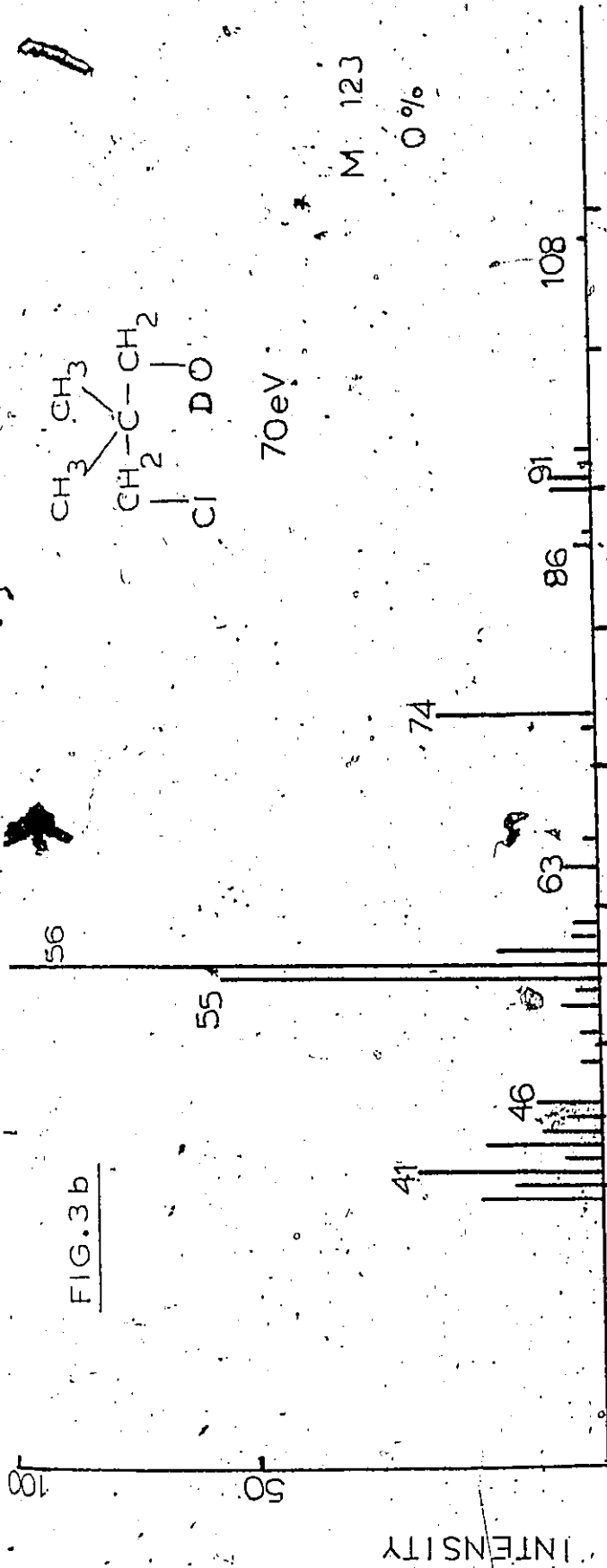
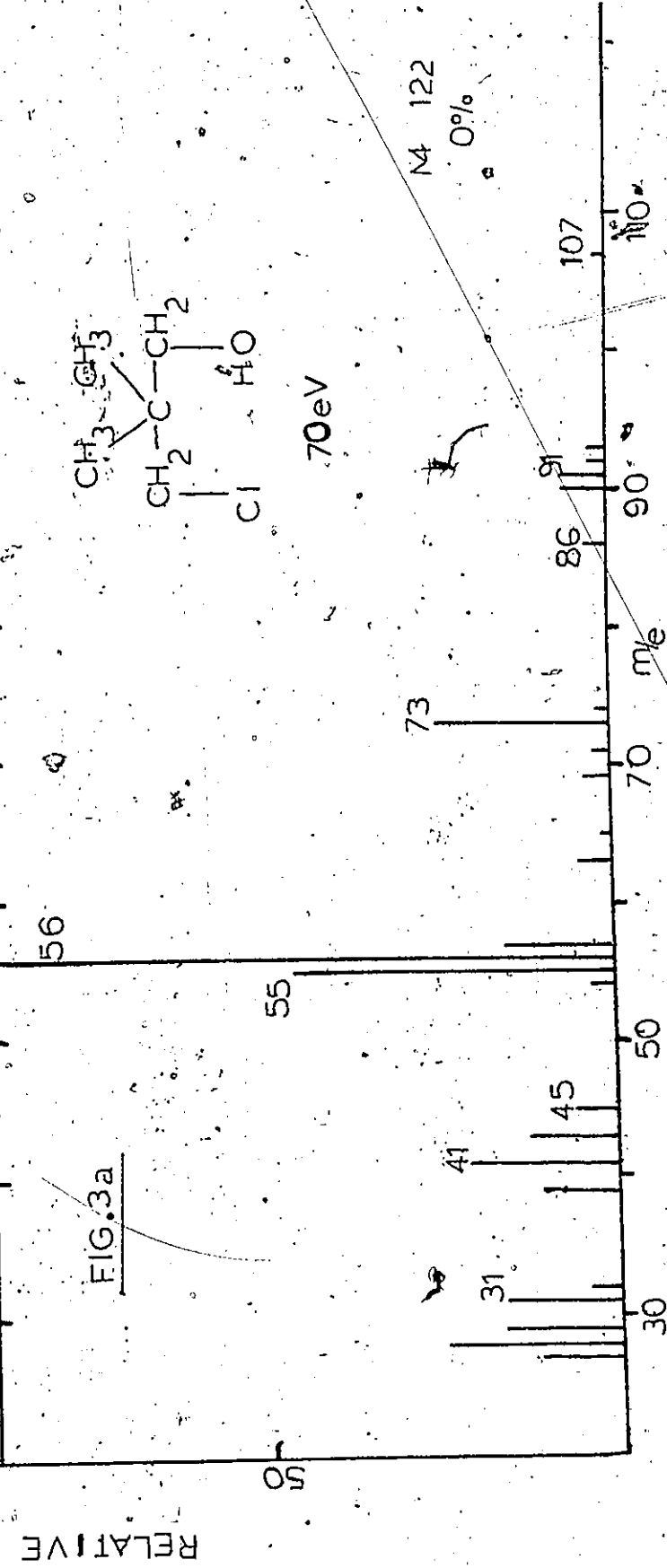
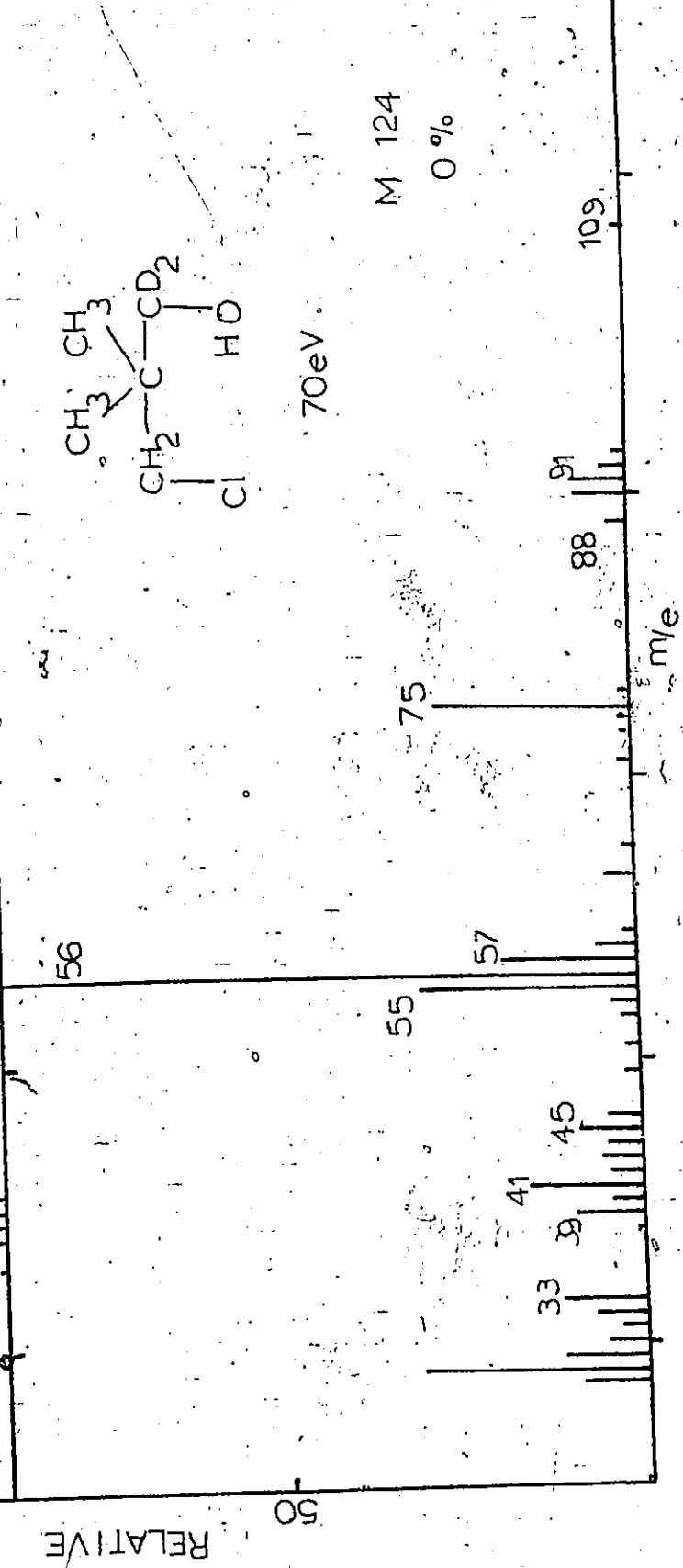
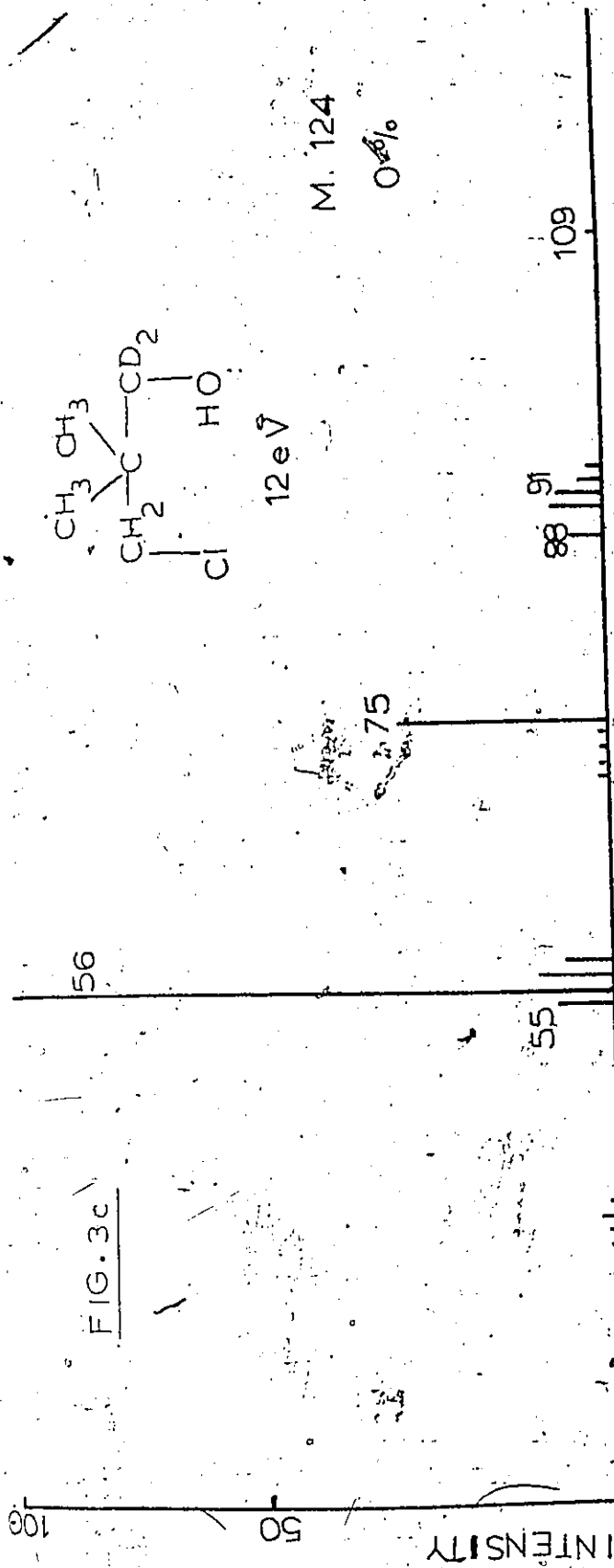
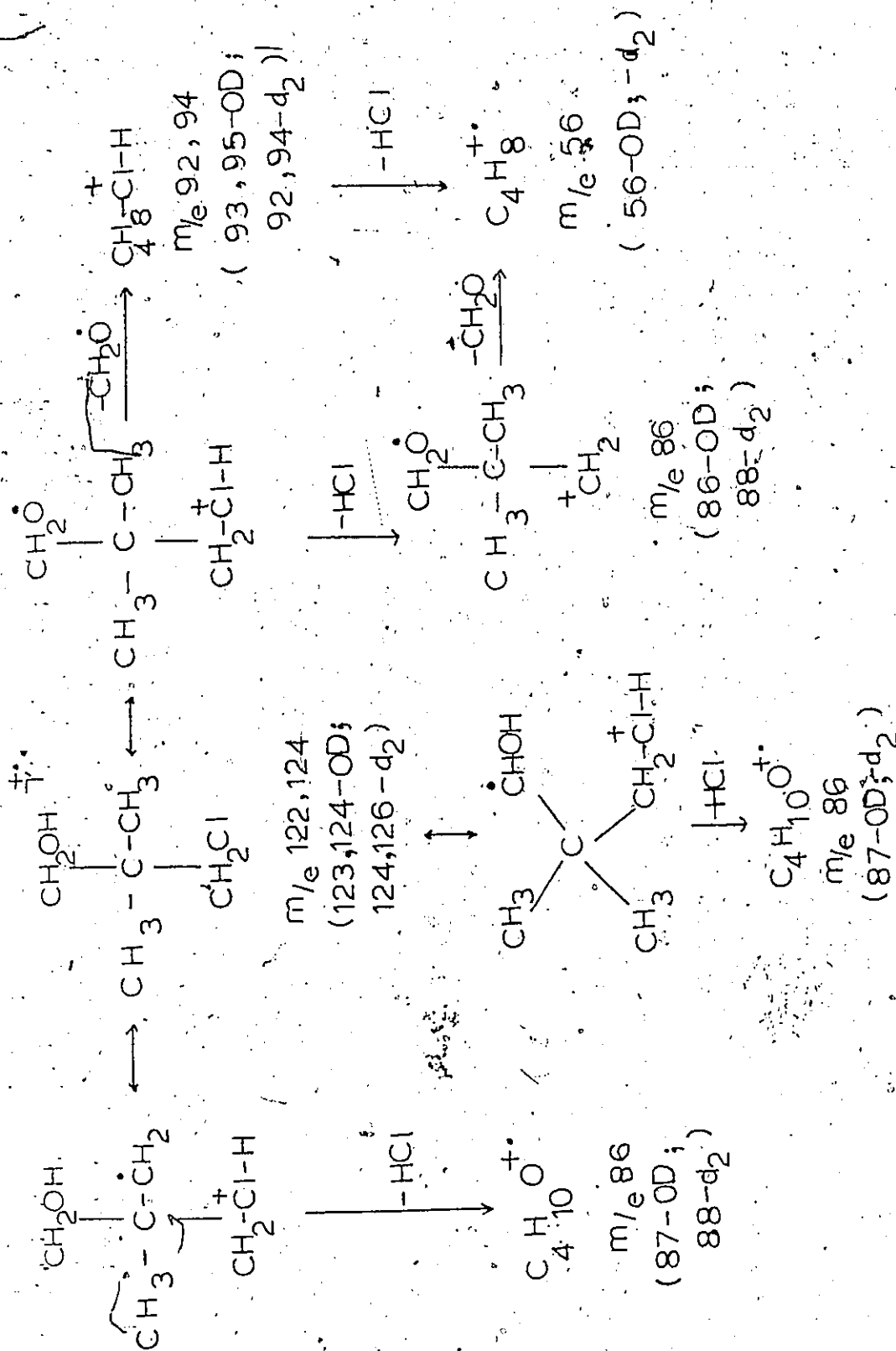


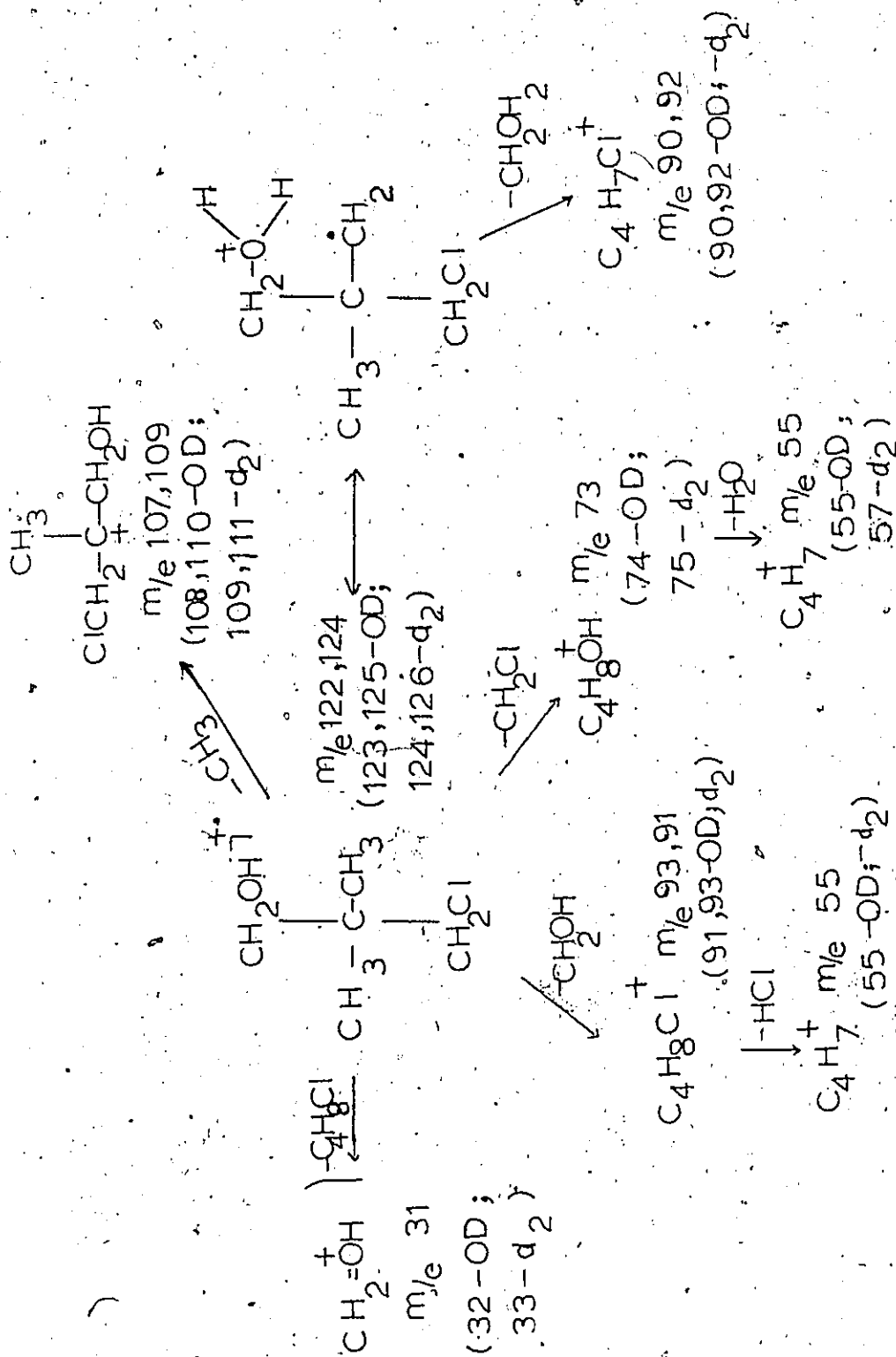
FIG. 3a







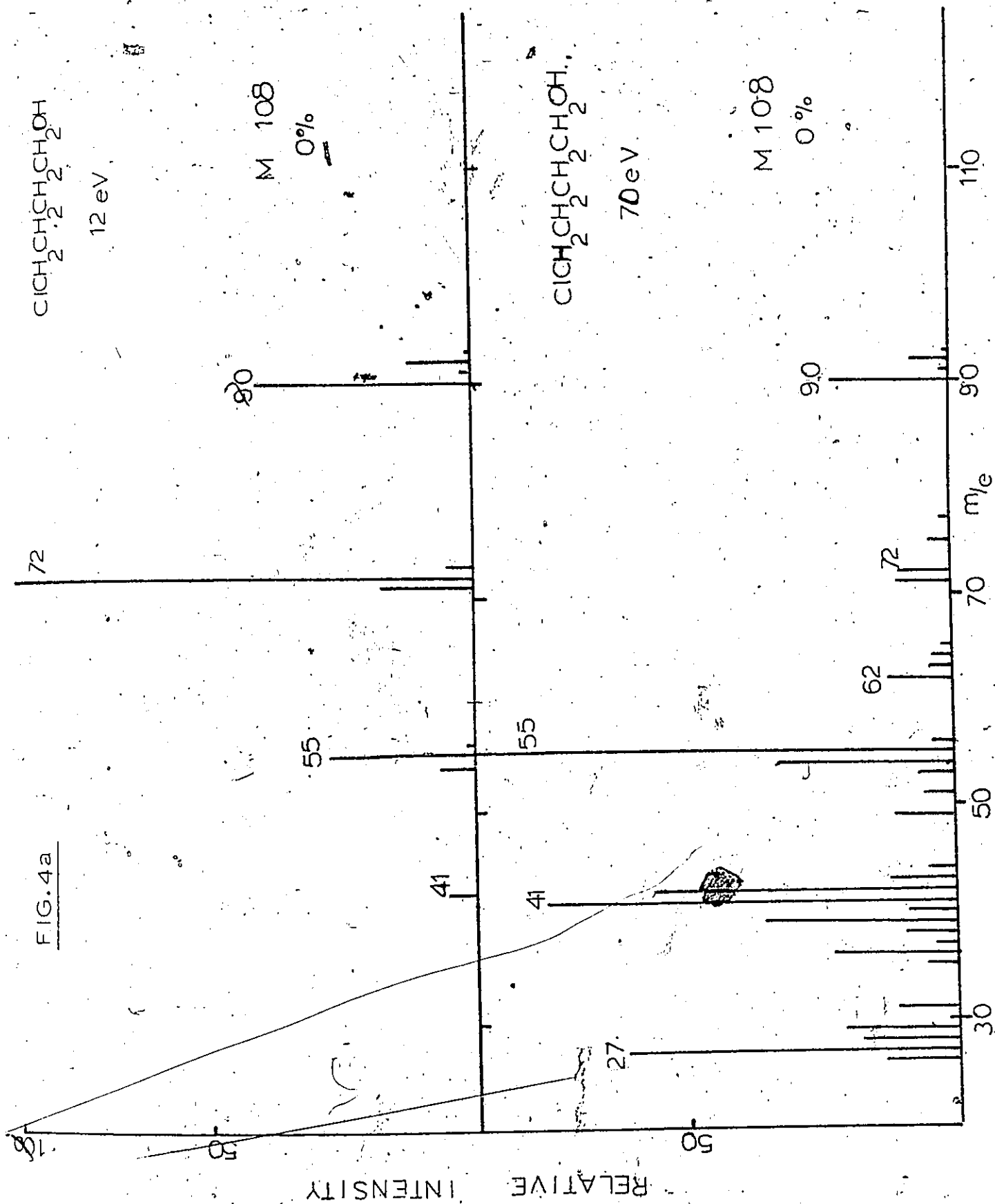
Scheme 7. Fragmentation mechanism for 3-chloro-2,2-dimethylpropanol-chlorine-hydroxyl, chlorine- β -methyl and chlorine- β -methylene interaction.

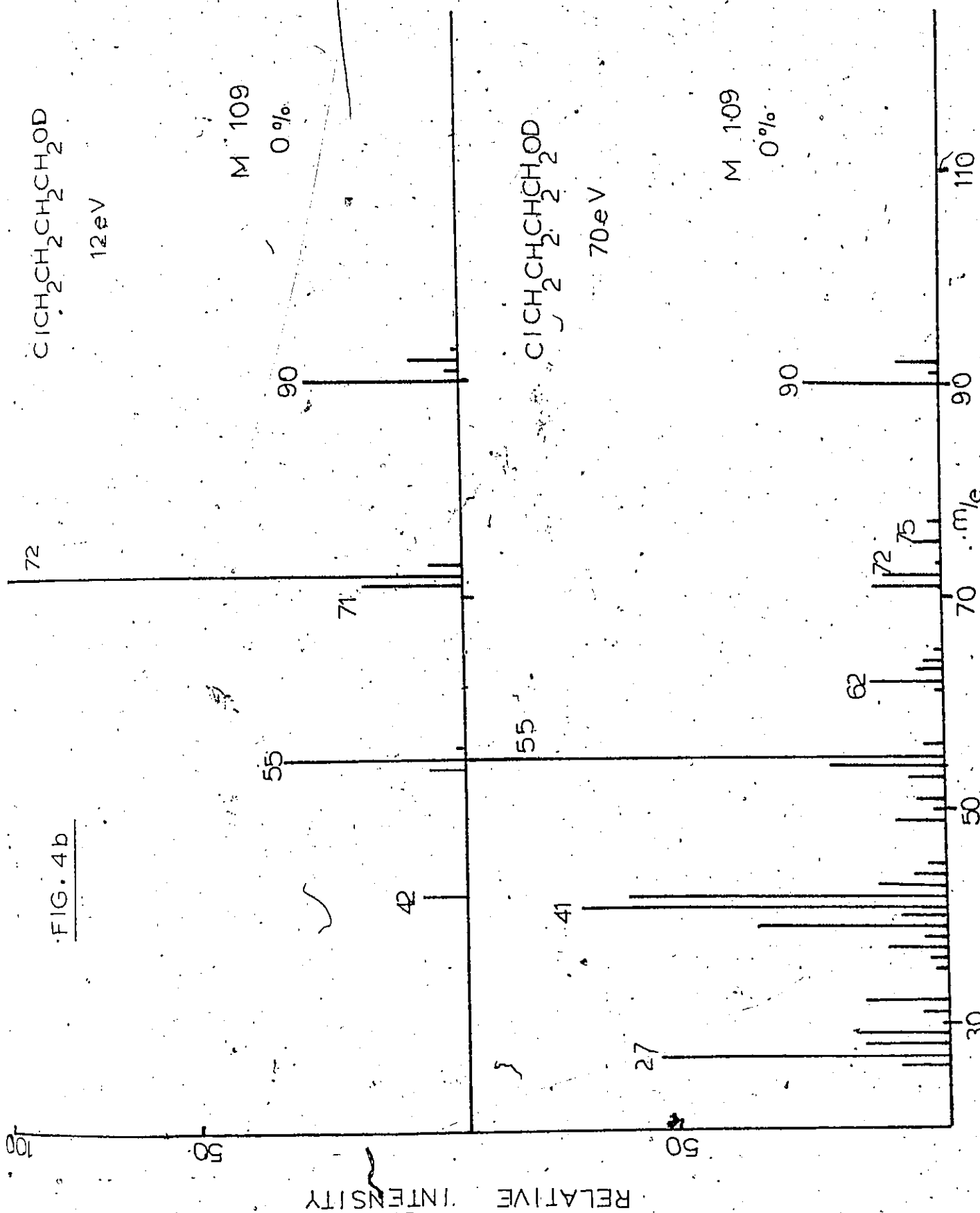


Scheme 8. Fragmentation mechanism for 3-chloro-2,2-dimethyl-propanol-hydroxyl- β -methyl interaction and the unrearranged molecular ion.

FIG. 4a

- 85 -





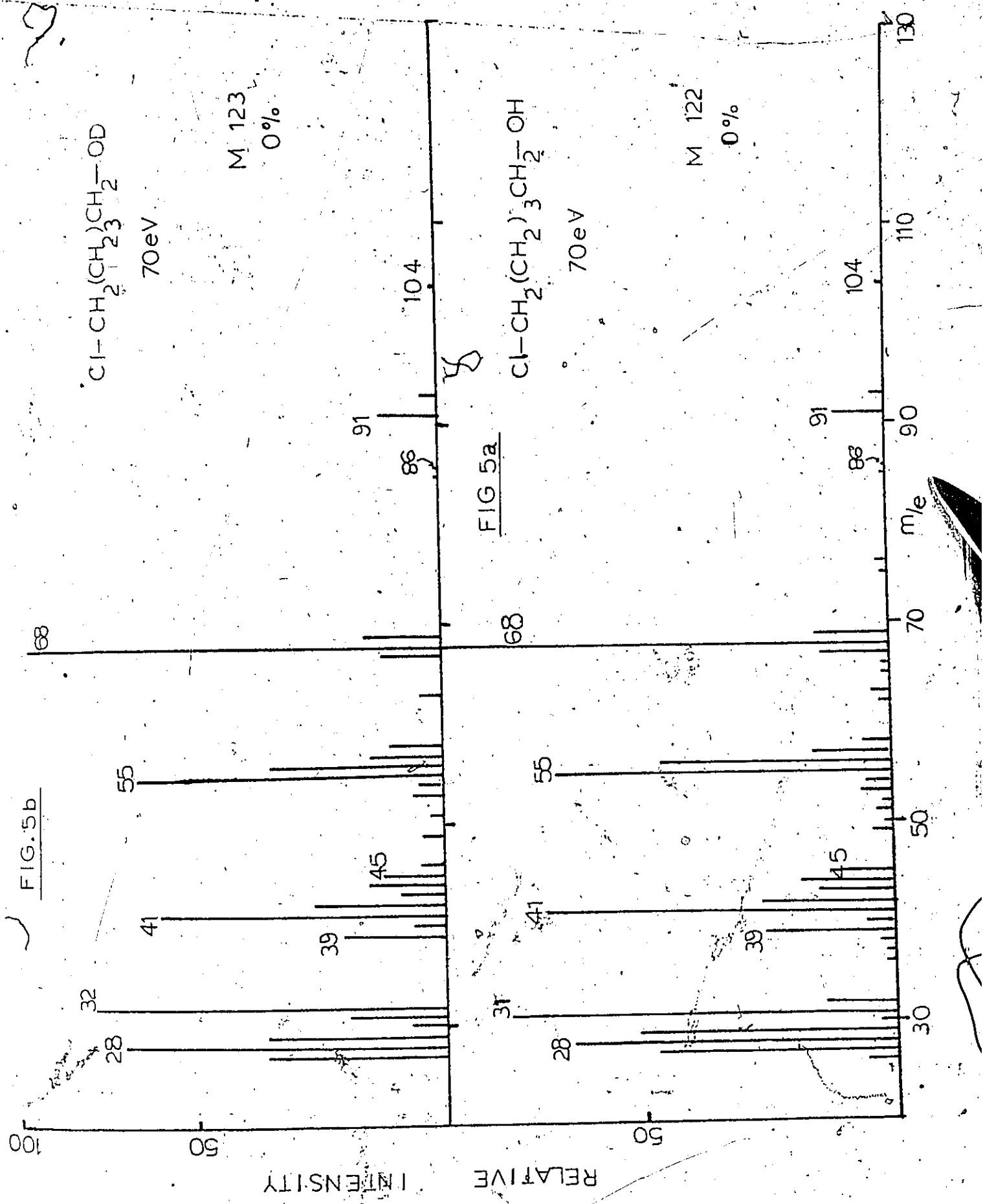
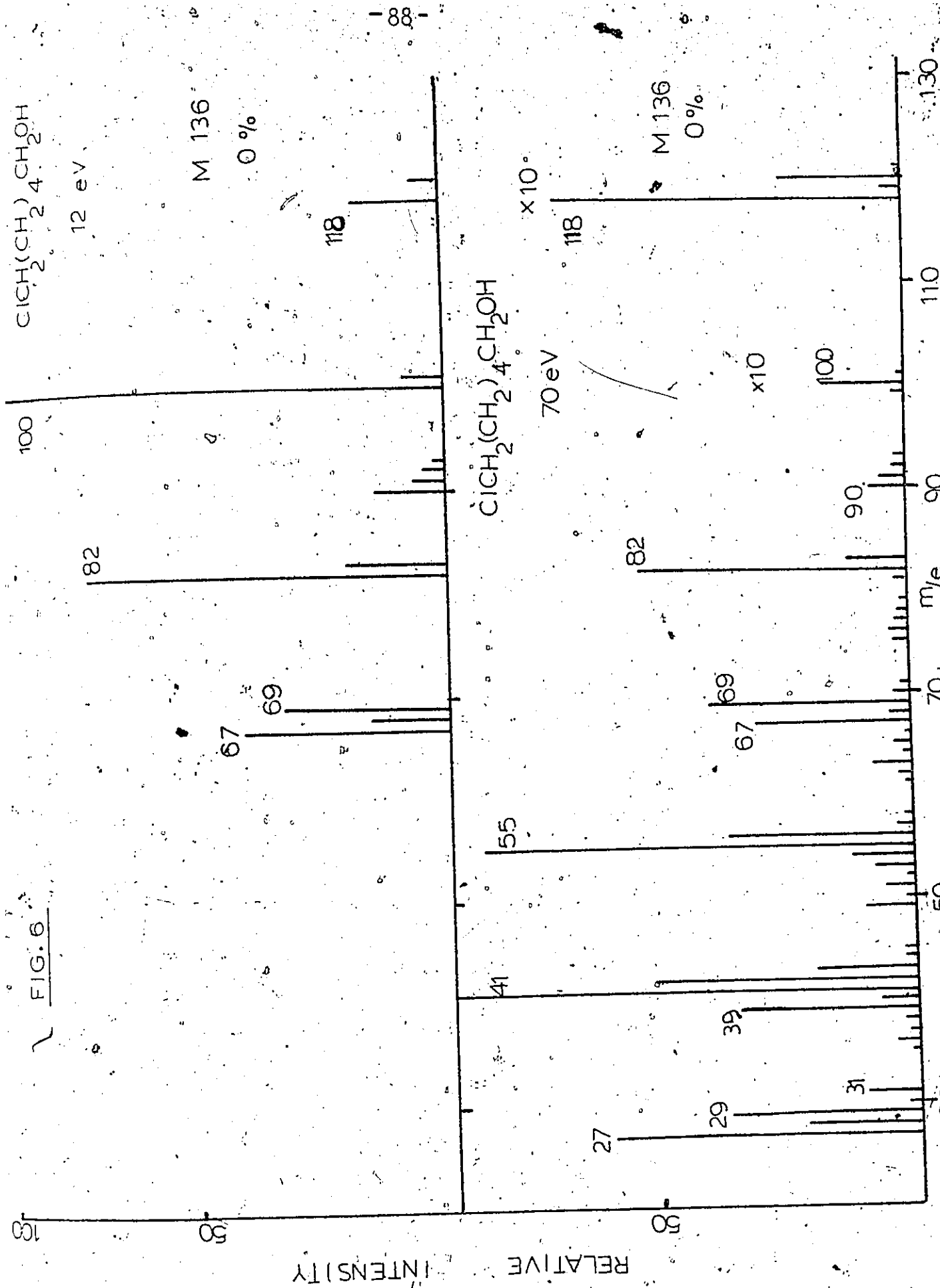


FIG. 6



CH_2OH . These are usually quite weak in intensity. When the hydroxyl groups are deuterated, of these ions only $\text{CH}_2=\text{OH}^+$ retains the label. This indicates that chlorine-hydroxyl and hydroxyl-methylene interaction is responsible for the loss of HCl and water respectively from the molecular ion. Loss of hydrochloric acid from molecular ions of the whole series of chlorohydrins studied, due to direct interaction of chlorine-hydroxyl and chlorine-methylene, is shown in Table 2. Their appropriate cyclic transition state ring sizes are included. Four conclusions may be drawn from the table. Firstly, both chlorine-hydroxyl and chlorine- β -methylene (and chlorine- β -methyl in the case of 3-chloro-2,2-dimethylpropanol) interact via six- and five-membered transition states respectively. These contribute to hydrochloric acid loss from the molecular ions of 3-chloropropanol and 3-chloro-2,2-dimethylpropanol respectively. The former interaction, however, is more favorable. Secondly, the elimination of hydrochloric acid arising from chlorine-hydroxyl interaction proceeds via a transition state of larger ring size (from 6 to 9 and/or larger). Similar mono-functional aliphatic chlorides and bromides^{16, 41, 64-65} favor a ring size of five. This is confirmed by deuterium labelling of the hydroxyl groups. The relative abundance of $(\text{M}-\text{HCl})^+$ due to this process falls sharply from eight to larger membered ring size. These ring sizes are indeed those normally associated with interactions between the ends of long chain molecules¹⁰¹⁻¹⁰². This parallels the behaviour in the formation of cyclic compounds by condensation reactions wherein 5, 6 and 7

Table 2.

Loss of HCl from Molecular Ions (70ev) of some chlorohydrins

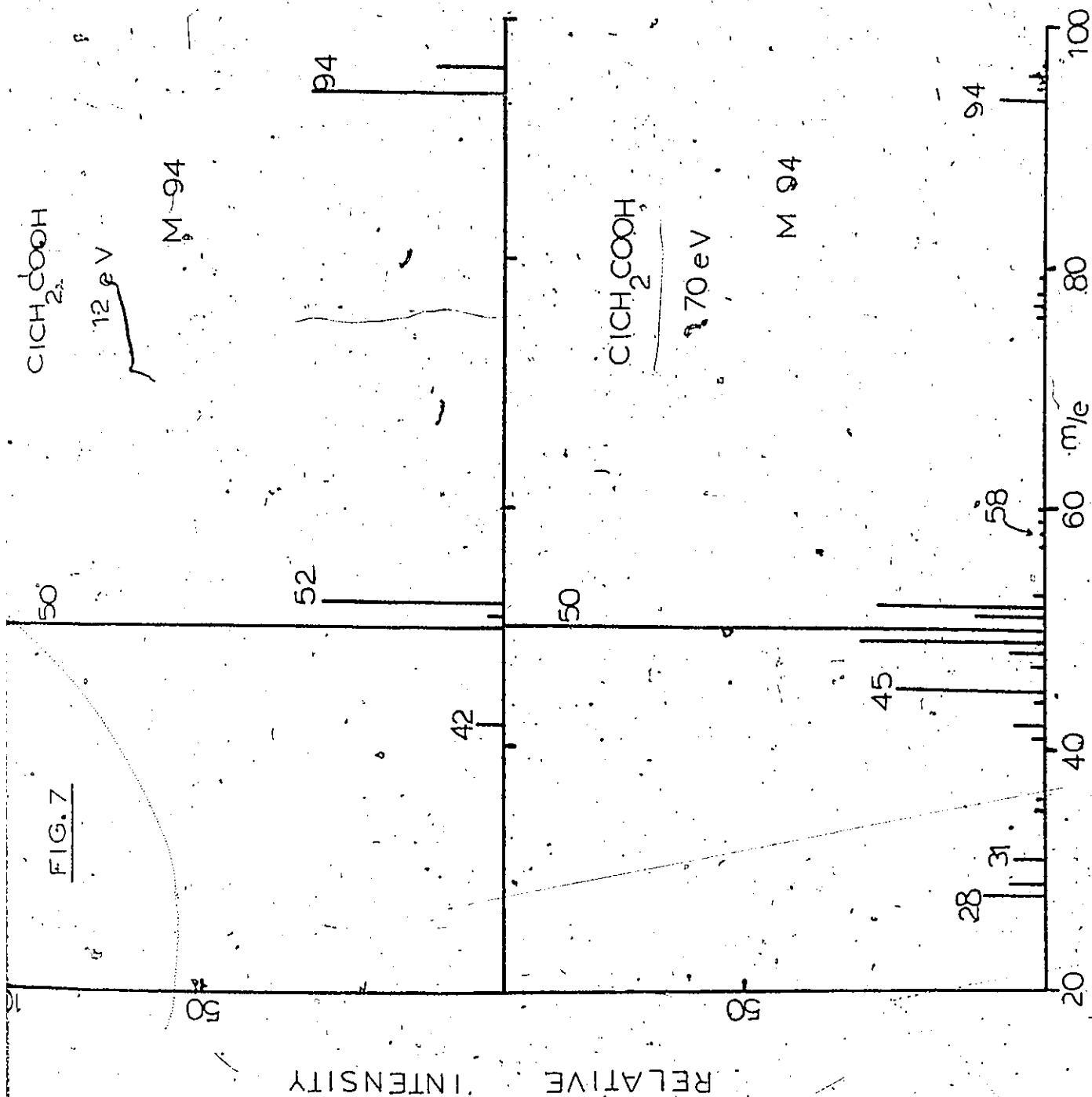
Compound	Chlorine-hydroxyl interaction	Ring size	Relative intensity	Chlorine-CH ₂ (or Cl-CH ₃) ² interaction	Possible ring size	Relative intensity
Cl(CH ₂) ₂ OH	0%	5	0%	0%	3-4	0%
Cl(CH ₂) ₃ OH	~60%	6	100%	~40%	3-5	68%
ClCH ₂ (CH ₂) ₂ CH ₂ OH	~95%	6	~4%	~5%	3 and 5	0.4%
Cl(CH ₂) ₄ OH	~100%	7	~10%	~0%	3-6	0%
Cl(CH ₂) ₅ OH	~100%	8	~0.5%	~0%	3-7	0%
Cl(CH ₂) ₆ OH	~100%	9	~2%	~0%	3-8	0%

membered rings were easily formed. Cyclization product yield also fell sharply from 8 to larger membered rings. Thirdly, the mechanisms due to chlorine-methylene (or chlorine-methyl) interaction proceeds only via a five-membered ring transition state (i.e. chlorine- β -methylene and/or chlorine- β -methyl interaction). Chlorine- γ -methylene or chlorine- δ -methylene interaction is of no importance in the molecular ion of the chlorohydrin series. This is again similar to the mechanism for the elimination of halogen acid in mono-functional aliphatic chlorides and bromides^{16, 41, 64-65}. Fourthly, elimination of HCl due to chlorine-hydroxyl interaction is probably a rearrangement process with a much lower activation energy than that due to chlorine-methylene interaction. This is clearly shown in Table 1 and 2. Here the former interaction is predominant over the latter for compounds 3-chloropropanol and 3-chloro-2,2-dimethylpropanol. No effective chlorine-methylene interaction gives rise to $(M-HCl)^+$ ion for the series starting 4-chlorobutanol to 6-chlorohexanol.

THE MASS SPECTRA OF SOME CHLOROACIDS

(A) Chloroacetic acid

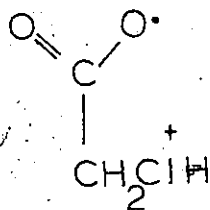
The mass spectra of chloroacetic acid is shown as Fig. 7. The proposed fragmentation mechanism is shown as Scheme 9. This molecule behaves quite simply. The fragment m/e 50, 52 results from CO_2 loss from the molecular ion following H atom transfer from carboxyl to chlorine via a five-membered cyclic intermediate. The concomitant hydrochloric acid loss from the



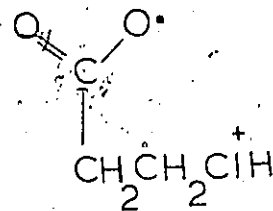
molecular ion is a very minor process. The abundance of m/e 58 is only 0.7%.

(B) 3-Chloropropanoic acid

The mass spectra of 3-chloropropanoic acid and 3-chloropropanoic acid-COOD are shown as Figs. 8a and b. The base peak is the fragment ion at m/e 73 (74-COOD), (M-Cl). In this molecule, although H atom transfer from carboxyl to chlorine may be geometrically facile (the transfer being via a six-membered ring) the concomitant HCl loss from the molecular ion is a very minor process. The abundance of m/e 72 (72-COOD) is only 1.3%. However, unlike the mass spectrum of chloroacetic acid, the fragment ion at m/e 64, 66 (65, 67-COOD), (M-CO₂), is very weak, being 3.3%. For chloroacetic acid, the analogous fragment ion (M-CO₂) is the base peak. The structures of the molecular ions of chloroacetic acid and 3-chloropropanoic acid leading to the formation of (M-CO₂) ions are (I) and (II) respectively (see Scheme 9 and 10),

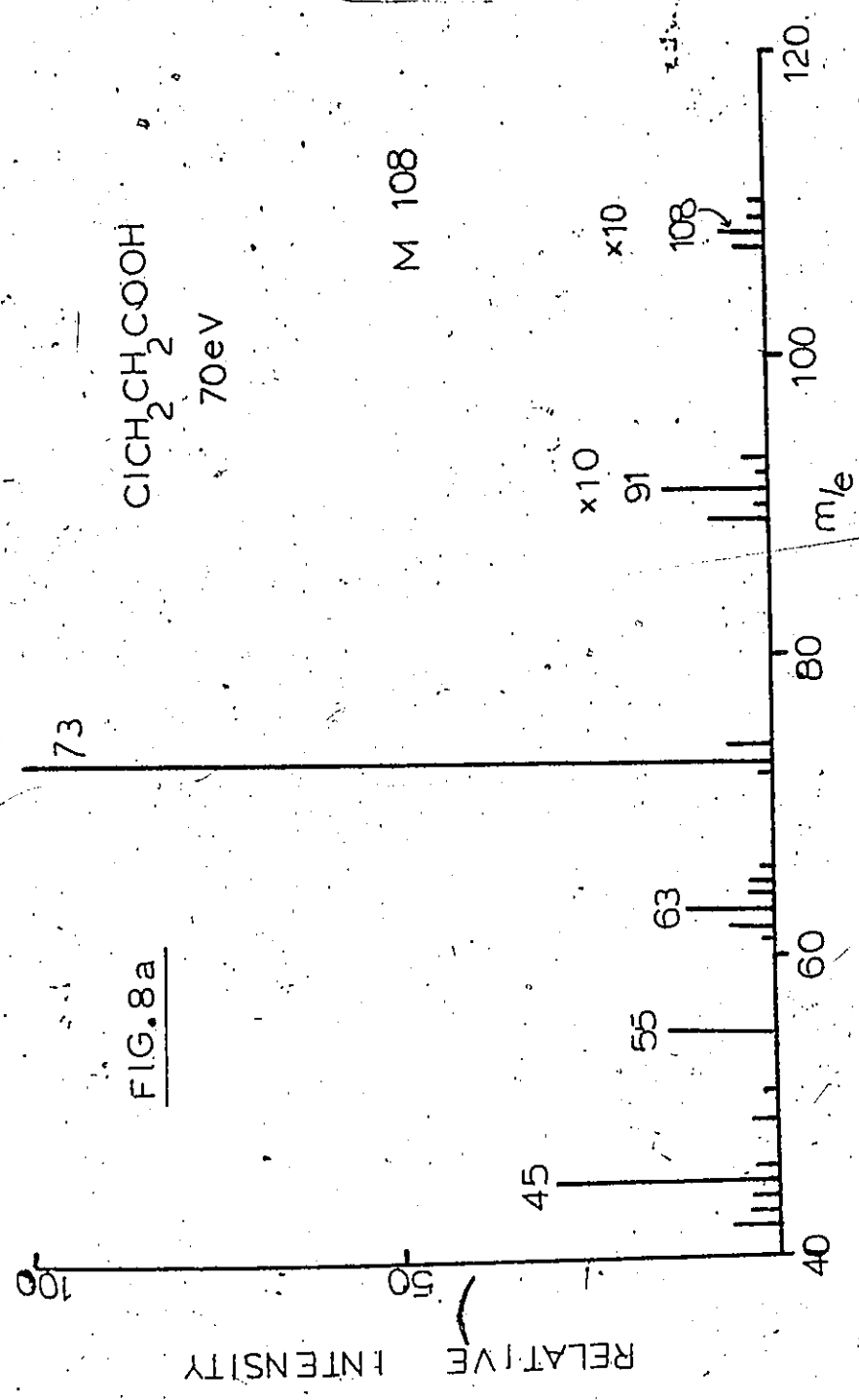


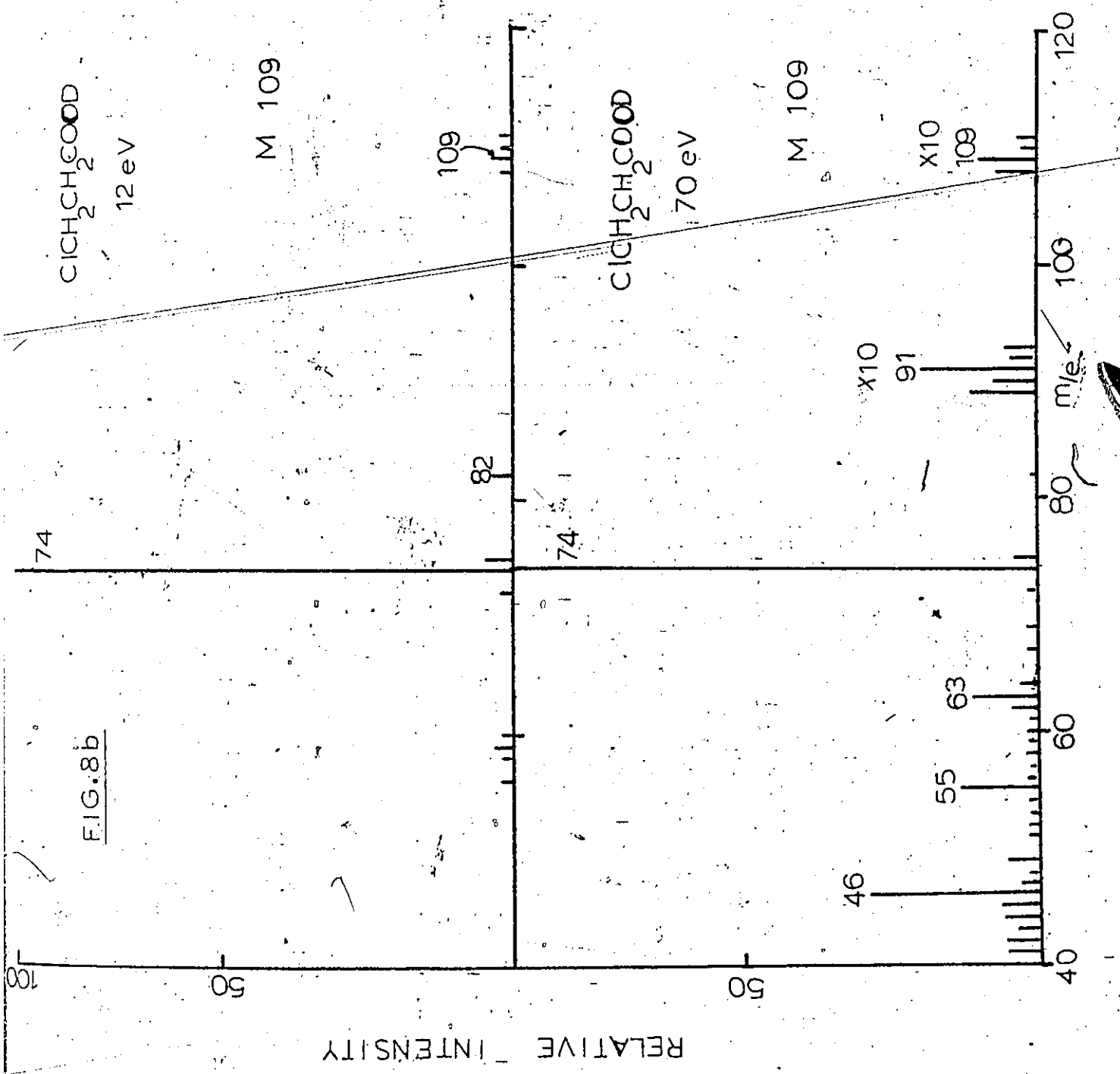
(I)

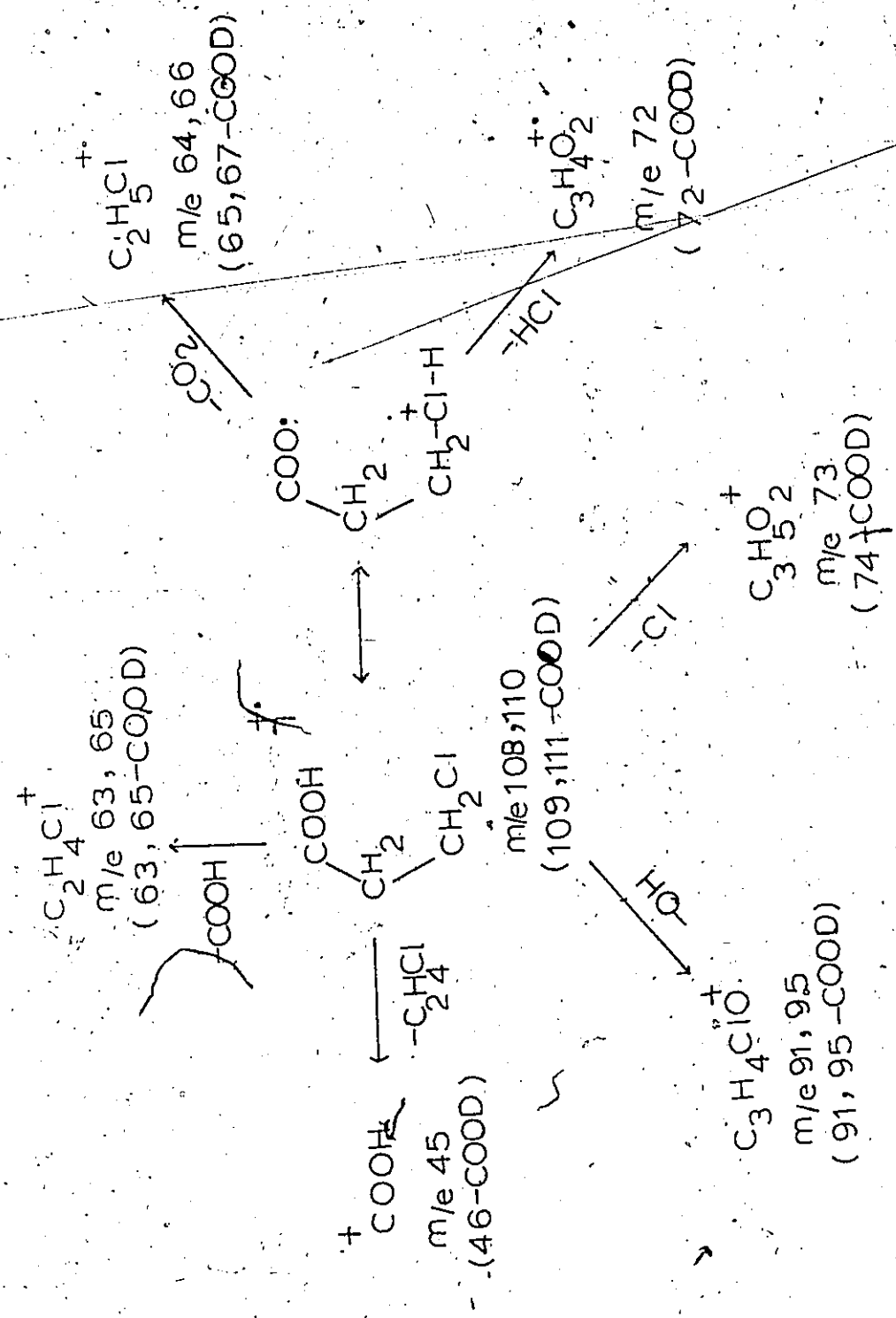


(II)

It is apparent that molecular ion of structure (I) is less stable than structure (II) and so yields (M-CO₂) fragment ion more readily.







Scheme 10. Fragmentation mechanism for 3-chloropropanoic acid.

The fragmentation for the molecular ion appears to be free of unexpected or difficult features and the proposed mechanism is shown as Scheme 10.

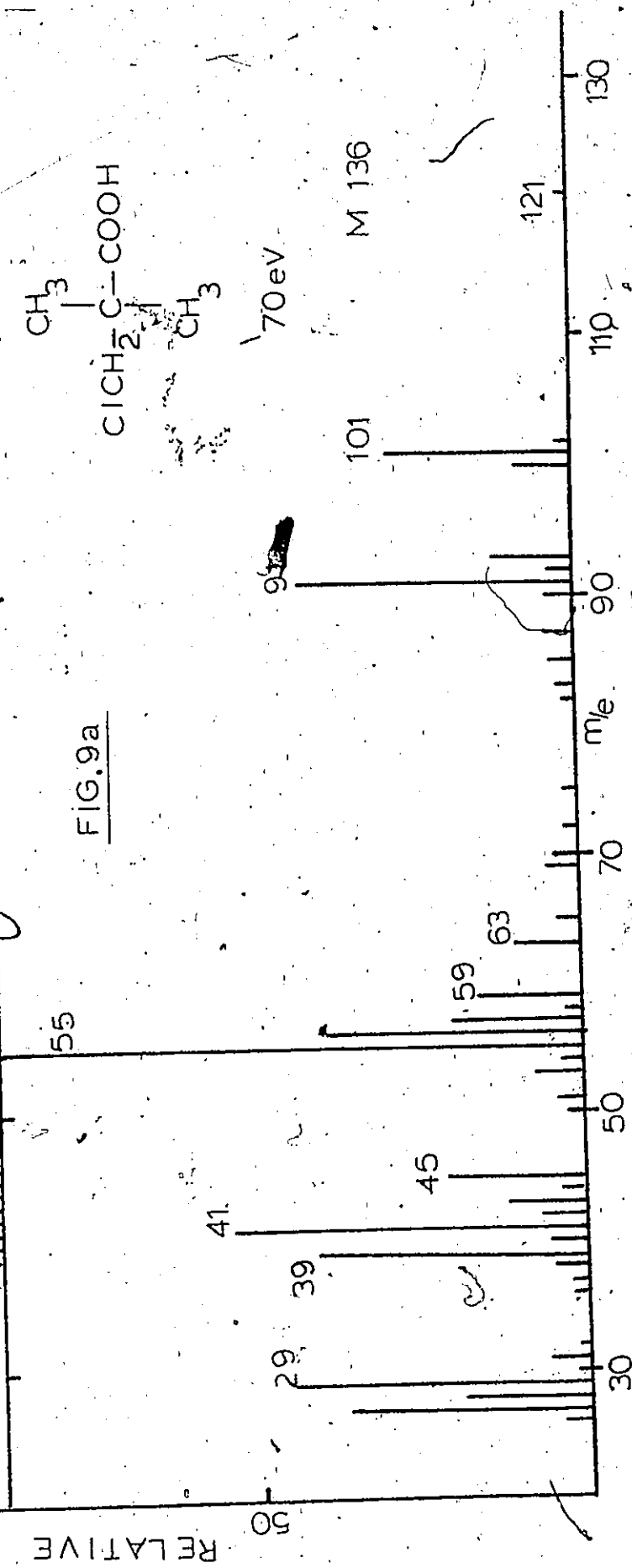
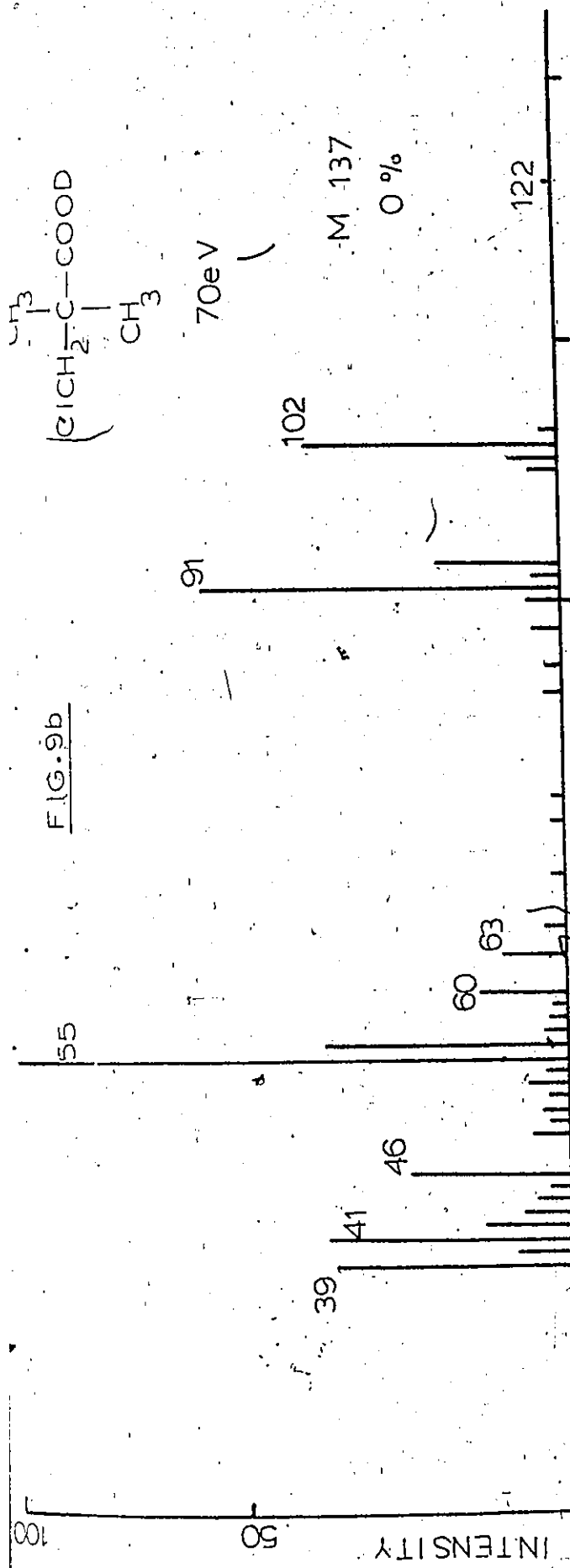
(C) 3-Chloro-2,2-dimethylpropanoic acid

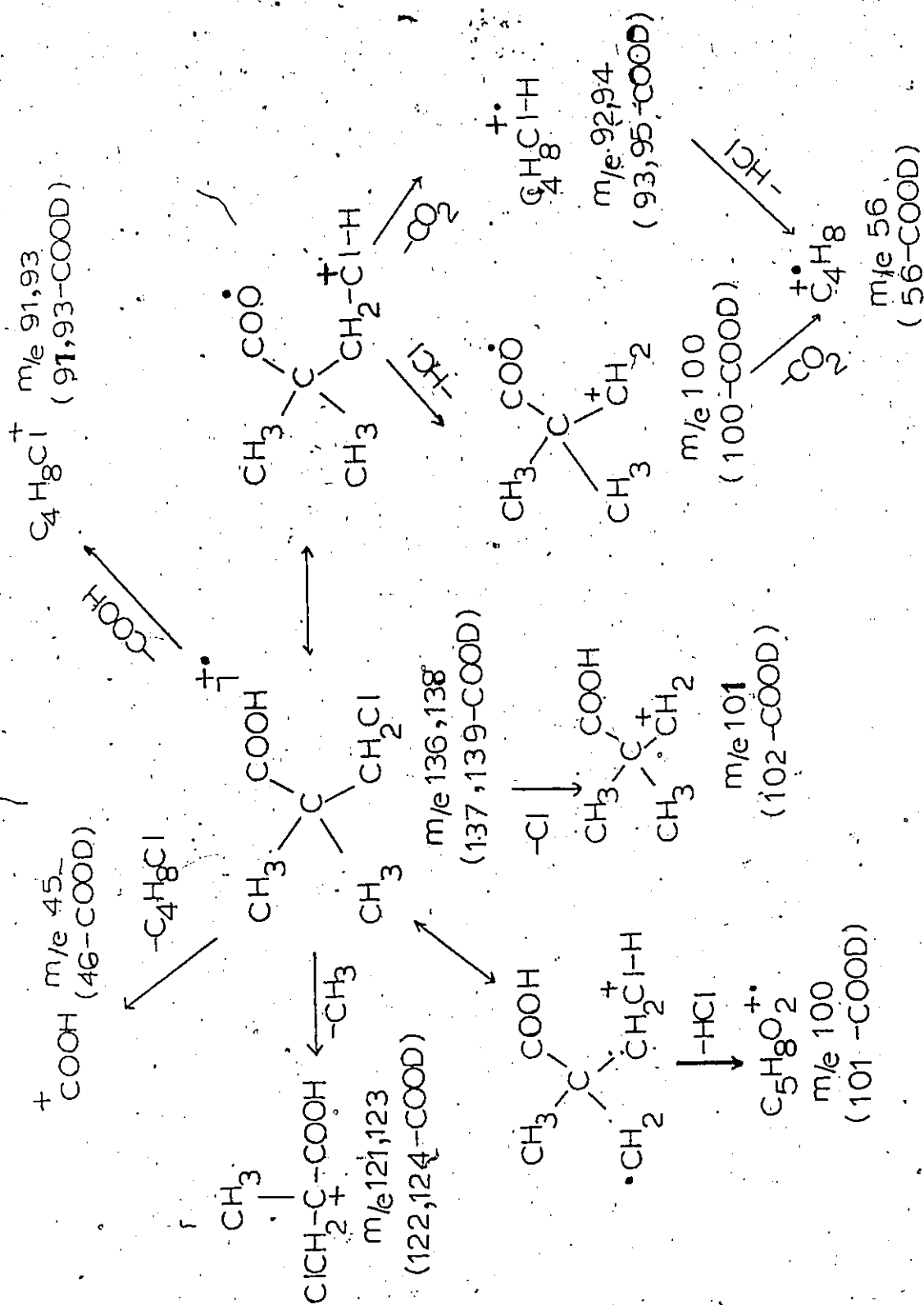
The mass spectra of 3-chloro-2,2-dimethylpropanoic acid and its carboxyl- d_1 analogue are shown as Figs. 9a and b. The base peak m/e 55 (55-COOD) is formed from $(M-COOH)^+$, m/e 91, 93 (91, 93-COOD). This is assumed to be $C_4H_8Cl^+$, the common intermediate discussed in Chapter 3. m/e 101 and 100 as shown in Fig. 9a, are formed by loss of Cl and HCl respectively from the molecular ion. The importance of the H atom in the methyl groups is seen from the carboxyl- d_1 spectrum (Fig. 9b). The loss of HCl from the molecular ion arises from two sources. These are chlorine-carboxyl and chlorine-methyl interaction. 50% of the total HCl (DCl+HCl) loss from the molecular ion comes from the former interaction and the other 50% from the latter. These involve six- and five-membered transition states respectively, as shown in Scheme 11.

(D) Summary and general discussion

Loss of hydrochloric acid from the molecular ions of the three chloroacids, chloroacetic acid, 3-chloropropanoic acid and 3-chloro-2,2-dimethylpropanoic acid, arises from chlorine-carboxyl and chlorine-methylene (and/or chlorine-methyl) interaction as shown in Table 3. Their appropriate ring sizes are included.

Although we have not studied the higher homologues of this series, two conclusions are obvious. Firstly, although





Scheme 11. Fragmentation mechanism for 3-chloro-2,2-dimethylpropanoic acid.

Table 3.
Loss of HCl from molecular ions of
Some Chloroacids

Compound	Relative abundance due to Cl-COOH interaction	Ring size	Relative Abundance due to Cl-CH ₂ (or Cl-CH ₃) interaction	Possible ring size
ClCH ₂ COOH	≤ 0.7%	5	0%	3
ClCH ₂ CH ₂ COOH	≤ 1.3%	6	0%	3 & 4
ClCH ₂ (CH ₂) ₂ COOH	≤ 4%	6	≤ 4%	3 & 5

chlorine-carboxyl interaction giving rise to (M-HCl) ion formation may be sterically favorable, it is only a very minor process. The appropriate ring sizes for this process are five- and six- and/or larger. Secondly, formation of (M-HCl) ion in 5-chloro-2,2-dimethylpropanoic acid indicates that chlorine- β -methyl as well as chlorine- β -carboxyl interaction are operating. We are unable to establish whether chlorine- β -methylene, chlorine- γ -methylene or chlorine- δ -methylene interactions are of any importance in the molecular ion for the 10 series. Further work on the higher homologues of this series should be able to provide the answer.

CHAPTER 5

CYCLOHEXENE AND METHYLCYCLOPENTENE ANDCYCLOHEPTENE AND 4-METHYLCYCLOHEXENE

The fragmentation mechanisms and energetics of the isomeric C_5H_8 hydrocarbons, spiropentane, cyclopentene, penta-1,3-diene and isoprene⁸⁰ and also the isomeric bicyclic and tricyclic C_7H_{10} hydrocarbons, norbornene and nortricyclene¹²² have been studied by Holmes and his co-worker. Fragmentations of the C_5H_8 molecules were for the most part found to proceed via common intermediates in which hydrogen atoms had lost their positional identity. Only spiropentane displayed any specific fragmentation behaviour related to its ground state geometry. In the case of the isomeric bicyclic and tricyclic C_7H_{10} hydrocarbons, except for the prominent retro Diels-Alder fragmentation of the molecular ion of the former, the decomposition pathways of the $C_7H_{10}^+$ ions were reported to be dissimilar and complex. The mass spectra of some isomeric C_6H_{10} ¹²³⁻¹²⁵ and some C_7H_{12} ¹²⁶⁻¹²⁷ molecules have been studied previously. H/D scrambling in the molecular ions prior to fragmentation (resulting from successive 1,3-allylic rearrangements) was believed to occur in these cyclic olefins^{125, 127}. This scrambling was reported to be slower than in acyclic olefins, because hydrogen scrambling was less important in the higher energetic molecular ions¹²⁵ (i.e. those which dissociate within the ion source). Relatively more hydrogen randomization

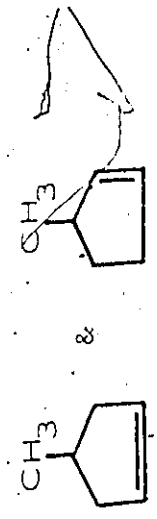
however, occurred in methylenecyclohexane than in 2-methylcyclohexene¹²⁷.

In this work, we describe detailed studies of the mass spectra of two isomeric cyclic C_6H_{10} hydrocarbons, methylcyclopentene and cyclohexene; and two C_7H_{12} isomers, 4-methylcyclohexene and cycloheptene. The chief purpose of these experiments was to discover whether the structural differences in the above molecules gave rise to identifiably different fragmentation pathways and also whether ions common with respect to both structure and energy content were involved. In particular, the problem of atom scrambling has been considered in some detail, not only with regard to the distribution of normal and metastable ion peak abundances in labelled compounds, but also with respect to observations on energy release in ion fragmentations.

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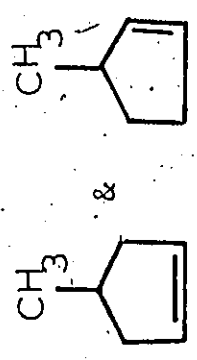
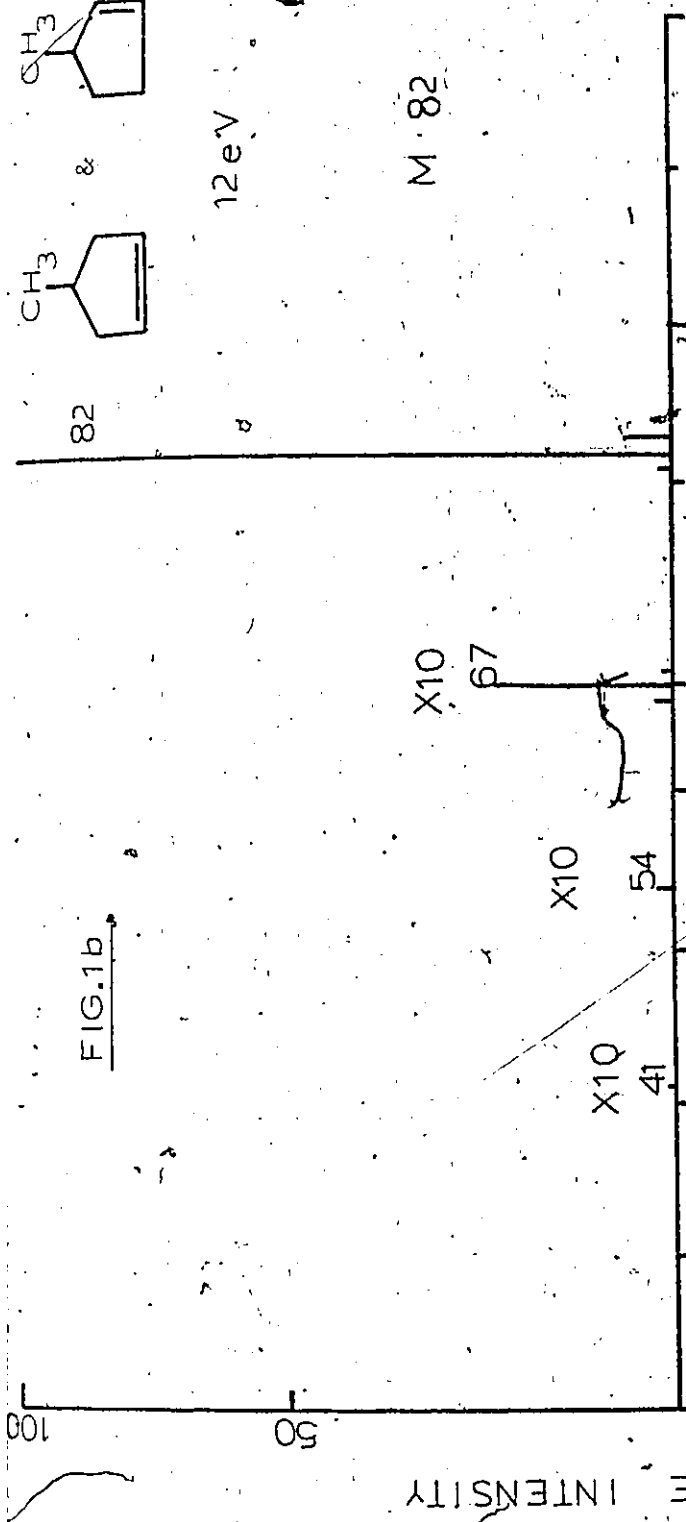
CYCLOHEXENE AND METHYLCYCLOPENTENE

The 70 and (nominal) 12 ev mass spectra of methylcyclopentene (mixture of 4-methylcyclopentene and 3-methylcyclopentene) are shown in Figs. 1a and b. The 70 and 12 ev mass spectra of cyclohexene are shown in Figs. 2a and b; they agree well with previous data¹²⁵. Table 1 lists the fourteen most abundant metastable ion peaks observed by a Daly detector (AEI MS-902) in the two mass spectra, their relative abundances and the fragmentations responsible for their genesis. In order to elucidate fragmentation mechanisms, the following labelled

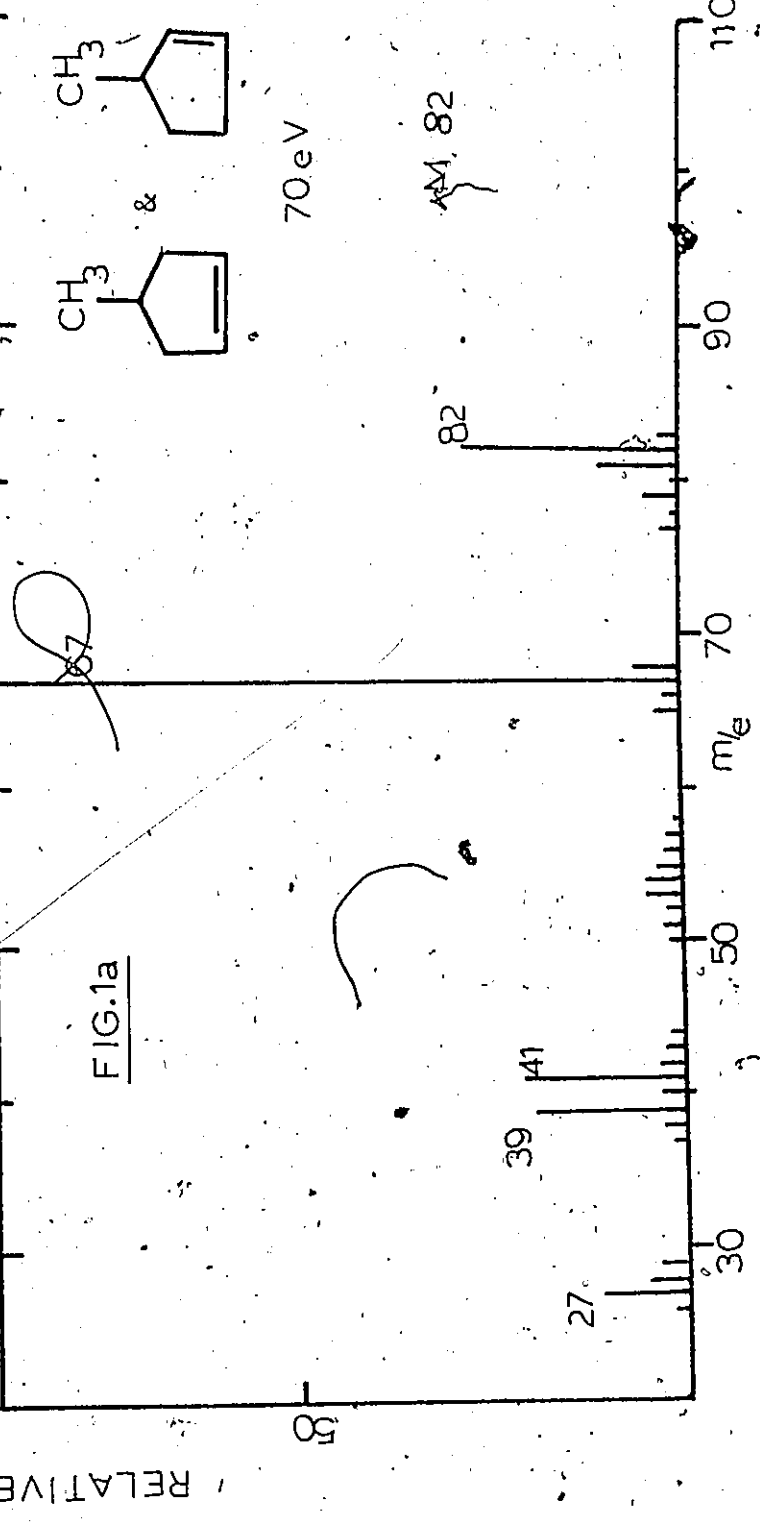


12 eV

M 82



70 eV



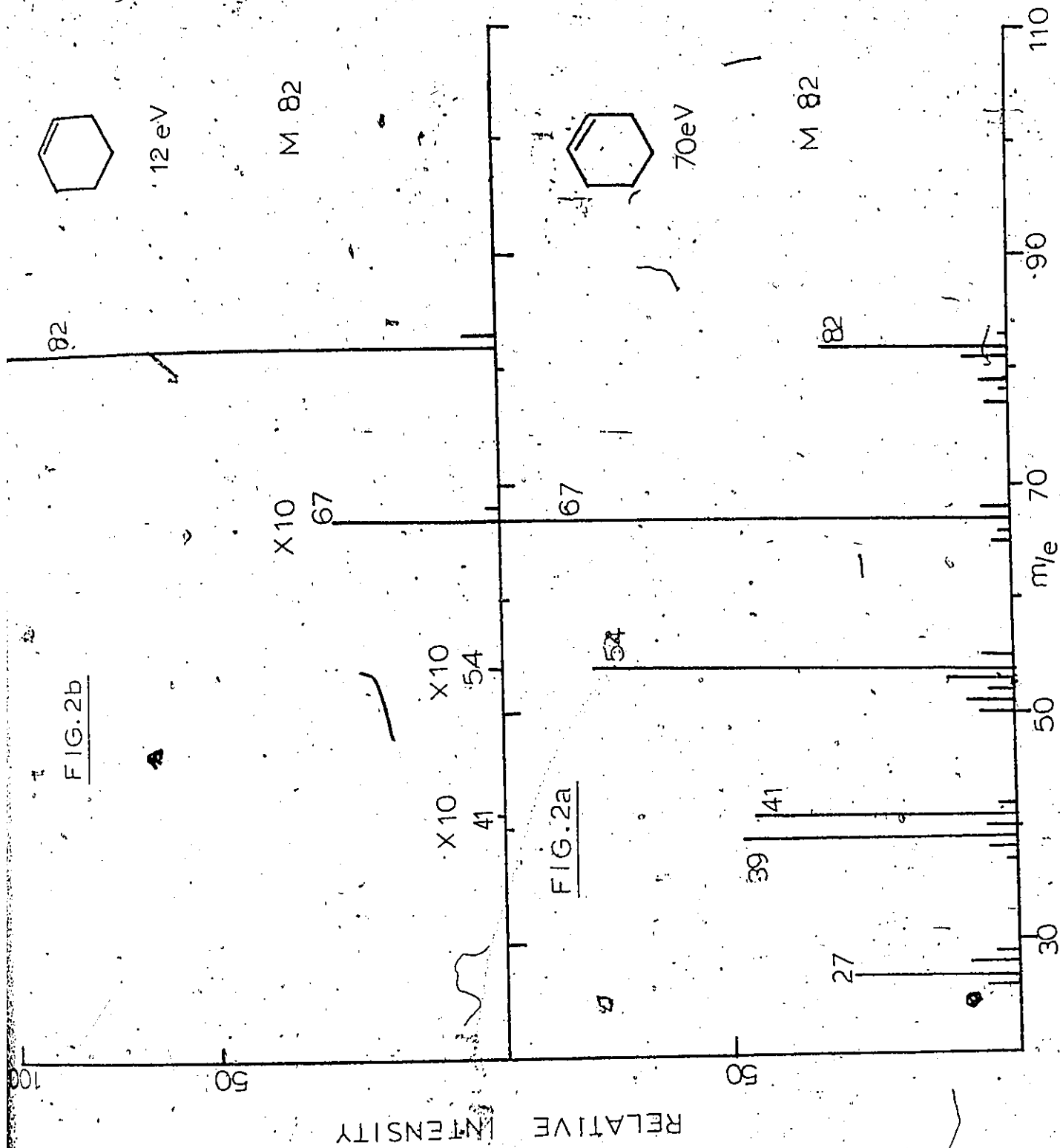


Table 1. Metastable ion peaks** observed in the 70ev mass spectra of cyclohexene and methylcyclopentene

Generating fragmentation	m ⁺ m/e	Relative abundance (70ev)	
		methylcyclopentene	Cyclohexene
$C_6H_{10}^{+} \rightarrow C_6H_9^{+} + H^{\bullet}$	80.0	0.1	0.1
$C_6H_{10}^{+} \rightarrow C_5H_7^{+} + CH_3^{\bullet}$	54.7	50.9	100
$C_6H_{10}^{+} \rightarrow C_4H_6^{+} + C_2H_4^{\bullet}$	35.6	0.2	0.3
$C_6H_{10}^{+} \rightarrow C_3H_5^{+} + C_3H_5^{\bullet}$	20.5	0.1	0.1
$C_6H_9^{+} \rightarrow C_6H_7^{+} + H_2$	77.1	60.4	32.9
$C_6H_6^{+} \rightarrow C_4H_4^{+} + C_2H_2$	34.7	1.1	0.9
$C_6H_5^{+} \rightarrow C_4H_3^{+} + C_2H_2$	33.8	1.1	1.7
$C_5H_7^{+} \rightarrow C_5H_5^{+} + H_2$	33.1	100	30.4
$C_5H_7^{+} \rightarrow C_3H_5^{+} + C_2H_2$	25.1	10.4	3.2
$C_5H_6^{+} \rightarrow C_3H_4^{+} + C_2H_2$	24.2	0.6	0.3
$C_5H_5^{+} \rightarrow C_3H_3^{+} + C_2H_2$	23.4	0.8	0.3
$C_4H_6^{+} \rightarrow C_3H_3^{+} + CH_3^{\bullet}$	28.2	10.4	43.0
$C_4H_4^{+} \rightarrow C_4H_2^{+} + H_2$	48.1	1.5	1.8
$C_3H_5^{+} \rightarrow C_3H_3^{+} + H_2$	37.1	4.5	5.7

** Measured by a Daly detector (MS 902S), see Chapter 1 (pp. 8-10) for description.

compounds were prepared (see experimental section for details) a mixture of 1-d₁-3-methylcyclopentene and 1-d₁-4-methylcyclopentene; 1-d₁-cyclohexene and 1,3,3-d₃-cyclohexene. The 70 and 12 ev mass spectra of each labelled compound are shown in Figs. 3a and b, 4a and b and 5a and b respectively. From Figs. 1 and 2, it can be seen that superficially, the same fragmentations occur in the mass spectra of the compounds, for example, there are three principal fragment ions, i.e. (M-CH₃)⁺, m/e 67; (M-C₂H₄)⁺, m/e 54; and (M-C₃H₅)⁺, m/e 41. For ease of comparison, the behaviour of fragment ion formation from molecular ions generated from both isomers will be discussed collectively.

(A) The (C₅H₇)⁺ ions, m/e 67, (M-CH₃)⁺

The formation of the fragment ion m/e 67 is interpreted as loss of a methyl radical from the molecular ion. Table 2 presents the observations on daughter and metastable ion peaks for the various labelled compounds (Corrections have been made for ¹³C and for small percentage of partially deuterated compounds). In the relative abundances of these peaks lies the major difference in the mass spectra of the isomers. In 1-d₁-methylcyclopentene, (M-CH₂D)⁺ is a relatively minor fragment compared with (M-CH₃)⁺ (with a relative ratio of 10.2:1.0 and 15.5:1.0 at 70 and 12 ev respectively). In 1-d₁-cyclohexene however, (M-CH₃)⁺ and (M-CH₂D)⁺ ions have a relative abundance ratio of 2.31 and 2.43 at 70 ev and 12 ev respectively. For a mono-deuterated methylcyclopentene and cyclohexene, complete randomization of hydrogen before or during fragmentation would yield CH₃: CH₂D losses in the ratio 2.33:1.00. Thus in both mono-

FIG. 3b

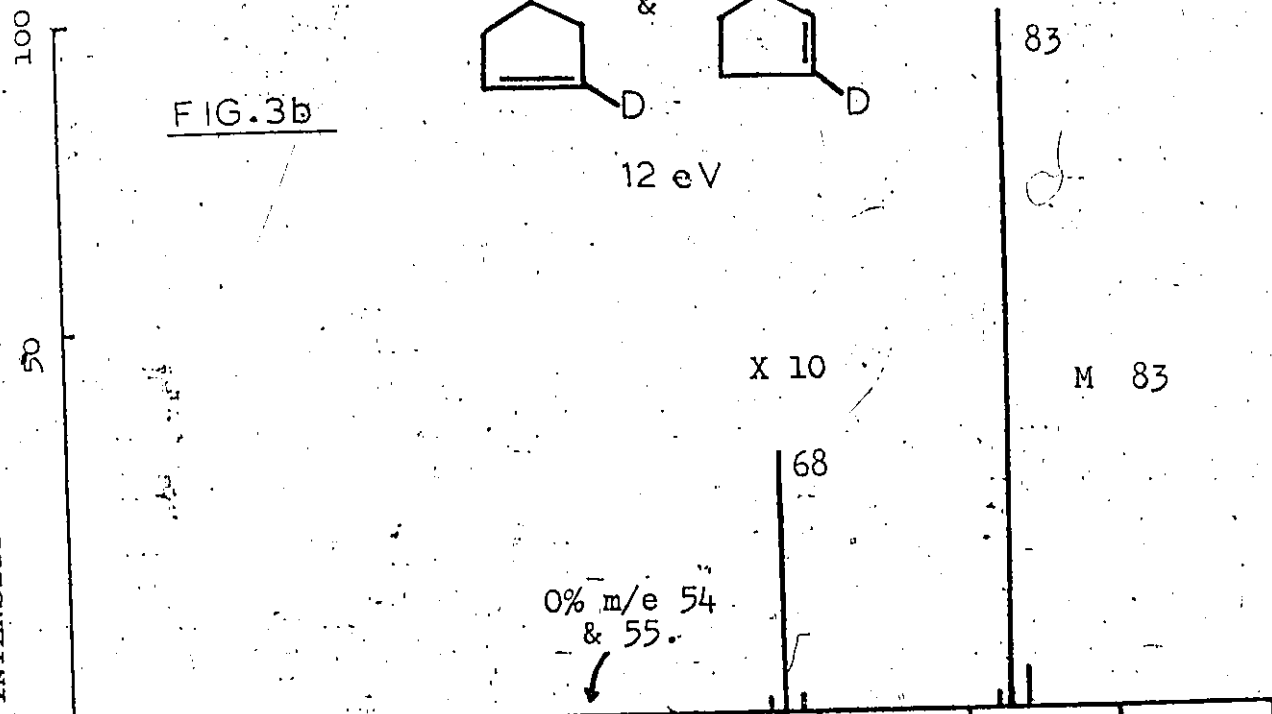
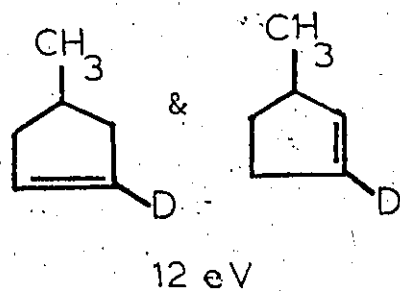
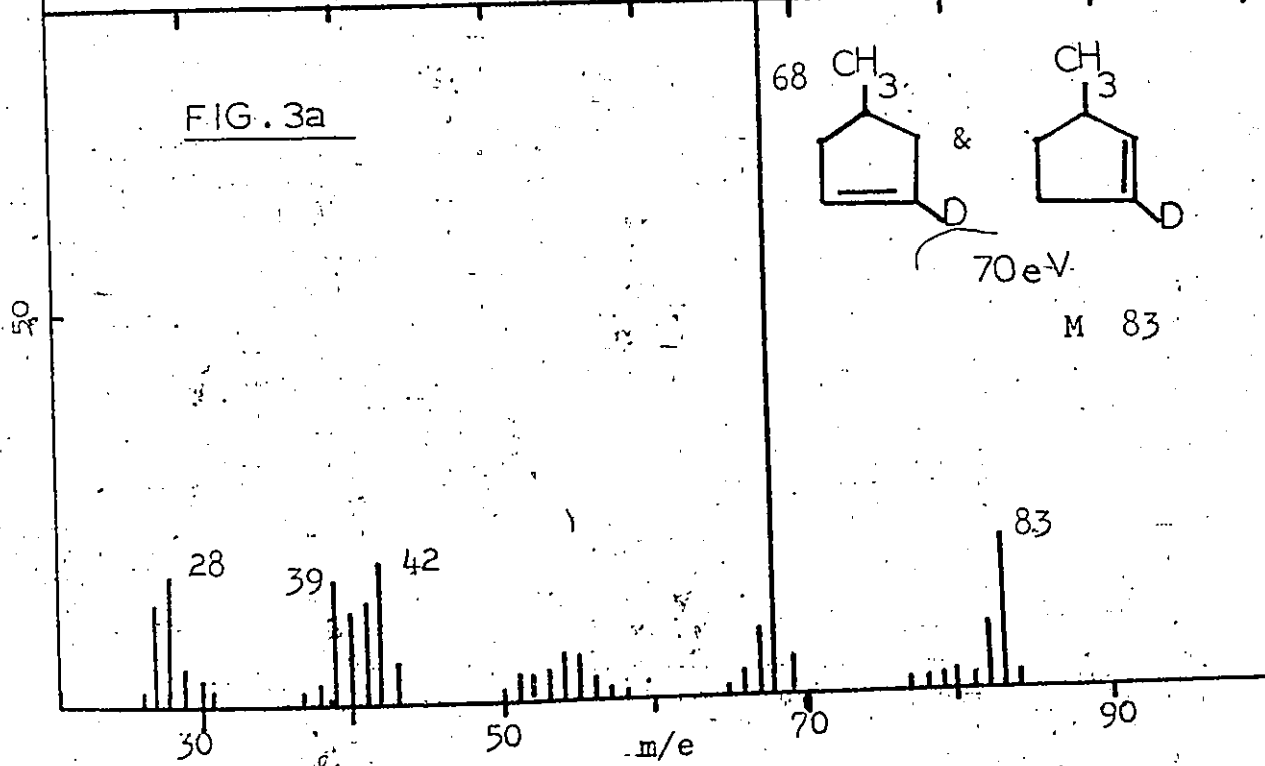
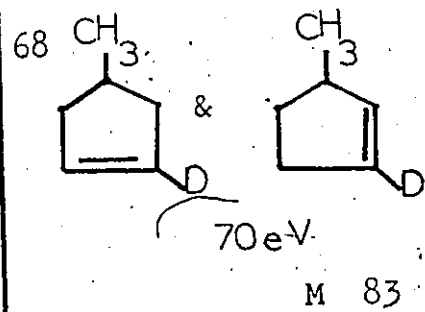
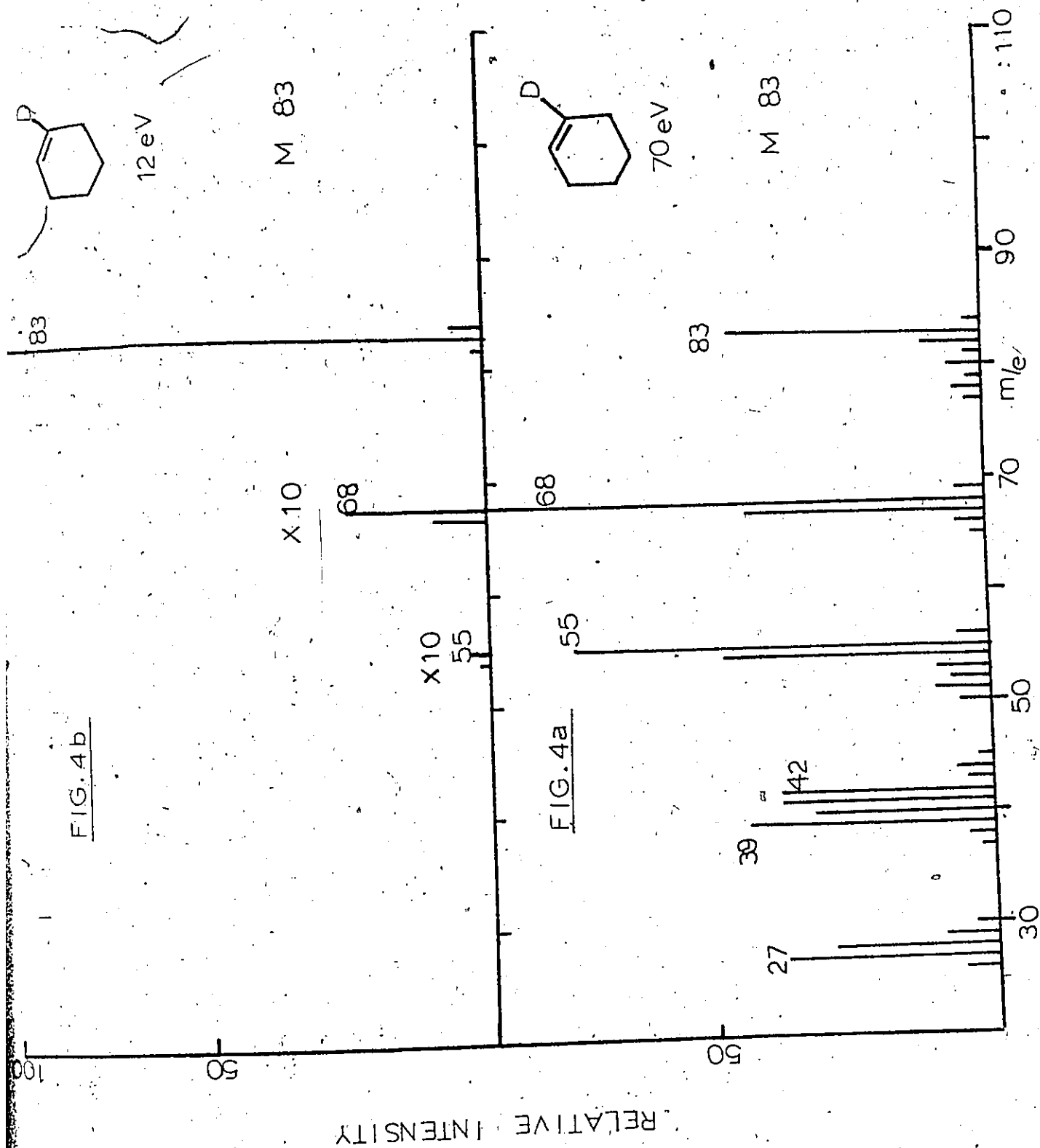


FIG. 3a





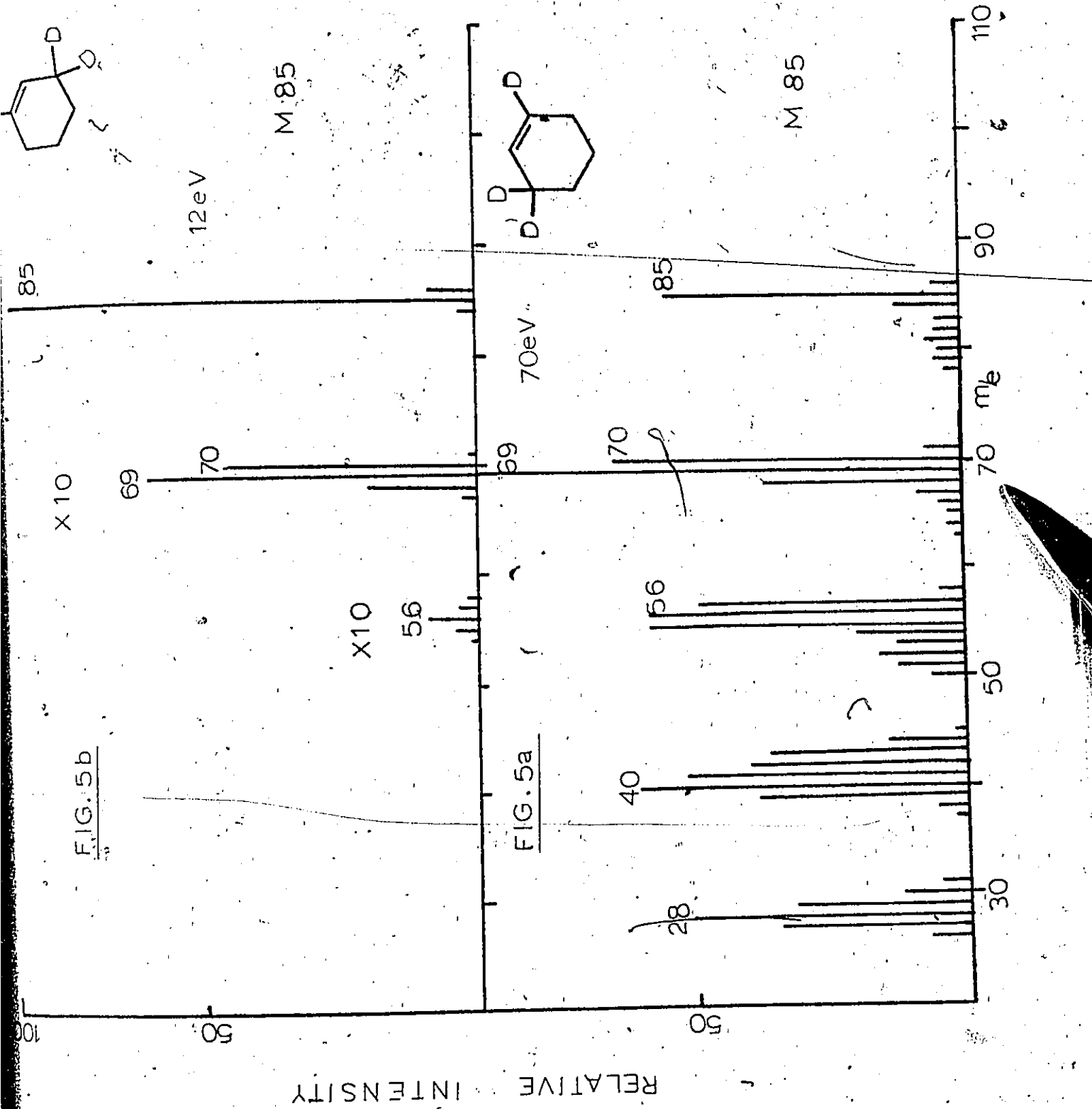


Table 2

Normal^a and metastable^b peak height intensities for methyl radical loss in the mass spectra of labelled cyclohexene and methylcyclopentene

	1d ₁ -methylcyclopentene (~ 98.4%-d ₁)	1-d ₁ -cyclohexene (~ 98%-d ₁)	1,3,3-d ₃ -cyclohexene (97%-d ₃ , 3%-d ₂)
m/e	Ratios $\frac{\text{Peaks}}{70\text{ev } 10\text{ev}}$ * Random	Ratios $\frac{\text{Peaks}}{70\text{ev } 10\text{ev}}$ * Random	Ratios $\frac{\text{Peaks}}{70\text{ev } 10\text{ev}}$ * Random
70	- - - - -	- - - - -	1.57 2.17 2.95 1.67
69	- - - - -	- - - - -	2.83 3.31 4.21 3.00
68	10.2 15.5 3.75 2.33	2.31 2.43 2.80 2.33	1.00 1.00 1.00 1.00
67	1.00 1.00 1.00 1.00	1.00 1.00 1.00 1.00	0.03 0.09 0.03 0.05

- (a) Correction for ¹³C and unlabelled contribution.¹⁰
 (b) Metastables separated by the method of Jennings.

deuterated compounds, fragment ion peak height measurements at high and low electron energies indicate that in the case of 1-d₁-cyclohexene, methyl loss involves essentially complete hydrogen scrambling with no isotope effect at 70 ev but a small isotope effect of 1.05 at 12 ev. In the case of 1-d₁-methylcyclopentene, practically only CH₃ loss was observed. This indicates that probably the entire (M-CH₃)⁺ ion in methylcyclopentene is due to the ejection of the methyl substituent.

Defocused metastable ion peak intensities for labelled methylcyclopentene and cyclohexene were measured and the results are included in Table 2. The metastable ion peak intensities for 1-d₁-cyclohexene indicate either, completely random selection of hydrogen in methyl loss with an isotope effect of 1.20 (see Table 2), or incomplete scrambling of hydrogen before fragmentation with or without an isotope effect. If the processes taking place in the ion source and the first field-free region are the same then more complete scrambling and larger isotope effects should be observed in the first field-free region metastable ion peaks. Since fragment ion peak abundance measurements show that methyl radical loss involves complete scrambling, metastable ion peak intensities should similarly show complete hydrogen scrambling for this fragmentation and thus deviation from random loss must indicate an isotope effect (1.20). To separate unambiguously the two factors, the fragmentation of another complementary deuterated species, 1,3,3-d₃-cyclohexene was also investigated. The results are summarized in Table 3 and are compared with the random statistical ratios. The observed/

Table 3

$(M-CH_3)/(M-CH_2D)$, $(M-CH_2D)/(M-CHD_2)$ and $(M-CHD_2)/(M-CD_3)$

for unimolecular metastable ions from deuterated

cyclohexenes (70 ev)

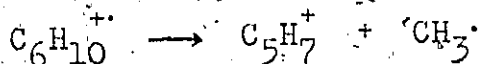
Compound	$(M-CH_3)/(M-CH_2D)$	$(M-CH_2D)/(M-CHD_2)$	$(M-CHD_2)/(M-CD_3)$
1-d ₁ -cyclohexene	2.80	--	--
Observed/Statistical	1.20±0.07	--	--
1,3,3-d ₃ -cyclohexene	0.70±0.07	4.21±0.07	39±16
Observed/Statistical	1.26±0.07	1.40±0.07	1.85±0.74

statistical ratios are the same (within experimental error) for the two labelled compounds. This is consistent with (i) complete H/D scrambling in these low-energy molecular ions and, (ii) an isotope effect of 1.20.

The defocused metastable ion peak abundance ratios for CH_3 and CH_2D loss, from the molecular ion of 1- d_1 -methylcyclopentene is 3.75. This is not reflected in the fragment ion peak abundance ratios of 11.2 and 15.5 at 70 and 12 eV respectively. It would appear that either the processes taking place in the ion source for methylcyclopentene are different from those occurring in the first field-free region, or that the observed daughter ion abundances indicate that practically the entire $(\text{M}-\text{CH}_3)$ ion in methylcyclopentene is due to the ejection of the methyl substituent (direct bond cleavage) from the unscrambled and unrearranged molecular ion, whereas metastable ion peak measurements reflect incomplete H/D scrambling of the unrearranged molecular ion before methyl radical is lost.

Holmes and Weese have recently discussed metastable ion peak shapes in detail¹²⁸. In the case of cyclohexene, for the $(\text{M}-\text{CH}_3)$ process, they were able to construct a pair of Gaussian curves which were summed to produce the observed metastable ion profile. It was stressed that having subtracted one Gaussian from the observed peak, the remainder was also of Gaussian shape. Although such adding and subtracting of Gaussian curves is a subjective process, somewhat insensitive to the chosen parameters, it is noteworthy that only two curves were required to reproduce the experimental observations. The physical significance of such two peaks would be that two distinguishable structures and/or

electronic excited states of the precursor ion were dissociating within the first field-free region. In the present study, the variation of metastable ion peak profile for the same process



as a function of the precursor ion's structure and origin (i.e. two different $C_6H_{10}^{+}$ precursor ions were generated from methylcyclopentene and cyclohexene) were examined. The effect of deuterium labelling on the metastable ion peak profile for the process has also been studied. The results are summarized as shown in Table 4. Here $w_{0.5}$ and % height define the Gaussian, and % abundance defines the proportions (areas), of each Gaussian component in the composite metastable ion peak. Fig. 6 shows the separation of the metastable ion peak of the process ($M-CH_3$) into two Gaussian components (A) and (B) for the compound cyclohexene. The metastable ion peaks for the processes ($M-CH_3$) and ($M-CH_2D$) for 1- d_1 -cyclohexene are identical with that of its unlabelled analogue and therefore are not reproduced. The metastable ion peaks for 1- d_1 -methylcyclopentene, however, can be separated into two Gaussian components (B) and (C), component (B) being one of the cyclohexene components for the same process. The ratio of Gaussian component (B) and (C) for the ($M-CH_3$) process, 52:48 (by area), is different to that of the process ($M-CH_2D$), being 51:69 (by area). These are shown in Figs. 7 and 8 and Table 4. Thus it can be concluded that there are at least two distinguishable structures and/or electronic excited states for each of the precursor ions, dissociating within the

Table 4. Separation of the Metastable

ion peak for the process ($C_6H_{10}-CH_3$)

into two Gaussian components

	Cyclohexene		1-d ₁ -cyclohexene		1-d ₁ -methylcyclopentene				
	(M-CH ₃)		(M-CH ₃)		(M-CH ₂ D)		(M-CH ₂ D)		
	Gaussian A	Gaussian B	Gau.A	Gau.B	Gau.A	Gau.B	Gau.C	Gau.B	Gau.C
a	60	31	60	31	60	31	70	31	70
%height ^b	29	71	29	71	29	71	29	49.5	50.5
% abundance (by area) ^c	44	56	44	56	44	52	48	31	69

(a) Half height width for the Gaussian component.

(b) % height of the Gaussian component.

(c) % abundance measured by area, indicating the proportion of each of the Gaussian component in the composite metastable ion peak.

FIG. 6

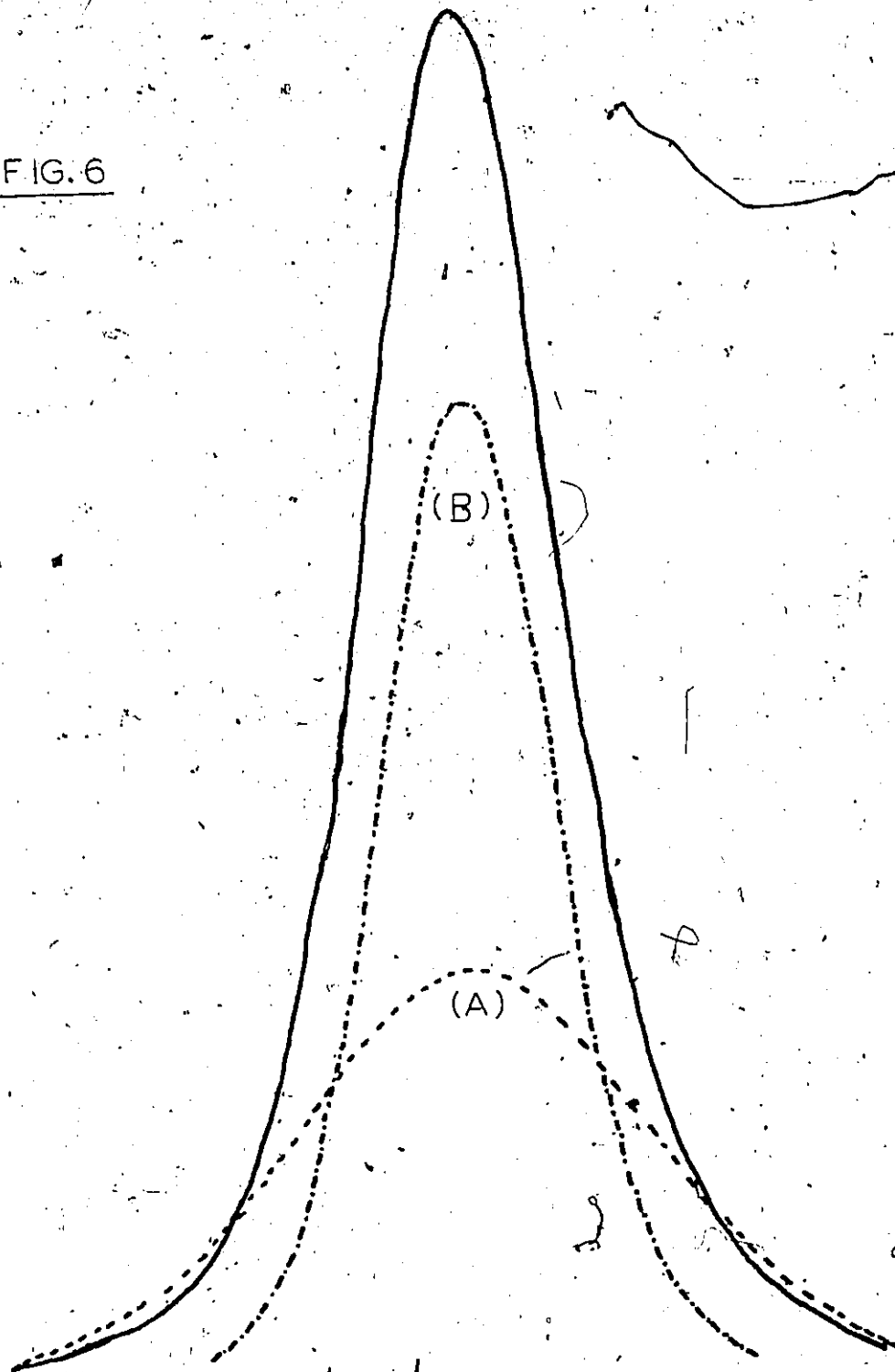


Fig. 6. Metastable ion peak for the cyclohexene generated dissociation, $M^+ \rightarrow C_5H_7^+ + CH_3$, separated into two Gaussian components (A) and (B).

FIG. 7

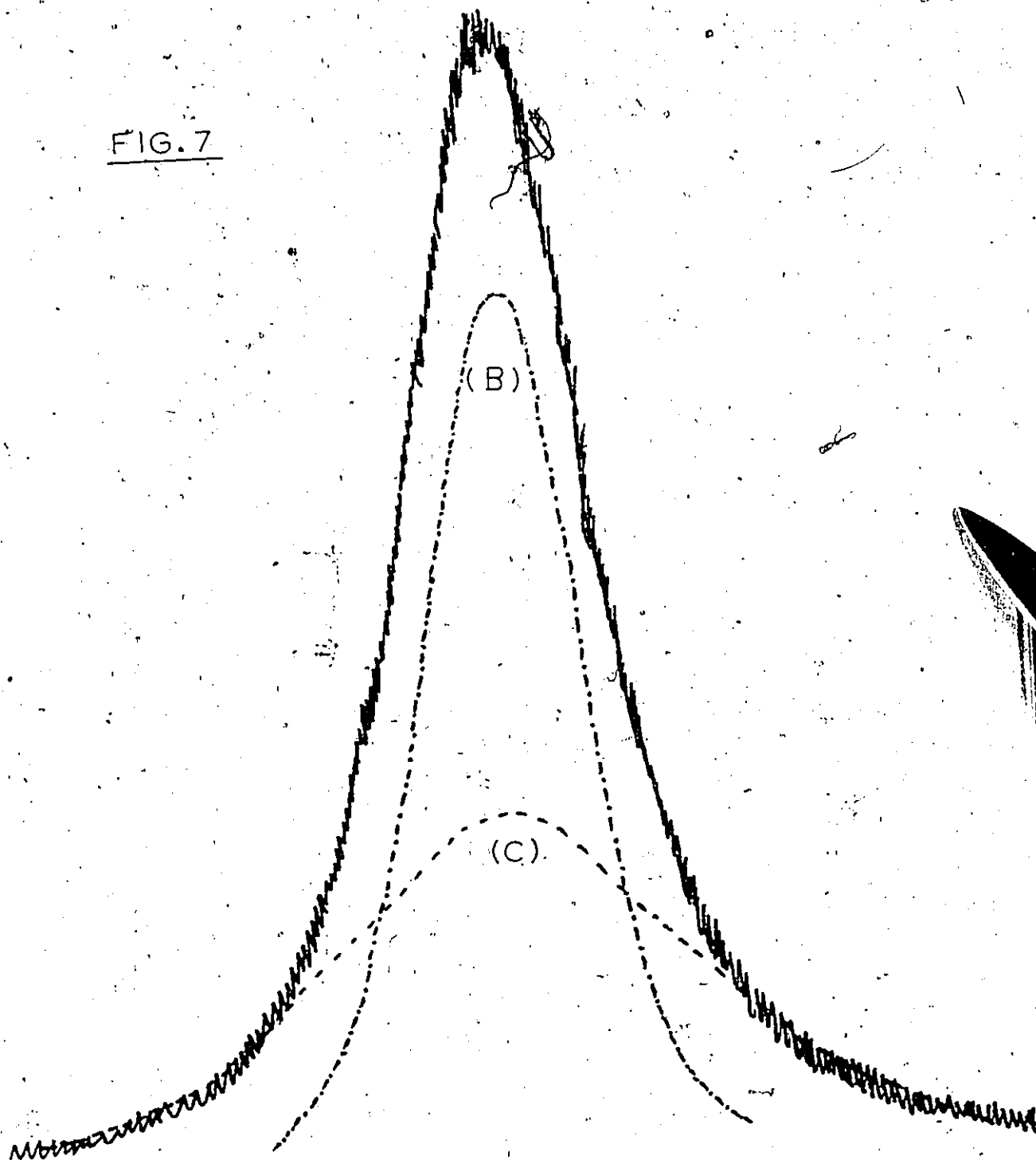


Fig. 7. Metastable ion peak for the 1-d₁-methylcyclopentene generated dissociation, $C_6H_9D^+ \rightarrow C_5H_7^+ + CH_3^+$, separated into two Gaussian component (B) and (C).

FIG. 8

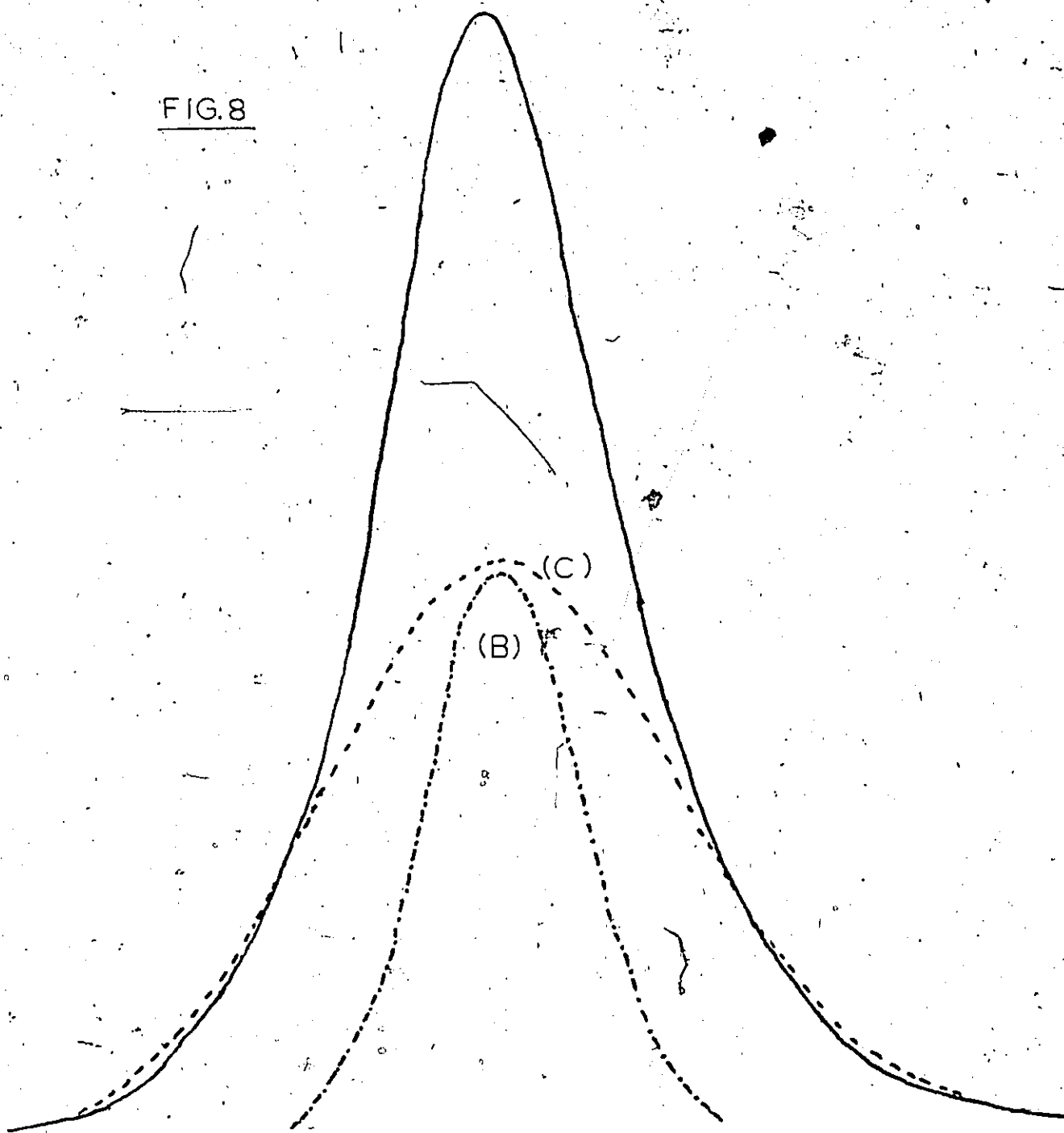


Fig. 8. Metastable ion peak for the 1-d₁-methylcyclopentene generated dissociation, $C_6H_9D^{+*} \rightarrow C_5H_7^{+} + CH_2D^{\cdot}$, separated into two Gaussian components (B) and (C).

first field-free region; one of the two being common to each precursor ion.

Since the overall relative metastable ion peak abundances for the processes $(M-CH_3)^+$: $(M-CH_2D)^+$ from 1-d₁-cyclohexene and 1-d₁-methylcyclopentene are 2.80 and 3.75 respectively (Table 2), the relative abundances of each structure can be determined. This is presented as Table 5.

Three interesting conclusions can be drawn from the results shown in Table 5. Firstly, in the case of 1-d₁-cyclohexene, two distinguishable structures (A) and (B) (designated by Gaussian (A) and (B) respectively) of the precursor ion were dissociating within the first field-free region. The $(M-CH_3)^+$: $(M-CH_2D)^+$ metastable ion peak areas are in the same ratio (2.80:1.00) for both structures and they are similarly greater than the random value (2.33:1.00), indicating an isotope effect (1.20). In the case of 1-d₁-methylcyclopentene however, the $(M-CH_3)^+$: $(M-CH_2D)^+$ metastable ion peak areas are in the ratios 2.61±0.15:1.00 and 6.29:1.00 for structures (C) and (B) respectively. The former is again considered to be complete random with a similar isotope effect (1.12±0.06). The latter is probably due to incomplete H/D scrambling of the molecular ion of structure (B) before fragmentation. Secondly, in agreement with the data for daughter ion observations on 1-d₁-methylcyclopentene for the $(M-CH_3)^+$ process, structure (B) is the incompletely scrambled and un rearranged molecular ion of methylcyclopentene, which loses the methyl radical by direct bond cleavage. To obtain structure (B) from cyclohexene however, involves a ring contraction of the

Table 5.

Relative Abundance of the processes $(M-CH_3)/(M-CH_2D)$

for the separated structures for the
labelled compounds

Process	1-d ₁ -cyclohexene		1-d ₁ -methylcyclopentene		Complete Random
	Gaussian A	Gaussian B	Gaussian B	Gaussian C	
(M-CH ₃)	2.80	2.80	6.29	2.61±0.15	2.33
(M-CH ₂ D)	1.00	1.00	1.00	1.00	1.00

cyclohexene molecular ion by allylic cleavage following by ring closure to give a methylcyclopentene molecular ion (i.e. structure (B)), during which complete H/D scrambling occurred. Thirdly structure (A) from cyclohexene and structure (C) from methylcyclopentene could be linear, formed by allylic cleavage of the cyclic molecular ions.

It is interesting to compare the loss of a methyl radical from methylcyclopentene and methylcyclohexene, with that observed in the mass spectra of methylcyclopentane and methylcyclohexane. Labelled compound peak measurements indicated that practically the entire $(M-CH_3)$ ion peak in methylcyclohexane¹²⁹ was due to the ejection of the methyl substituent. 50% of the $C_5H_9^+$ ion yielded from methylcyclopentane¹²⁹ however derived from the expulsion of the methyl substituent, the rest coming from ring carbons. Exactly the opposite trends were observed in the case of methyl cyclic olefins. As observed in the present study, almost the entire $(M-CH_3)^+$ ion was due to the ejection of the methyl substituent from the methylcyclopentene molecular ion. In 2-methylcyclohexene¹²⁷, only 60% of the methyl loss was due to loss of the substituent, the other 40% was derived from an internal carbon atom. In the present study, about 88% of the CH_3 loss originated from the substituent for the isomer 4-methylcyclohexene, results for which will be discussed later in this chapter.

(B) The $(C_4H_6)^+$ ions, m/e 54, $(M-C_2H_4)^{++}$

In the relative abundances of these peaks lie the major difference in the mass spectra of the isomers. In methylcyclo-

pentene, $(M-C_2H_4)^+$ is a relatively minor fragment (5% base peak).

In cyclohexene it is 75% of the base peak (see Figs. 1a and 2b).

This is not too surprising as it has been suggested previously that the elimination of ethylene from cyclohexene following electron impact was a retro Diels-Alder reaction^{1f, 125, 130-131}.

In the case of the unrearranged methylcyclopentene molecular ion, a retro Diels-Alder reaction was not operative. The

evidence upon which this earlier suggestion was based was however, rather tenuous. The relative normal and metastable ion

peak intensities for ethylene loss in the mass spectra of 1-d₁-cyclohexene, 1,3,3-d₃-cyclohexene and 1-d₁-methylcyclopentene

are reproduced in Table 6. The normal peak intensities for the $(M-C_2H_4)$ and $(M-C_2H_3D)$ processes from 1-d₁-methylcyclopentene

are weak and were not measured. Thus from Table 6, the measured values for the processes from 1-d₁-cyclohexene are very close to

those calculated assuming random loss of hydrogen. For cyclohexene, our results confirm those of Derrick, Falick and

Burlingame¹²⁵. Their results indicated that by field ionization,

scrambling of the hydrogen by 1,3-allylic rearrangements in

3,3,6,6-d₄-cyclohexene was observed to begin within 1×10^{-11} sec

and to be complete within 1×10^{-9} sec (in electron impact

reactions, the source residence time is 10^{-6} to 10^{-5} sec). The

elimination of ethylene from cyclohexene is thus postulated to

be formally a retro Diels-Alder reaction. It has been suggested

previously that the elimination of ethylene from cyclohexene,

norbornene¹²², 4-vinylcyclohexene¹³², methylcyclohexenes^{127, 131}

and 1-propenylcyclohexene¹³³ was a retro Diels-Alder reaction.

Table 6.
Normal^a and Metastable^b peak intensities for
ethylene loss in the mass spectra of
labelled cyclohexene and methyl-
cyclopentene

m/e	1-d ₁ -methylcyclopentene (≥98.4%-d ₁)	1-d ₁ -cyclohexene (≥98%-d ₁)	1,3,3-d ₃ -cyclohexene (97%-d ₃ , 3%-d ₂)
	Ratios Peaks 70ev 10ev m Random	Ratios Peaks 70ev 10ev m Random	Ratios ^c Peaks 70ev 10ev m Random
57	- - -	- - -	5.0-5.0 - 5
56	- - -	- - -	5.5 11.3 - 15
55	- - - 2.4 1.5	2.2 ±0.5 2.0 1.5 1.5	5.7 5.6 - 9
54	- - - 1.0 1.0	1.0 1.0 1.0 1.0	0.2 0.7 - 1

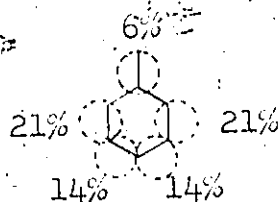
(a) Normal peak intensities for the processes from methylcyclopentene are weak and were not measured; corrected for carbon-13 contribution.
(b) Metastables separated by the method of Jennings.¹⁰
(c) Not measured.

H/D randomization of labelled 4-vinylcyclohexene¹³² and 1-methylcyclohexene¹²⁷ before or during the retro Diels-Alder reaction has been reported. In the case of norbornene¹²² however, no evidence even for partial hydrogen-deuterium scrambling preceding this dissociation of the molecular ion in either the first or second field-free regions was observed. The retro Diels-Alder reaction for the elimination of ethylene from methylcyclohexene has been studied here and is discussed later in this chapter.

For methylcyclopentene, in the normal mass spectrum, the fragment ion $(M-C_2H_4)^+$ is weak and was not measured. For 1-d₁-methylcyclopentene however, it was possible to measure the defocused metastable ion peak abundance ratio and the result is included in Table 6. The measured value (2.41 : 1.00) compared with the complete random value (1.50 : 1.00) indicates either (i) incomplete H/D scrambling or, (ii) complete scrambling with an isotope effect (1.60). It is formally possible that the methylcyclopentene molecular ion isomerizes to that of cyclohexene before undergoing the retro Diels-Alder elimination characteristic of the latter. A feasible mechanism for this isomerization is allylic fission followed by hydrogen migration from side chain methyl group to adjacent carbon and then ring closure to form a cyclohexene molecular ion. If this is the case, the observed value would indicate incomplete H/D scrambling without an isotope effect, since no isotope effect was observed for the $(M-C_2H_4)$ process in cyclohexene.

Labelling data for cyclopentane⁵¹ indicated that ethylene might either be lost from the scrambled cyclic molecular ion, or from an open-chain radical ion in which various hydrogen migrations

might occur. In cyclohexane^{43,129} the loss of ethylene originated from the cyclic parent ion by single bond cleavage mechanisms. In methylcyclopentane¹²⁹ some 80% of the ethylene carbons originated from the ring. In methylcyclohexane¹²⁹ the contributions of various parts of the molecule to C_2H_4 formation can be estimated:



The percentage figures indicated the operation of a significant isotope effect. This conclusion was based on deuterium retentions in the resultant $C_5H_{10}^+$ ions from α -d₁-, 2-d₁- and 4-d₁-methylcyclohexane¹²⁹.

(C) The $(C_3H_5)^+$ ions, m/e 41, $(M-C_3H_5)^+$

The $C_3H_5^+$ ion, m/e 41, in methylcyclopentene and cyclohexene is mainly due to $(M-C_3H_5)^+$. The 70 ev mass spectra of 1-d₁-methylcyclopentene and 1-d₁-cyclohexene yield 1:1 ratio for the ions m/e 41, $(M-C_3H_4D)^+$, and m/e 42, $(M-C_3H_5)^+$ corresponding to m/e 41 for the unlabelled compounds. Random loss of hydrogen also requires a ratio of 1:1 in both cases. In 1-d₁-cyclohexene however, specific loss of C_3H_5 or C_3H_4D also would give a $(M-C_3H_5)^+ : (M-C_3H_4D)^+$ ratio of 1:1. The latter possibility can be ruled out because in the mass spectrum of 1,3,3-d₃-cyclohexene m/e 44, $(M-C_3H_5)^+$ was observed; this requires randomization of hydrogen. A feasible mechanism for the formation of

m/e 42, $(M-C_3H_5)^+$; from the labelled compound is shown in Scheme 1. Here as in the case of the $(M-C_2H_4)^+$ process, the methylcyclopentene molecular ion is proposed to isomerize to that of a cyclohexene molecular ion, following the same mechanism, before or during loss of the (C_3H_5) species.

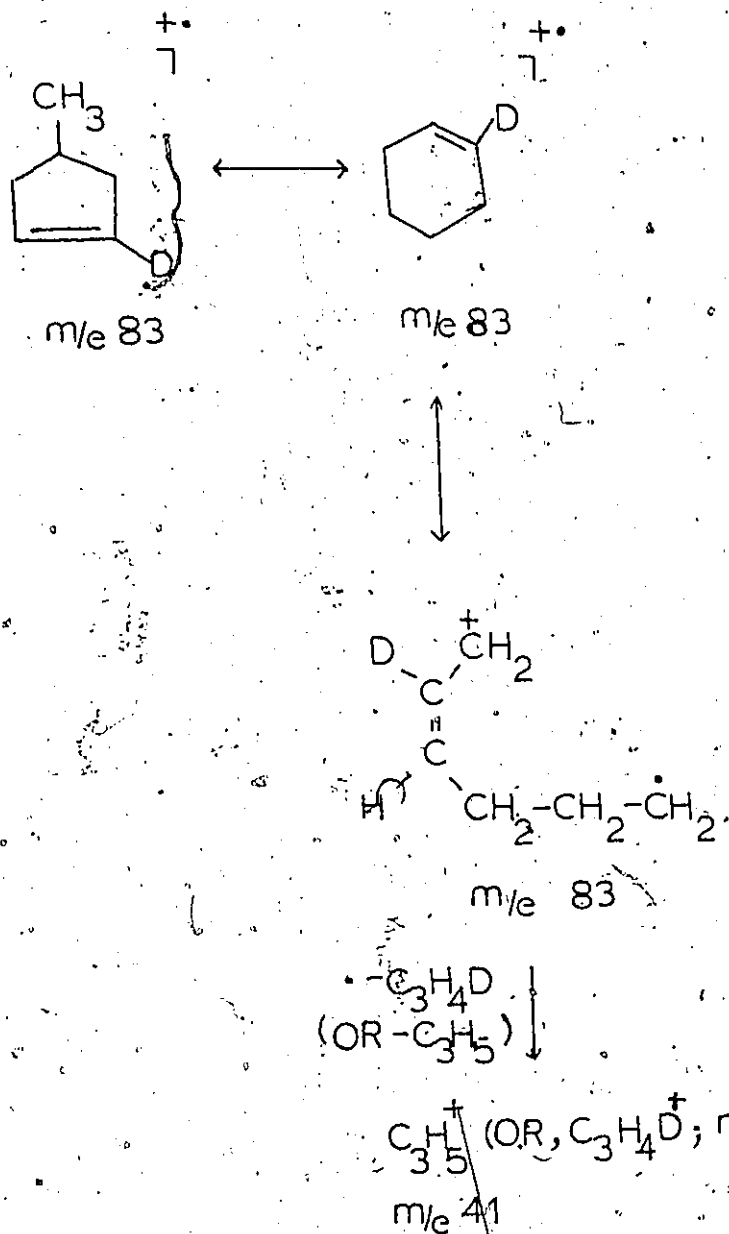
(D) The $(M-H)^+$ ions, m/e 81, $(C_6H_9)^+$

The loss of a hydrogen atom from the molecular ions of both isomers gives rise to a flat-topped metastable ion peak with a small energy release of 0.05 ev. Theoretical and experimental shape comparison of flat-topped metastable ion peaks, obtained from hydrogen atom loss from these and some other hydrocarbon molecular ions has been a subject of study by Holmes and Weese in this laboratory¹²⁸. Both $(M-H)^+$ ions fragment by losing ethylene to give a minor fragment ion $C_4H_5^+$, confirmed by the presence of the appropriate metastable ion peaks. The first field-free metastable ion peak abundance ratios for $(M-1, -C_2H_4)$ and $(M-1, -C_2H_3D)$ in the mass spectra of 1-d₁-cyclohexene and 1-d₁-methylcyclopentene are 1.32 and 1.25 respectively. The random loss ratio is 1.25.

(E) Kinetics of the formation of m/e 54, $(M-C_2H_4)^+$; and

m/e 67; $(M-CH_3)^+$ for the mass spectra of cyclohexene and methylcyclopentene

In the mass spectra of cyclohexene, the formation of $(M-C_2H_4)^+$ ion involves only direct bond dissociations whereas the formation of $(M-CH_3)^+$ ion involves extensive intramolecular rearrangement. These observations for the two processes can be



Scheme 1. Fragmentation mechanism for the loss of C_3H_5 from the molecular ion in the mass spectrum of methylcyclopentene.

explained by employing the general consequences of Quasi-Equilibrium Theory¹³⁴⁻¹³⁵.

The differences between high and low energy spectra in terms of the Quasi-Equilibrium Theory have been frequently expressed in the recent literature¹³⁶. In particular, the property has often been employed that rearrangement reactions tend to predominate over direct cleavage reactions as the electron energy is decreased. This principle may be expressed¹³⁷ in terms of the simplified equation of the Quasi-Equilibrium Theory (equation 1).

$$k = \nu \left(\frac{E - E_a}{E} \right)^{S-1} \dots \dots \dots (1)$$

where E is the internal energy of the species reacting, E_a is the activation energy, ν , the frequency factor, k, the first order rate constant and S is the number of effective harmonic oscillators in the decomposing ion.

For cyclohexene at low electron energy, the ratio $k_{(M-CH_3)}/k_{(M-C_2H_4)}$ is 18 (Fig. 1b), where $k_{(M-CH_3)}$ and $k_{(M-C_2H_4)}$ are the rate constants for the elimination of CH_3 and C_2H_4 respectively from the cyclohexene molecular ion. Measurements of the abundance of metastable transitions in the second-field free region (between the electric sector and the magnetic sector), indicate that at ca. 1×10^{-6} sec, $k_{(M-CH_3)}$ for m/e 67 is approximately 300 times greater than that for $k_{(M-C_2H_4)}$ for m/e 54. Since it is the low-energy precursor ions which undergo metastable ion

decomposition and give rise to normal ion peaks at low electron energies, the observation of intense metastable and normal ion peaks at low ev for methyl loss from cyclohexene and the comparable very weak metastable peak and normal peaks at low ev for ethylene loss corresponding to direct bond cleavage, implies that the former process has the lower activation energy. Electron impact appearance potential measurements for cyclohexene confirmed this. The activation energy for the formation of $(M-C_2H_4)^+$ ion was about 0.5 ev higher than that for the formation of $(M-CH_3)^+$ ion^{124, 131}. This is in agreement with the Quasi-Equilibrium Theory prediction.

It should be noted that the frequency factor for a typical simple cleavage is high and approaches the bond vibrational frequency, while that for a rearrangement is low. However, according to equation (1), the lower activation energy for a rearrangement reaction may offset its low frequency factor. Thus the combination of low E_a and ν , typical of rearrangements, results in a much slower rise of k with E than is found for direct bond cleavage fragmentation (see Fig. 9). In cyclohexene, loss of an ethylene is expected to have high frequency factor while loss of a methyl radical (following extensive rearrangement) should have a low frequency factor. The preceding factors account for the importance of direct bond cleavage, i.e. ethylene loss, compared to rearrangement reaction, i.e. methyl radical loss from cyclohexene molecular ion at 70 ev.

Another important consequence of the Quasi-Equilibrium Theory postulates and the effect of E_a and ν on reaction rates is

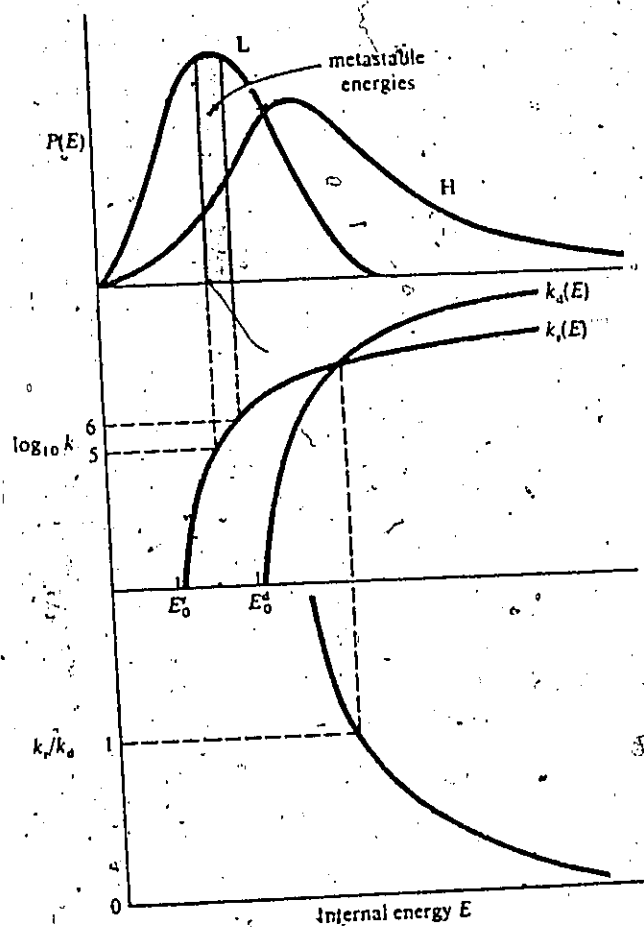


Fig. 9. Rate and energy curves for rearrangement (r) and direct cleavage (d) reactions, H and L represent high and low-energy distributions respectively.

that hydrogen scrambling is a low E_a /low ν process. Hence a rapid process such as direct bond cleavage can hardly be accompanied by hydrogen randomization though this may be extensive or complete during slower fragmentations. This conclusion can be illustrated with reference to the 1-d₁-cyclohexene spectrum studied here (Table 6). Rapid elimination of ethylene (ion source generated fragments) from 1-d₁-cyclohexene, a retro Diels-Alder reaction, involves the loss of a hydrogen atom at some site other than C₃ and C₄ (see Table 6, 70 and 12 ev), but scrambling is slow and thus is incomplete. Metastable ion peak measurements, however, indicate that H/D scrambling is complete before loss of ethylene takes place. In other words, the rates of H/D scrambling for the above low energy species are enhanced to a greater degree than the rates of the elimination reactions.

Another prediction from the Quasi-Equilibrium Theory is that the primary deuterium isotope effect in mass spectra increases with decreasing internal energy. Moreover an isotope effect is important in rearrangement reactions. For direct bond cleavages however, isotope effects are usually insignificant. This is observed here. For 1-d₁-cyclohexene, it is found that there is no observable isotope effect operating on the loss of ethylene (direct bond cleavage) from the molecular ion, even in the first field-free region. However, the isotope effect operating on the loss of a methyl radical (a rearrangement process) from the completely scrambled ion increases with decreasing internal energy (1.00, 1.05 and 1.20 in the 70 and 12 ev ion sources and the first field-free region respectively).

The same trend can be observed in the 1,3,3-d₃-cyclohexene compound (also Table 6). Similar observation was reported for the losses of H and D from the molecular ions of deuterated toluenes and cycloheptatrienes².

Contrary to the fragmentation mechanism for the mass spectrum of cyclohexene, normal peak height measurement indicates that in methylcyclopentene, (M-C₂H₄)⁺ ion is relatively minor, because a retro Diels-Alder reaction is not operative. The formation of the (M-CH₃)⁺ ion however, involves mostly direct bond dissociation from the unscrambled and unrearranged molecular ion. At 70 and 12 ev, the (M-CH₃)/(M-C₂H₄) ratios are 20:1 and 100:1 respectively. The relative metastable ion abundance ratio for the (M-CH₃) and (M-C₂H₄) processes is found to be approximately 250:1 (second field-free region). These results indicate that the methylcyclopentene molecular ion may extensively rearrange to the cyclohexene ion, before or during the loss of ethylene. The activation energy for the cyclohexene ion formation from the methylcyclopentene molecular ion however, is large compared to the activation energy for the elimination of ethylene from the cyclohexene ion produced by rearrangement. It is also larger than the activation energy for the (M-CH₃) process (direct bond cleavage).

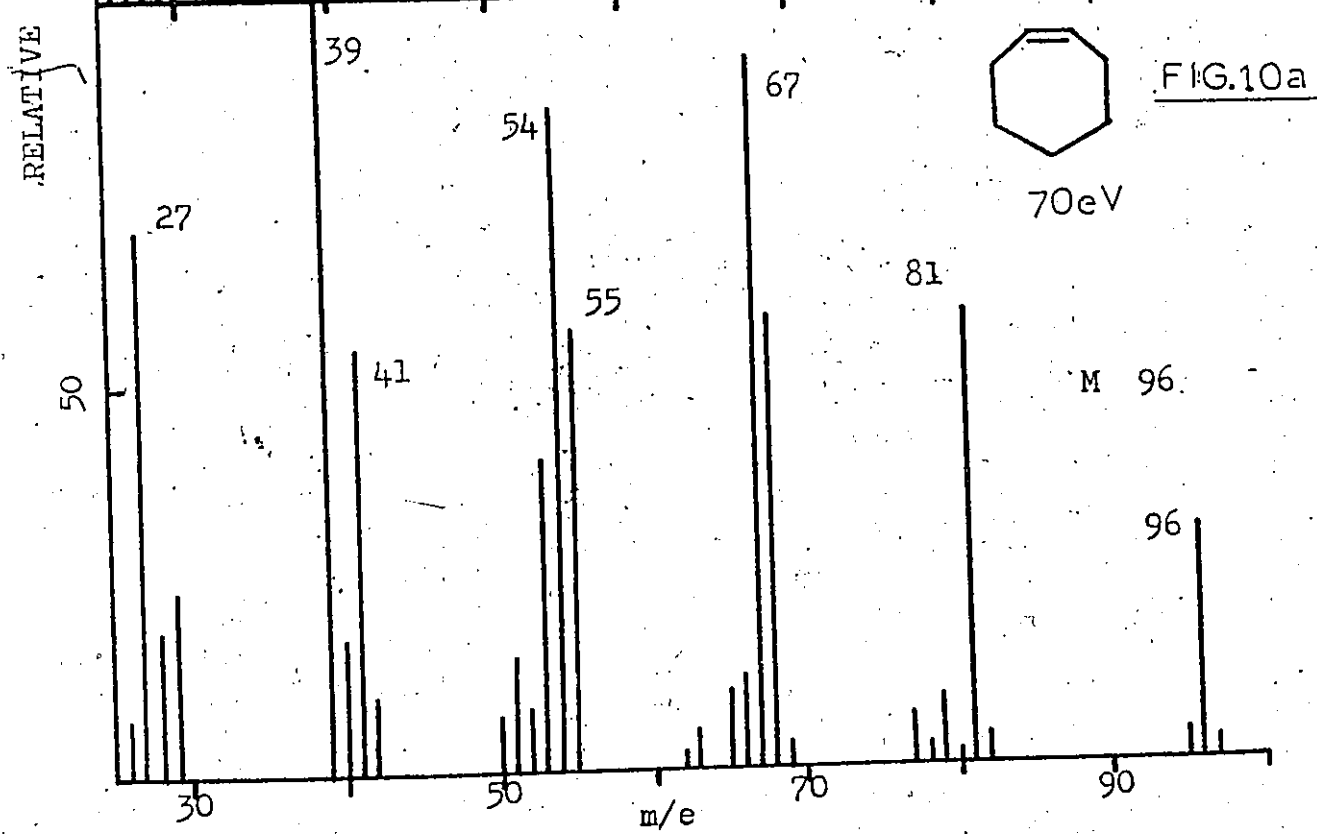
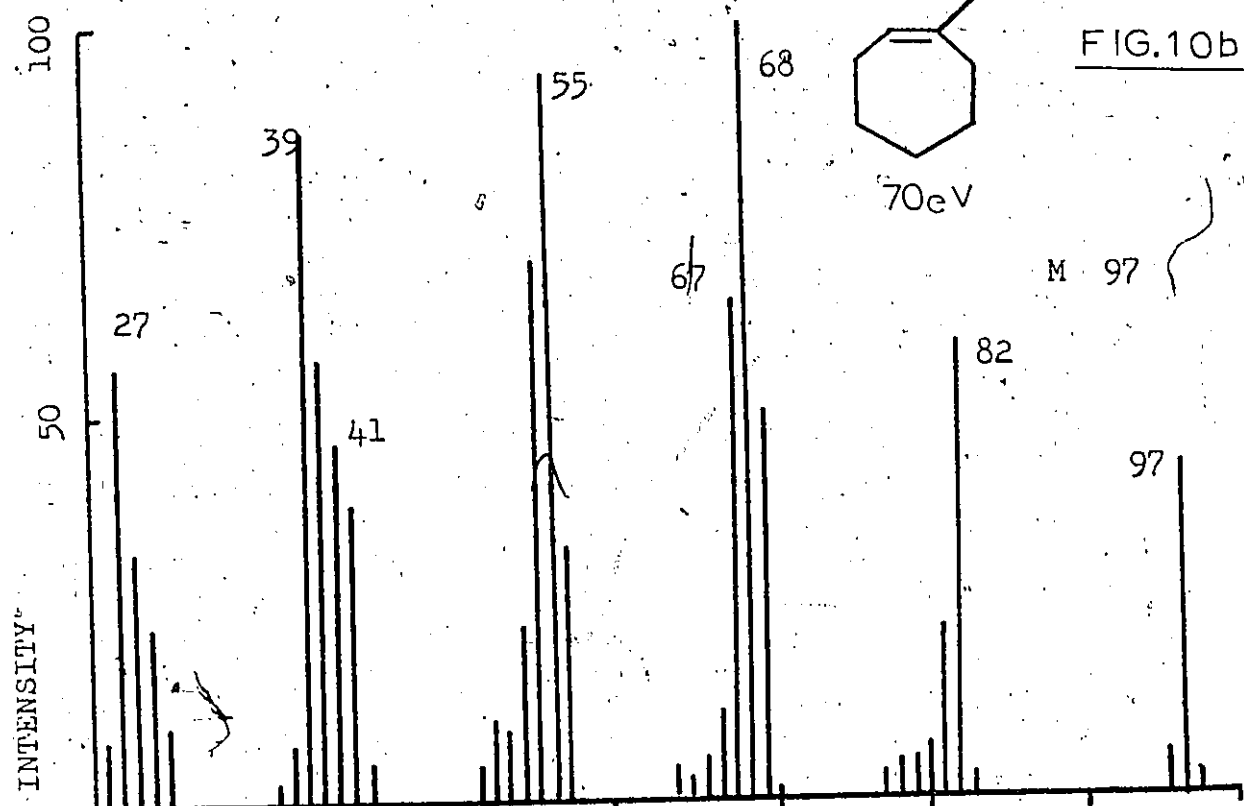
THE MASS SPECTRA OF CYCLOHEPTENE AND 4-METHYLCYCLOHEXENE

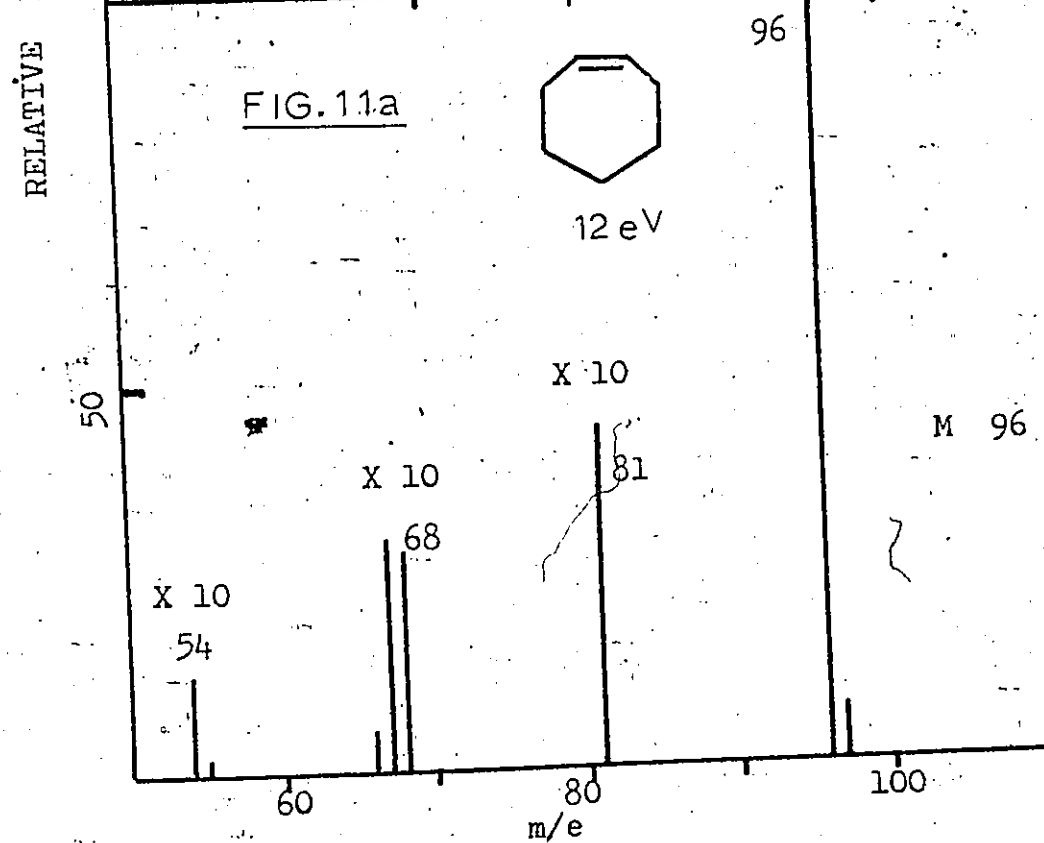
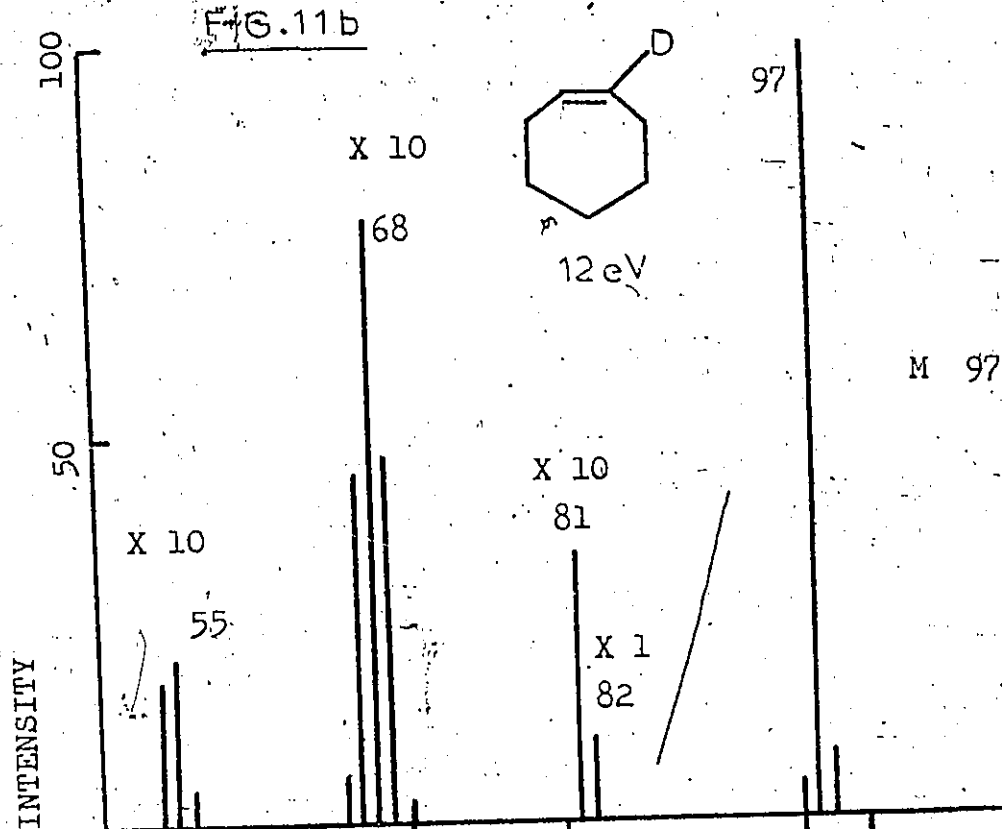
This mass spectral study of cycloheptene and 4-methylcyclohexene is an extension of the homologues of cyclohexene and

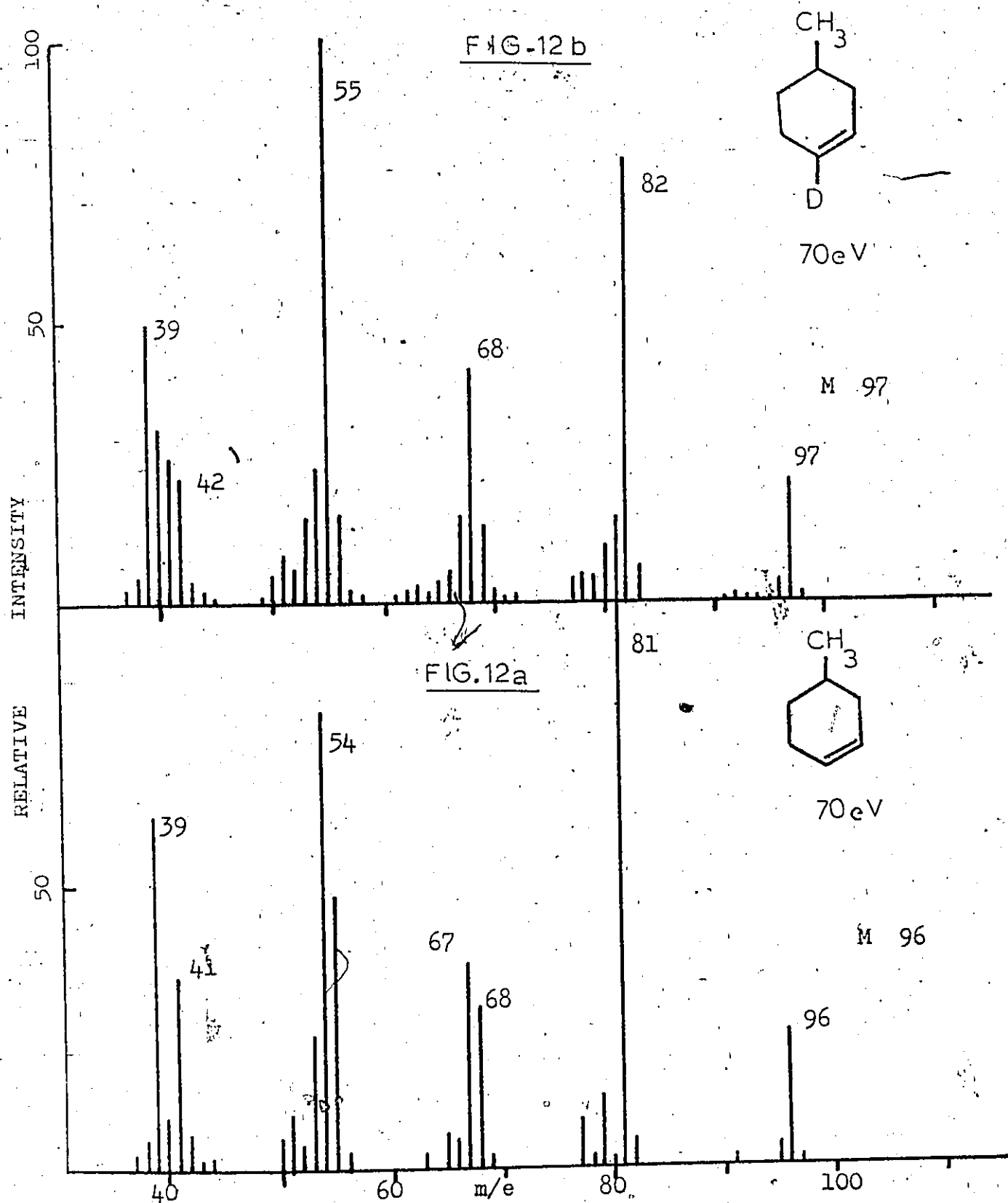
methylcyclopentene described in the preceding section. The chief purpose of these experiments was to discover what similarities could be observed in their fragmentation mechanisms and the energetics thereof. The problem of atom scrambling has been considered in some detail with regard to the distribution of normal and metastable ion peak abundances in labelled compounds.

The 70 and 12 ev mass spectra of cycloheptene and 4-methylcyclohexene are shown in Figs. 10a and 11a; and 12a and 13a respectively. The 70 ev mass spectrum of the 4-methylcyclohexene is in good agreement with previously tabulated data^{131, 138}.

The same fragmentations for both isomers appear to take place. This is confirmed by metastable transitions as shown in Table 7. The relative abundances of the major peaks are however, different as is clearly shown in Figs. 10 to 13. The primary fragment ions from both molecular ions are $(M-CH_3)^+$, $(M-C_2H_4)^{++}$, $(M-C_2H_5)^+$, $(M-C_2H_6)^{++}$, $(M-C_3H_5)^+$ and $(M-C_3H_6)^{++}$. This is shown in the 12 ev mass spectra in Figs. 11a and 13a. 1-d₁-cycloheptene and 1-d₁-4-methylcyclohexene were prepared and their 70 and 12 ev mass spectra were examined in order to determine fragmentation pathways and ion structures in detail. Their 70 and 12 ev mass spectra are shown as Figs. 10b, 11b; 12b and 13b respectively. For ease of comparison, the behaviour of fragment ion formation from molecular ion generated from both isomers will be discussed together.







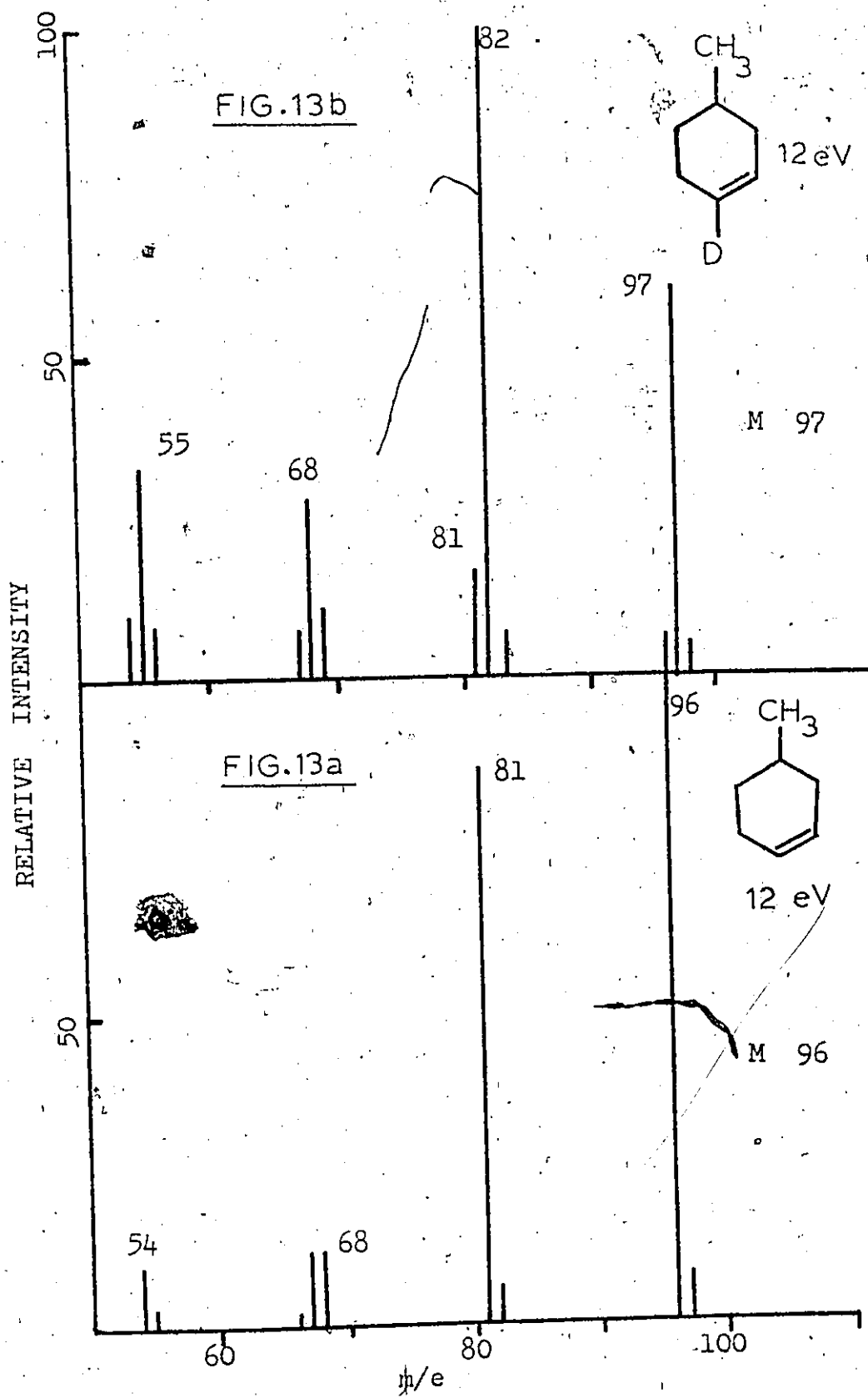


Table 7. Metastable ion peaks ** observed in the 70ev mass spectra of cycloheptene and 4-methylcyclohexene

Generating fragmentation	m [*] m/e	Relative abundance (70ev)	
		4-methylcyclohexene	Cycloheptene
$C_7H_{12}^{+\bullet} \rightarrow C_6H_9^+ + CH_3^\bullet$	68.3	74.3	30.5
$C_7H_{12}^{+\bullet} \rightarrow C_5H_8^{+\bullet} + C_2H_4$	48.2	1.4	1.0
$C_7H_{12}^{+\bullet} \rightarrow C_5H_7^+ + C_2H_5^\bullet$	46.8	-	1.9
$C_7H_{11}^+ \rightarrow C_5H_7^+ + C_2H_4$	47.3	4.8	1.4
$C_7H_{11}^+ \rightarrow C_5H_6^+ + C_2H_5^\bullet$	45.8	-	0.5
$C_7H_{11}^+ \rightarrow C_7H_9^+ + H_2$	91.0 ^a	3.3	1.9
$C_7H_{10}^{+\bullet} \rightarrow C_5H_6^{+\bullet} + C_2H_4$	46.3	1.9	1.0
$C_7H_9^+ \rightarrow C_7H_7^+ + H_2$	89.0 ^a	2.4	1.4
$C_6H_9^+ \rightarrow C_6H_7^+ + H_2$	77.1 ^a	47.1	17.1
$C_6H_6^{+\bullet} \rightarrow C_4H_4^{+\bullet} + C_2H_2$	34.7	~ 1.0	1.0
$C_6H_5^+ \rightarrow C_4H_3^+ + C_2H_2$	33.8	1.0	1.0
$C_5H_8^{+\bullet} \rightarrow C_5H_7^+ + H^\bullet$	66.0 ^a	100	100
$C_5H_7^+ \rightarrow C_5H_5^+ + H_2$	63.1 ^a	10	11.4
$C_5H_7^+ \rightarrow C_3H_5^+ + C_2H_2$	25.1	1.4	1.9
$C_4H_7^+ \rightarrow C_3H_3^+ + CH_4$	27.7	3.8	6.2
$C_4H_6^{+\bullet} \rightarrow C_3H_3^+ + CH_3^\bullet$	28.2	27.1	18.1
$C_4H_5^+ \rightarrow C_4H_4^+ + H^\bullet$	51.0	3.8	5.2
$C_4H_5^+ \rightarrow C_4H_3^+ + H_2$	49.1 ^a	1.9	1.9
$C_3H_5^+ \rightarrow C_3H_3^+ + H_2$	37.1 ^a	2.9	2.9

** Measured by a Daly detector (MS 902S), see Chapter 1 (pp. 8-10) for description.

^a "Flat top" metastable ion peak

(A) The $C_6H_9^+$ ion, m/e 81, (M-CH₃)

Table 8 presents the observation on daughter and metastable ion peaks for 1-d₁-cycloheptene and 1-d₁-4-methylcyclohexene. For cycloheptene, all hydrogen atoms have lost their identity. This indicates that considerable rearrangement takes place before the methyl radical is lost. For 1-d₁-4-methylcyclohexene, relative abundances of ions m/e 82 and 81 at 70 and 12 ev are 7.0:1.0 and 6.0:1.0 respectively. Moreover, the ratio of their generating metastable ion peaks from M⁺ is 10:1. Complete hydrogen randomization requires a ratio of 3:1. These results indicate that at least 87% of the methyl radical originates from the substituent. The mass spectra of labelled 1-methyl-d₃-cyclohexene has been studied by Stark and co-worker¹²⁷ who found that normal peak measurements indicated only 60% of methyl radical loss was due to loss of the substituent. The other 40% was derived from an internal carbon atom.

The behaviour of the low energy, metastable ion generating molecular ions of cycloheptene and 4-methylcyclohexene are worthy of more attention. Careful study of the defocused metastable ion peak shapes for the (M-CH₃) process indicates that both compounds have the same profile. Also they all have two things in common. Firstly, they are very broad at the skirts such that values of n of 1.5 or less are needed in an expression of the form¹²⁸,

$$h = e^{-\rho w^n} \quad n \leq 1.5 \dots \dots \dots (2)$$

Table 8.

Normal^a and Metastable^b peak intensities for methyl radical loss in the mass spectra of labelled cycloheptene and 4-methylcyclohexene

	1-d ₁ -4-methylcyclohexene (≥ 98%-d ₁)				1-d ₁ -cycloheptene (96%-d ₁)			
m/e	Peaks		Ratios		Peaks		Ratio	
	70ev	10ev	m*	Random	70ev	10ev	m*	Random
82	7.0	6.0	10.0	3.0	3.0	3.0	3.0	3.0
81	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0

(a) Correction for ¹³C and unlabelled contribution.

(b) Metastables separated by the method of Jennings¹⁰.

to describe the broad peak base. Here h is the peak height, w its corresponding width and β and n are constants. Secondly the value of n which fits the base profile is much too small to fit the profile above the half-height. The observed profile is considered to be made up from two (or more) Gaussian type peaks of "pure" shape that fit an expression of the form,

$$h = e^{-\beta w^2} \dots \dots \dots (3)$$

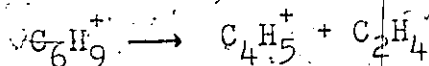
This suggests that the metastable generating molecular ions of the two C_7H_{12} isomers rearrange to at least two common structures before methyl radical loss. It is possible that one of the common structures is cycloheptene and 4-methylcyclohexene is a methylcyclohexene molecular ion which fragments by direct bond cleavage, losing the methyl substituent. In cycloheptene, the molecular ion has to rearrange extensively to form a methylcyclohexene molecular ion. During this time complete H/D scrambling will have taken place. In 4-methylcyclohexene however there is only partial scrambling in the molecular ion before or during direct bond cleavage for methyl substituent ejection. This observation is similar to that obtained from cyclohexene and methylcyclopentene. We also propose that one of the common structures for the (M-CH₃) process is the methylcyclopentene molecular ion in which direct bond cleavage occurred and the methyl substituent is ejected.

Dissociation of $C_6H_9^+$

The major fate of the $C_6H_9^+$ ion is to dissociate by loss of a hydrogen molecule. It gives a flat-topped metastable ion

peak ($m^* = 77.0$). The average energy release associated with the unlabelled molecules was calculated using the width of the peak at the "horns" and substituting in the appropriate equation¹²⁸. The energy release was estimated to be 0.40 ev. This value is independent of the precursor molecules (cycloheptene and 4-methylcyclohexene). The C_6H_{10} isomers, cyclohexene and methylcyclopentene also display an identical "flat-topped" metastable. Thus the constancy of both energy release and shape as described above is further evidence in support of a common species, $C_6H_9^+$. The relative abundances of metastable ion peaks for the loss of a hydrogen molecule (H_2 and HD) from the $C_6H_9D^+$ ion from both 1-d₁-cycloheptene and 1-d₁-4-methylcyclohexene were measured. They were found to be 5.0:1.0 and 5.6:1.0 respectively by area measurement. These indicate an isotope effect of 1.45 and 1.60 respectively if complete hydrogen scrambling has taken place (complete hydrogen scrambling requires a ratio of 5.5:1). This is typical of hydrogen atom or hydrogen molecule elimination from hydrocarbon ions⁸⁰.

Another secondary dissociation of some interest is the process,



The first field-free region metastable ion peaks for 1-d₁-cyclohexene and 1-d₁-methylcyclopentene are in the ratios 1.32:1.00 and 1.25:1.00 respectively. This is compatible with the random value (1.25:1.00). Similar results would be expected in the present case of 4-methylcyclohexene and cycloheptene.

(B) Dissociations of the molecular ions by ethylene,
ethyl and ethane loss

The 12 ev mass spectra of cycloheptene and 4-methylcyclohexene are shown in Figs. 11a and 13a respectively. Under these conditions, peaks arising from secondary fragmentation are essentially absent. The former compound shows three major peaks in the m/e 65-68 cluster, namely m/e 68, ($M-C_2H_4$); m/e 67, ($M-C_2H_5$) and m/e 66, ($M-C_2H_6$). However, for 4-methylcyclohexene, only the first two processes are important. It would appear that these processes may necessitate considerable rearrangement before fragmentation. Table 9 presents the observation on daughter and metastable ion peak for the labelled compounds for these three processes. For cycloheptene, all hydrogen atoms have lost their identity. This indicates that for these three fragmentations, extensive rearrangement takes place before ethylene, ethyl and ethane are lost. Normal peak measurements for 1-d₁-4-methylcyclohexene indicate almost complete and incomplete scrambling of hydrogen in the molecular ion before the loss of ethyl and ethylene respectively. The mechanism of formation, fragmentation behaviour and structures of the ions $C_5H_8^+$ and $C_5H_7^+$ will be described separately as follows.

The $C_5H_7^+$ ion, m/e 67, ($M-C_2H_5$)

The $C_5H_7^+$ ion is prominent in the mass spectra of cycloheptene (base peak) and 4-methylcyclohexene. This ion is also base peak in the mass spectra of all C_5H_8 isomers⁸⁰ and also cyclohexene, methylcyclopentene and cyclooctene. It thus represents an important species in such C_nH_{2n-2} homologues.

Table 9.

Normal^a and Metastable^b peak intensities for ethylene,
ethyl and ethane losses in the mass spectra of
1-d₁-4-methylcyclohexene and 1-d₁-cycloheptene

	1-d ₁ -4-methylcyclohexene (≥ 98%-d ₁)			1-d ₁ -cycloheptene (≥ 96%-d ₁)		
	Ratios			Ratios		
	Peaks		m [*]	Peaks		m [*]
m/e	70ev	10ev		70ev	10ev	
69	12.4	9.1	n.o. ^c	44.5	55.4	21
68	40.7	27.3	n.o. ^c	96.5	98.0	59
67	15.2	7.1	n.o. ^c	63.7	58.6	47
66	-	-	n.o. ^c	44.5	8.0	11

- (a) Correction for ¹³C and unlabelled contribution.¹⁰
 (b) Metastables separated by the method of Jennings.
 (c) Not observed.

Therefore, information as to its structure and fragmentation behaviour is clearly desirable. For both cycloheptene and 4-methylcyclohexene (normal peak data), all hydrogen atoms have lost their identity, showing that extensive rearrangement takes place before ethyl loss. A reasonable route to this ion would incorporate an allylic cleavage followed by a hydrogen atom transfer to form the ethyl group which could then be lost by direct cleavage. This mechanism was favored by Kihstle and Stark¹²⁷ in their study of 2-methylcyclohexene.

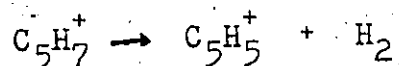
It has been found that the heats of formation of $C_5H_7^+$ ion generated from $C_6H_{10}^+$ precursors (two of them being cyclohexene and methylcyclopentene) by methyl radical loss are all 199 ± 2 kcal/mole¹³⁹. The daughter ion, $C_5H_7^+$, thus appears to be a common ion at threshold. The heats of formation of $C_5H_7^+$ ion generated from C_5H_8 molecules by hydrogen atom loss however were all 210 ± 2 kcal/mole⁸⁰. This suggests the possibility of a higher energy species than that observed in the study of C_6H_{10} molecules. It would be interesting to study the heats of formation of $C_5H_7^+$ ions produced from the higher C_nH_{2n-2} homologues.

Dissociations of $C_5H_7^+$

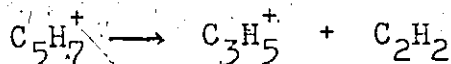
The major dissociation pathway for this important ion is by acetylene loss ($m^* 25.1$). Holmes⁸⁰ has studied this process in the mass spectra of four C_5H_8 isomers. He found from metastable ion studies of labelled molecules, that acetylene loss involved complete hydrogen atom scrambling in the ion prior to dissociation. It is not unreasonable to expect that similar

observations can be obtained in the mass spectra of methylcyclopentene, methylcyclohexene, cyclohexene and cycloheptene studied in this work.

Holmes⁸⁰ also studied the process



for this ion. This endothermic reaction ($\Delta H_f C_5H_5^+ - \Delta H_f C_5H_7^+ \geq 254 - 210 \geq 44$ kcal/mole) is accompanied by a ~~di~~ flat-topped metastable ion peak. The energy release was estimated to be 0.12 ev and was independent of the precursor molecules (spiro-pentane, cyclopentene, piperylene, isoprene, methylcyclopentene, methylcyclohexene, cyclohexene and cycloheptene). The constancy of both shape and energy release as described above is evidence in support of a common dissociating species $C_5H_7^+$. The first field-free region metastable ion peak areas for the $(C_5H_7-H_2)$ process in 1-d₁-cyclohexene and 1-d₁-methylcyclopentene are in the ratio 5.00:1.00 and 4.57:1.00 for loss of H₂ and HD respectively. This is greater than the random value (2.5:1.0) indicating an isotope effect of 1.83 to 2.00. Besides, these metastable ion peaks are superimposable upon each other. This is further evidence for a common structure for the $C_5H_7^+$ ions. It is worthwhile to emphasize here that there are at least two types of $C_5H_7^+$ ions. Firstly if a $C_5H_7^+$ ion is observed as an ion generated in the first field free region, then it must have been produced from low energy $C_5H_8^+$ or $C_5H_7R^+$ species (R=CH₃, C₂H₅ or C₃H₇). Secondly if one studies the two processes



these $C_5H_7^+$ ions must have involved appreciably higher energies in their formation in order that their dissociations can now be seen in the first field-free region.

The $C_5H_8^+$ ion, m/e 68, (M- C_2H_4)

Table 9 lists the appropriate observations on daughter ions and metastable ion peaks for 1-d₁-cycloheptene and 1-d₁-4-methylcyclohexene. For cycloheptene, all hydrogen atoms have lost their identity. This suggests that for this fragmentation considerable rearrangement takes place prior to ethylene loss. For 4-methylcyclohexene however, scrambling of hydrogen is not complete before or during ethylene loss. Kinstle and Stark in their study of the mass spectra of various labelled 2-methylcyclohexenes¹²⁷ proposed that allylic isomerization of the 2-methylcyclohexene molecular ion to 3- and 4-methylcyclohexene ions preceded dissociation. It was also suggested that the 2-methylcyclohexene and 3-methylcyclohexene ions undergo a retro Diels-Alder reaction by losing ethylene, in a ratio of approximately 2:1. Another route however, which incorporates an allylic cleavage followed by ethylene loss cannot be ruled out.

Dissociation of $C_5H_8^+$

The major dissociation pathway for this ion in the mass spectra of these compounds is by hydrogen atom loss. Second

field-free metastable ion peaks observed from an A.E.I. MS 902S instrument are roughly of Gaussian shape. Holmes⁸⁰ has studied this process originated from the molecular ions of some C_5H_8 hydrocarbons, using a single focusing Hitachi RMU-6D and an A.E.I. MS 902S instrument equipped with a β -slit. With the former instrument these metastable ion peaks were again roughly of Gaussian shape. With the latter when observed by the acceleration voltage scan method¹⁰ under conditions of good energy resolution, the peaks were found to be of the "flat-top" variety.

(C) Rapid dissociation of the molecular ions

The 12 ev mass spectra of 4-methylcyclohexene (Fig. 13a) and cycloheptene (Fig. 11a) show two major peaks in the m/e 50-55 cluster, namely m/e 54, $(M-C_3H_6)^+$ and m/e 55, $(M-C_3H_5)^+$. The former species is the predominant one. There is no strong metastable ion peak corresponding to their formation from M^{++} or $(M-1)^+$. Thus it is concluded that loss of propane and C_3H_5 radical takes place rapidly in the ion source. In order to help identify such processes, low electron energy mass spectra (12 ev) were examined. Under these conditions few peaks arising from secondary fragmentation are present.

The behaviour of 4-methylcyclohexene is less clear cut than that of cycloheptene*. In the 12 ev mass spectrum of the unlabelled 4-methylcyclohexene, the relative intensities of ions m/e 54, $(M-C_3H_6)^+$; and m/e 55, $(M-C_3H_5)^+$ are approximately 5:1 (after ^{13}C correction). In 1-d₁-4-methylcyclohexene under similar conditions, the relative abundance of m/e 54, $(M-C_3H_5D)^+$; *which shows complete H/D randomization before or during the loss of C_3H_5 and C_3H_6 species (see Fig. 11b).

m/e 55, $(M-C_3H_6)^{+}$ and $(M-C_3H_4D)^{+}$; and m/e 56, $(M-C_3H_5)^{+}$ are 1.00:5.00:0.78. In the absence of any isotope effect for these fast processes, the relative peak ratio $(M-C_3H_5D)^{+}$: $(M-C_3H_6)^{+}$, and $(M-C_3H_4D)^{+}$: $(M-C_3H_5)^{+}$ are 1.00:4.65 and 1.00:2.23 respectively. Random loss both require 1:1. This indicates incomplete scrambling of the molecular ion before dissociation, with or without an isotope effect. The single deuterium attached to olefinic carbon thus appears to be preferentially retained. Kinstle and Stark in their study of the mass spectrum of 2-methylcyclohexene¹²⁷ proposed that the 2-methylcyclohexene molecular ion rearranged to 4-methylcyclohexene ion. This ion was then expected to undergo a retro Diels-Alder reaction to produce a butadiene $C_4H_6^{+}$ radical ion by losing the original methyl substituent. This is consistent with the observation that the spectrum of the CD_3 -compound exhibited an m/e 54 peak but no m/e 57 peak. Our present results confirm this proposal. The fragmentation patterns of 2-methylcyclohexene and 3-methylcyclohexene were extremely similar to that of 4-methylcyclohexene studied here. However, the intensity of $C_4H_6^{+}$, m/e 54, $(M-C_3H_6)$ from 4-methylcyclohexene was reproducibly larger than that of m/e 54 from the other two isomers¹³¹. This is consistent with 1,3-allylic rearrangement in the molecular ions. The peak ratio $(M-C_3H_6)$: $(M-C_3H_5D)$ of 4.65:1.00 indicates that about 18% of the olefinic C_1 deuterium of the decomposing 4-methylcyclohexene molecular ion has scrambled to C-4 or C-5, prior to the retro Diels-Alder reaction for the formation of butadiene radical ion.

(D) Summary and conclusion

Although the mass spectra of these two C_7H_{12} molecules are superficially similar, there are some fast fragmentations of the molecular ion of 4-methylcyclohexene which reflect ground state molecular geometry. These are the losses of methyl, ethylene and propane. All fragmentations of the molecular ion of cycloheptene, as well as ethyl and C_3H_5 losses from the molecular ion of 4-methylcyclohexene involve complete or almost complete hydrogen atom scrambling. The fragment ions $C_6H_9^+$ and $C_5H_7^+$ from both molecules each pass through a common intermediate prior to dissociation. The chief evidence for the above conclusions came from detailed studies of metastable ion peak abundance and shapes in labelled analogues.

APPENDIX I
EXPERIMENTAL

All mass spectra were obtained using an Hitachi Perkin-Elmer RMU-6D instrument. Metastable defocusing studies were carried out on a RMU-6E or an AEI MS 902S using the methods described by Kiser et al.¹⁴⁰ and Jennings¹⁰ respectively. Unless otherwise stated all spectra were run at 70 ev. Samples were introduced via an all-glass liquid inlet system. This and the ion source were maintained at temperatures below 50°C to avoid thermal decompositions.

Deuterium labelling

Whenever materials labelled with deuterium in a hydroxyl or a carboxyl group were analyzed, the instrument was previously "deuterated" by insertion of D₂O through the liquid inlet system prior to and during analysis. This minimized exchange within the instrument and thus assured high percentage labelling. To deuterate the hydroxyl or a carboxyl group, the sample was dissolved in D₂O (warming if required) and the solvent subsequently removed under vacuum. Good labelling was usually obtained after three to four such treatments.

Sample purity

All prepared liquid samples were purified first, by distillation according to the procedures reported in the literature describing the particular preparation. All compounds were purified by gas-liquid chromatography before their mass spectra were determined.

The purity of labelled compounds (deuterium and ^{13}C) was determined from the shift of the molecular or other suitable fragment ion peaks (where the molecular ion peak is absent).

Neopentyl compounds

Neopentyl alcohol and its 1,1- d_2 analogue were prepared by reduction of pivaloyl chloride with LiAlH_4 and LiAlD_4 respectively.

Neopentyl- ^{13}C -1,1- d_2 alcohol and neopentyl- ^{13}C alcohol were prepared by reacting t-butyl lithium with $^{13}\text{CO}_2$ followed by reduction of the acid with LiAlD_4 and LiAlH_4 respectively¹⁴¹.

Neopentyl bromides and chlorides were prepared by treating the appropriate alcohol with triphenylphosphine dibromide and dichloride respectively in dimethylformamide¹⁴².

$\text{C}_4\text{H}_8\text{X}^+$ ions

2-Bromo-1-chloro-2-methylpropane and its 1,1- d_2 analogue:

2-methyl-2-propen-1-ol and its 1,1- d_2 analogue were prepared by reduction of 2-methyl-2-propenyl acid with LiAlH_4 and LiAlD_4 respectively. The alcohols were then reacted with triphenylphosphine in excess carbon tetrachloride (25°C , 2 days) to produce 2-methyl-2-propenyl chloride and its labelled analogue¹⁴³. Addition of 30% HBr in glacial acetic acid yielded the products required¹⁴⁴.

3-Chloro-2,2-dimethylpropanol and its 1,1- d_2 analogue were prepared by reduction of β -chloropivalic acid (Aldrich) with LiAlH_4 and LiAlD_4 respectively.

1,3-Dichloro-2,2-dimethylpropane and its $1,1-d_2$ analogue were produced by the reaction of triphenylphosphine in excess carbon tetrachloride ($25^{\circ}C$, 3 days) with 3-chloro-2,2-dimethylpropanol¹⁴³.

1-Bromo-3-chloro-2,2-dimethylpropane and its $1,1-d_2$ analogue were produced by the reaction of triphenylphosphine dibromide in excess methylene chloride ($25^{\circ}C$, 3 days) with 3-chloro-2,2-dimethylpropanol and its $1,1-d_2$ analogue respectively.

3-Bromobutanol and its $1,1-d_2$ analogue were formed by addition of HBr (30% HBr in glacial acetic acid) to crotonic acid¹⁴⁵, followed by reduction of the bromoacid with $LiAlH_4$ and $LiAlD_4$ respectively.

3-Bromo-1-chlorobutane and its $1,1-d_2$ derivative were produced by the reaction of triphenylphosphine in excess carbon tetrachloride ($25^{\circ}C$, 3 days) with 3-bromobutanol and its $1,1-d_2$ analogue respectively¹⁴⁵.

1-Bromo-2-chloro-2-methylpropane was formed by the reaction of triphenylphosphine dibromide in excess methylene chloride ($25^{\circ}C$, 3 days) with 2-methyl-2-propen-1-ol and its $1,1-d_2$ analogue respectively, followed by the addition of HCl in glacial acetic acid ($25^{\circ}C$, 14 days).

Chlorohydrins and chloroacids

Ethylene chlorohydrin (2-chloroethanol), 99%: Aldrich Chem. Co.

2-Chloro-1,1- d_2 -ethanol was prepared by the reduction of

chloroacetic acid with $LiAlD_4$.

Trimethylene chlorohydrin (3-chloropropanol): Aldrich Chem. Co.

3-Chloro-1,1-d₂-propanol was produced by the reduction of

3-chloropropanoic acid with LiAlD₄.

3-Chloro-2,2-dimethylpropanol and its 1,1-d₂ analogue (see

C₄H₈X⁺ ions section)

Tetramethylene chlorohydrin (4-chloro-1-butanol): J.T. Baker

Chem. Co.

Pentamethylene chlorohydrin (5-chloro-1-pentanol): Pealtz &

Bauer Inc.

Hexamethylene chlorohydrin (6-chloro-1-hexanol): Aldrich Chem. Co.

Chloroacetic acid: British Drug Houses Ltd.

3-Chloropropanoic acid: Aldrich Chem. Co.

β-Chloropivalic acid: Aldrich Chem. Co.

Cyclic C₆H₁₀ and C₇H₁₂ isomers

Cyclohexene and its 1-d₁ analogue were prepared by the reduction of cyclohexanone by LiAlH₄ and LiAlD₄ respectively, followed by dehydration of the appropriate alcohol in hexamethylphosphoric triamide¹⁴⁶.

1,3,3-d₃-cyclohexene was similarly prepared as above, except 2,2,6,6-d₄-cyclohexanone and LiAlH₄ were used. 2,2,6,6-d₄-cyclohexanone was prepared by three equilibrations of cyclohexanone, D₂O and trace of NaOD at reflux temperatures overnight.

Methylcyclopentene (mixture of 4-methylcyclopentene and 3-methylcyclopentene) and d₁-methylcyclopentene (mixture of 4-methyl-2-d₁-cyclopentene and 3-methyl-1-d₁-cyclo-

pentene) were prepared by the reduction of 3-methylcyclopentanone by LiAlH_4 and LiAlD_4 respectively, followed by dehydration of the appropriate alcohol in hexamethylphosphoric triamide¹⁴⁶.

Cycloheptene and 4-methylcyclohexene and their 1-d₁ analogues were prepared similarly as in the case of cyclohexene and its 1-d₁ analogue, except cycloheptanone and 4-methylcyclohexanone were used respectively.

PART II

THE PYROLYSIS OF 2- and 3-CHLOROPENTANE

CHAPTER 1INTRODUCTION

The pyrolysis of alkyl halides have recently been reviewed by Maccoll¹. Therefore, no attempt has been made here to cover this topic in detail, except to give a general understanding of mechanisms, substituent effects, isotope effects, stereochemistry, rearrangements, surface effects and direction of elimination.

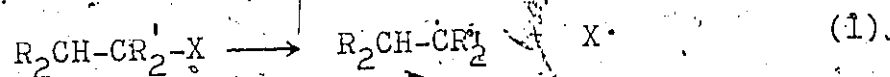
(A) Mechanism of homogeneous gas phase pyrolysis of alkyl halides

Three basic types of mechanism have been used in the interpretation of homogeneous gas phase pyrolyses. They are:

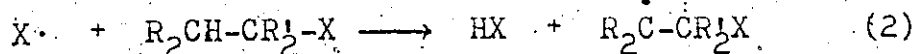
- (i) A radical non-chain mechanism,
- (ii) A radical chain mechanism, and,
- (iii) A unimolecular elimination reaction.

Any substance decomposes mainly by the path involving the least activation energy. This path, also, depends on the structure of the reactant molecule and the temperature of the reaction system.

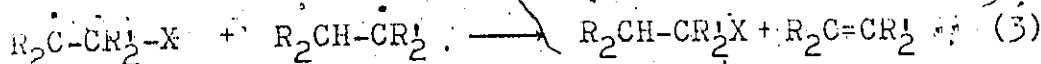
The radical mechanisms (i and ii) are multistep processes and both are initiated by homolysis:



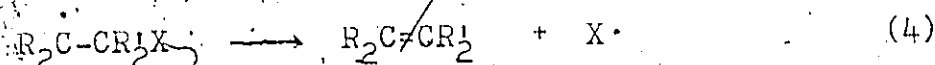
where X is a halogen atom and R_2CH-CR_2 is an alkyl group. The radical nonchain mechanism may lead to products by a radical abstraction of a hydrogen atom from the starting material:



and finally by a disproportionation of two radicals:



Steps (1) and (2) can lead to a radical chain mechanism if the radical $R_2C-CR_2^1X$ decomposes to the product and a radical, $X\cdot$,



As Maccoll¹ has clearly pointed out, the radical non-chain mechanism would require an activation energy at least equal to the homolytic bond dissociation energy, $D(R''-X)$, of the $R''-X$ bond. For most of the alkyl halides discussed in Maccoll's recent review¹, the bond dissociation energy is much larger (15 to 30 kcal/mole) than the energy of activation. On this ground alone, the radical nonchain mechanism is unlikely for the pyrolysis of alkyl halides, except in very special cases, such as the pyrolysis of allylic halides¹.

The radical chain mechanism can be excluded by the following observations. The reactions appear to: (1) lack induction periods, and, (2) are unaffected by radical chain sensitizer (bromine and allyl bromide) and radical inhibitors (cyclohexene and toluene). There are compounds which do not give good first-order unimolecular kinetics unless inhibitors are present¹. For example, primary bromides pyrolyze by both radical chain and unimolecular mechanisms. Therefore, in order to study the unimolecular homogeneous reaction only, it is necessary to employ an inhibitor (e.g. cyclohexene) that

eliminates the radical chain process. Free radical processes increase in the series RCl, RBr and RI and decrease with increasing branching of the alkyl group R.

Thus it is possible to study the unimolecular, homogeneous mechanism of the pyrolysis of alkyl chlorides and bromides essentially free of radical chain reactions if suitable radical inhibitors are available. Unimolecular elimination reactions of alkyl chlorides and bromides are often referred to as involving four-centered, six-centered or possibly other membered ring transition states. These reactions are characterized by moderately low energies of activation ($E_a \sim 36-61$ kcal/mole), Arrhenius frequency factors around 10^{13} and entropies of activation ranging from a small positive value to a small negative value.

Since 1955, MacColl and colleagues¹⁻² have favored a very polar transition state in the gas phase unimolecular homogeneous dehydrohalogenation of alkyl chlorides and bromides leading to the intermediate formation of a tight carbonium halide ion-pair. They have stated that "the major factor influencing the rate is the stability of the carbonium ion in the ion pair"¹⁻². Five observations were presented in support of the ion-pair theory.

- (1) Activation energies were lowered and rates raised by α -substitution with electron-releasing groups.
- (2) Only minor changes in the rate occurred from β -substitutions.
- (3) A strong correlation existed between energies of activation and corresponding heterolytic bond dissociation energies. Little correlation however, was seen between energies of activation and homolytic bond dissociation energies.
- (4) Wagner-Meerwein

rearrangements occurred in gas phase halide pyrolyses. (5) A close similarity between gas phase elimination and polar substitutions (S_N1) and elimination reaction (E_1) in polar solvents existed. These arguments were discussed in detail in two recent reviews by Maccoll and his co-worker¹⁻². They favor the ion-pair theory mainly because the great body of theory available to account for ionic reactions of organic compounds in polar solvents may be applied to these gas phase heterolytic reactions.

However, the ion-pair intermediate, if it exists in the gas phase, must not be as generally conceived in polar solvents. For example, Harding, Maccoll and Ross³ failed to show that D-(+)-2-chlorooctane racemized at a rate greater than it eliminated hydrochloric acid (an experiment which has often been used as a test for a rapid reversible equilibrium between the ground state and the reactive ion-pair intermediate⁴).

Benson and Bose⁵ have favored a semi-ion-pair mechanism. Using this model, O'Neal and Benson⁶ calculated energies and entropies of activation. Their values agreed remarkably well with the experimentally reported values for their four-centered transition state reactions.

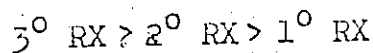
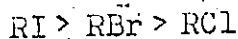
It appears that all data reported, with the possible exception of the Wagner-Meerwein rearrangements, could be explained by a highly polar transition state which proceeds directly to products without the formation of an ion-pair intermediate.

(B) Substituent effects

There is convincing evidence that the major factor which determines the thermal stability of alkyl halides is the heterolytic strength of the C-X bond. Maccoll¹⁻² has stated repeatedly, "while there is no correlation between the energies or free energies of activation and homolytic bond dissociation energies, there is a clear correlation with heterolytic bond dissociation energies". He has suggested the following equation as a reasonable estimate of the activation energy (E(HX)),

$$E(HX) = 0.29 D(R^+X^-) \quad (5)$$

where $D(R^+X^-)$ is the heterolytic bond dissociation energy. The rate sequences are:



where $3^\circ RX$, $2^\circ RX$ and $1^\circ RX$ represent tertiary, secondary and primary halides respectively.

Maccoll¹ has recently reviewed various group substitution effects on the rate of pyrolysis of alkyl halides. For example, it is apparent that electron-releasing groups at the α -position (Table 1) and to a much lesser extent at the β -position (Tables 2 to 4) increased the rate of elimination. This is illustrated for α -methyl substitution on chlorides where the relative rates of ethyl, isopropyl and t-butyl chlorides were 1:150:25000. The ratio was even greater for bromides and iodides (Table 1).

Table 1

Comparative Arrhenius Parameters and Relative Rates
for the α -methylated series of Alkyl Halides¹

Compound	Ethyl			Isopropyl			t-Butyl		
	$\log A$ sec ⁻¹	E_a kcal/m	Rel. Rate	$\log A$ sec ⁻¹	E_a kcal/m	Rel. Rate	$\log A$ sec ⁻¹	E_a kcal/m	Rel. Rate
Chloride (360°)	13.75	57.8	1	13.52	50.8	150	13.75	45.0	25000
Bromide (325°)	13.11	53.0	1	13.32	47.5	160	13.51	41.3	46000
Iodide (285°)	13.76	50.5	1	13.81	45.5	102	13.26	37.6	35400

Average Arrhenius parameters and rate constant ratios for the primary β -methylated series¹ are shown in Table 2.

Values for n-propyl and isobutyl iodides are not available.

Similar values were obtained for the secondary β -methylated (and β -ethylated) series as shown in Table 3. Values for 2-pentyl bromide are not available.

The series of tertiary β -methylated chlorides and bromides studied by Wong and Maccoll¹² and Harden¹³⁻¹⁴ respectively is of interest. Here the three β -hydrogen atoms of t-butyl chloride

(bromide) had been progressively replaced. The Arrhenius parameters and relative rates for the series are shown in Table 4.

It was thought better in calculating rate ratios to use the single set of results obtained by one worker than the average values

(shown in parentheses) for t-butyl and t-amyl chlorides. An

interesting conclusion to be made from these relative rate ratios is that β -methyl substitution is a second-order effect on the

carbon-halogen bond rather than a first-order effect on the carbon-hydrogen bond. This follows from the fact that, through the series

shown in Table 4, the carbon-hydrogen bond changes from primary to secondary to tertiary and then back to primary, while the rate constant increases uniformly down the series.

(C) Isotope effects

The magnitude of the deuterium isotope effect in the pyrolysis of ethyl-d₄ chloride¹⁵ and bromide¹⁶ was reported by

Blades and his co-workers as being 2.20 and 2.17 respectively.

The isotope effect was weakly temperature dependent. These

authors stated that their data might serve as direct support for

Table 2

Comparative Arrhenius Parameters and Relative Rates for the Primary β -methylated series¹

Halide	Ethyl	n-Propyl	iso-Butyl
Chloride			
E_a , kcal/mole	57.8	55.1	56.1
$\log A$, sec ⁻¹	13.75	13.47	13.94
Relative rate (440°C)	1	3.6	4.7
Bromide			
E_a , kcal/mole	53.0	51.1	50.4
$\log A$, sec ⁻¹	13.11	13.03	13.05
Relative rate (400°C)	1	3.4	7.3

Table 3

Comparative Arrhenius Parameters and Relative Rates for
the Secondary β -methylated (γ -methylated) series

Halide	iso-Propyl	sec-butyl	2-Pentyl	3-Pentyl
Chloride				
E_a , kcal/mole	50.3 ⁷	50.6 ⁸	50.7 ⁷	51.0 ⁷
$\log A$, sec ⁻¹	13.4 ⁷	14.00 ⁸	14.1 ⁷	14.4 ⁷
Relative rate (351°C)	1 ⁷	3.2 ⁸	13.6 ⁷	5.6 ⁷
Bromide				
E_a , kcal/mole	47.8 ⁹	43.8 ¹⁰	--	45.4 ¹¹
$\log A$, sec ⁻¹	13.2 ⁹	12.6 ¹⁰	--	13.5 ¹¹
Relative rate (650°C)	1 ⁹	2.3 ¹⁰	--	5.0 ¹¹

Table 4

Comparative Arrhenius Parameters and Relative Rate Constant
Ratio for the Tertiary β -methylated series

Halide	E_a (kcal/mole)	$\log A$ (sec^{-1})	Rel. rates
$\text{CH}_3\text{C}(\text{CH}_3)_2\text{Cl}^{12}$	45.0(45.0)	13.77(13.73)	1
$\text{CH}_3\text{CH}_2\text{C}(\text{CH}_3)_2\text{Cl}^{12}$	44.2(45.1)	13.82(14.24)	2.3
$(\text{CH}_3)_2\text{CHC}(\text{CH}_3)_2\text{Cl}^{12}$	42.3	13.38	4.7
$(\text{CH}_3)_3\text{CC}(\text{CH}_3)_2\text{Cl}^{12}$	41.9	13.80	18.0
$\text{CH}_3\text{C}(\text{CH}_3)_2\text{Br}^{14}$	42.2	14.00	1
$\text{CH}_3\text{CH}_2\text{C}(\text{CH}_3)_2\text{Br}^{13}$	40.5	13.60	3.2
$(\text{CH}_3)_2\text{CHC}(\text{CH}_3)_2\text{Br}^{14}$	39.0	13.54	7.5

the four-center mechanism often given for these reactions in which the carbon-hydrogen and carbon-halogen bonds are broken simultaneously with bond formation between hydrogen and halogen. Curtin and Kellom¹⁷ reported an isotope effect of 2.7 and 1.4 respectively for the pyrolysis of erythro- and threo-2-deutero-1,2-diphenyl-ethyl bromide and chloride at 400°C. Good¹⁸ found the rate ratio of pyrolysis of isopropyl-d₆ bromide to isopropyl bromide was 1:2.5 and was not temperature dependent. Subject to error due to the presence of a competing radical chain mechanism, these data seems to support Blades and his co-workers' point of view, i.e., a four-center transition state mechanism for the pyrolysis of alkyl halides.

(D) Stereochemistry

Cis-elimination is expected for the unimolecular homogeneous gas phase elimination of alkyl halides. This involves a quasi-four-membered ring transition state. This was clearly brought out by Barton and his co-workers¹⁹⁻²⁰. Curtin and Kellom¹⁷ experimentally examined the stereochemistry in this reaction by studying the thermal elimination of erythro- and threo-2-deutero-1,2-diphenylethyl bromide and chloride at 400°C. They showed that cis-elimination from the bromide predominated by a factor of about 2. The isotope effect was thus 1.4. The erythro- and threo-chlorides each gave the same mixture (73% deuterated trans-stibene and 27% undeuterated). This suggested that each isomer reacted by a mechanism in which only isotopic discrimination (a factor of 2.7) was operative. Their results are not clear-cut due to the possible occurrence of isomerization of the starting material

and/or products during reactions at the temperature employed.

Also the possibility of decomposition by a nonspecific free radical process cannot be ruled out. Recently, Yuan²¹ found that the relative rates of pyrolysis of 2,2,5,5-d₄-cyclopentyl chloride to cyclopentyl chloride was 1:2 and was not temperature dependent. More significantly, elimination of HCl and DCl with a relative ratio of 2:1 was found in the pyrolysis of cis-2-d₁-cyclopentyl chloride. Elimination of HCl only was found in the case of trans-2-d₁-cyclopentyl chloride. These data clearly demonstrated that a four-center, cis-elimination mechanism is operative in the gas phase pyrolysis of cyclopentyl chloride. Similar observations were obtained by McGillivray²² in his study of the pyrolysis of exo-norbornyl chloride.

(E) Rearrangements

A Wagner-Meerwein rearrangement, leading to hydrogen chloride and methylbutenes was first reported by Maccoll and Swinbourne²³⁻²⁴ in the pyrolysis of neopentyl chloride (450°C). They proposed for this homogeneous gas phase reaction an ion-pair mechanism. Anderson and Benson²⁵ however, favored a radical chain mechanism for this reaction. Recently Shapiro and Swinbourne²⁶⁻²⁷ suggested that a mixed unimolecular and radical chain mechanism would best explain the results with the former amounting to about 40% of the reaction. The pyrolysis of this compound is thus complex and rather poorly understood.

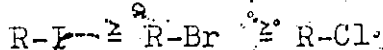
Bornyl and isobornyl chlorides were reported to yield camphene, tricyclene and bornylene²⁸⁻³¹. Herndon³² questioned the significance of the Wagner-Meerwein rearrangement for these

pyrolyses, due to the fact that bornylene undergoes a retro-Diels-Alder reaction. The pyrolysis of *exo*-norbornyl chloride has been studied recently by McGillivray²². It was found that no Wagner-Meerwein rearrangement occurred.

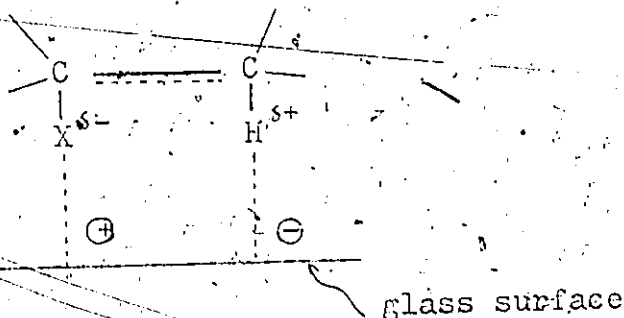
Robinson²³ has recently reported the pyrolysis and rearrangement of alkyl substituted 1,1-dichloro-cyclopropanes. He presented these data in support of the quasi-ionic isomerization of a cyclopropyl cation to an allylic cation.

(F) Surface effects in gas phase reactions

The usual test for the homogeneity of a gas phase reaction is to increase the surface:volume ratio of the reaction vessel. The rate will normally be increased when all or part of the reaction occurs on the surface. There are two most commonly used reaction vessel surfaces in gas phase kinetics studies. These are "clean" pyrex glass (or silica) and carbon coated glass (or silica). Carbon coatings can be produced by the pyrolysis of olefins and halogen-containing compounds. It can also be produced by prolonged "seasoning" of the substance whose pyrolysis is being investigated. Silica displays polar characteristics. This is clearly shown in the pyrolysis of polar compounds, particularly alkyl halides in which halogen acid is eliminated^{25, 24}. The pyrolytic sensitivity towards "clean" glass surfaces is expected in terms of heterolytic bond dissociation energies $D(R^+X^-)$ of the carbon-halogen bond, i.e.,



Shapiro and Swinbourne³⁶ examined the kinetics of the pyrolysis of alkyl chlorides catalyzed by a pyrex surface. They believed that the polar glass surface assisted charge separation in reactant molecules. The physical picture was that of a simple attachment of the electronegative chlorine atom to an electro-positive surface site, i.e.,



The heterogeneity in alkyl halide pyrolysis increases from primary to tertiary compounds³⁶. The "seasoned" reaction vessel surface was believed to eliminate the wall effect and give reproducible and homogeneous rates. The thin carbonaceous film produced in reaction vessel "seasoning" acted as a non-polar skin on the polar glass surface of the reaction vessel and was believed to be catalytically inert. As a generalization, at high temperature (above 500°C) all organic compounds will deposit pyrolytic carbon on glass surfaces.

Holbrook³⁷ reported the observation of a strong electron spin resonance signal from allyl bromide carbon. He suggested those supposedly inert surfaces, catalyzed some gas phase reactions. Holbrook and Rooney³⁸ found that both the rate of pyrolysis of sec-butyl chloride and the distribution of n-butene isomers in the products were dependent on the origin and the treatment of the

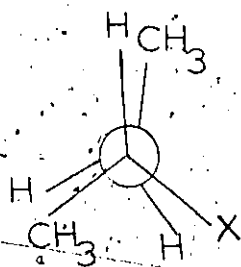
carbon surface. They showed carbon derived from the ethyl chloride pyrolysis was less active towards the sec-butyl chloride pyrolysis than those derived from the pyrolysis of cis-but-2-ene and allyl bromide. Holmes and Ruo³⁹ studied the odd electron concentration and chemical activity of pyrolytic carbons produced from various compounds towards the isomerization of cis-but-2-ene to its other isomers. They showed that although the odd-electron content was approximately the same in all the carbons, their chemical activity was different, in so far as isomerization of cis-but-2-ene is concerned. Thus, they concluded that carbon produced from cis-but-2-ene pyrolysis was less active towards isomerization than the carbon produced from allyl bromide pyrolysis.

Most of the simple alkyl halides decompose by a molecular elimination process. Some, however, are accompanied by a free radical chain process. The homogeneity of the process is checked by investigating the effect of changing the surface:volume ratio of the reaction vessel. If the reaction is completely homogeneous, varying the surface:volume ratio has no effect on the rate of pyrolysis.

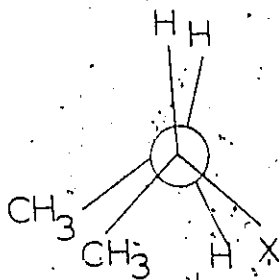
(G) Direction of elimination

So far the overall rate studies have shown that in alkyl halides, the transition state involves an appreciable charge separation between the carbon and halogen bond. Apart from the charge distribution in the transition states, little is known about the geometry of elimination, except in the case of the pyrolysis of cyclopentyl chloride²¹ and exo-norbornyl chloride²². These two pyrolyses involved cis-elimination of hydrogen chloride

and a four-center transition state. Such information could be obtained from a study of isomeric products whose geometry may reflect that of the transition state. Maccoll suggested that¹ if co-planarity was a requirement of the transition state in the elimination reaction, then the trans products for the pyrolysis of sec-butyl halides should predominate over the cis products, as can be seen from the projections I and II.



(I)



(II)

I, which leads to the trans olefin is less sterically hindered than II which leads to the cis compound. The trans-form is also favored by thermodynamic stability. The simplest monohalo compounds for which more than one olefin may be produced in the elimination of halogen acid are sec-butyl halides. These compounds pyrolyse by simple elimination of halogen acid^{8,40-41;44;10,42-44;45}, and the three isomers of n-butene are produced. Maccoll and Stone⁴⁰ and Heydtmann and Rinck^{8, 41} have studied the pyrolysis of sec-butyl chloride. Their studies do not throw any satisfactory light on the geometry of the elimination reaction because there were certain experimental problems in determining the three ratios of the n-butene isomers. Halogen acid produced in the reaction acts as a good catalyst in the isomerization of the n-butenes. Thus

one cannot hope to get true ratios of the isomers from the reaction if an appreciable concentration of the halogen acid is allowed to accumulate in the reaction system. In the case of Maccoll and Stone's studies, they decomposed the halide to nearly its half life and the acid was not removed from the reaction vessel. Heydtmann and Rinck decomposed the halide to nearly 100% conversion and obviously there could be a great deal of isomerization of n-butenes.

The surface of the reaction vessel, as described before, also plays a role in the pyrolysis. The polar surface acts as good catalysts for isomerization of n-butenes. Heydtmann and Rinck^{8, 41} used potassium chloride, which is quite polar. Maccoll and Stone⁴⁰ used the carbon coating produced from allyl bromide and reduced this effect in their studies to a good extent. However, Holmes and Ruoff³⁹ showed that a heterogeneous isomerization was catalyzed by the pyrolytic carbons obtained from allyl bromide. They studied^{46, 54} all the three butene isomers on this surface and calculated the equilibrium constants which were in good agreement with other workers⁴⁷⁻⁵². From the study of different carbonaceous coatings produced from allyl bromide, cis-but-2-ene, ethyl bromide and 3-chloro-2-methylpropene, they showed that cis-but-2-ene carbon coating was the least active towards the isomerization of the n-butenes. Thus, Capozzi⁴⁴ recently studied the pyrolysis of sec-butyl chloride and bromide using the carbon coating produced from cis-but-2-ene. He pyrolyzed the sec-butyl halides to a maximum of 15% so that the amount of halogen acid produced in the reaction was insufficient to cause any isomerization of the

n-butenes produced. It was found that the activation energy for the production of cis-but-2-ene was significantly lower than those for the production of but-1-ene and trans-but-2-ene. Possible reasons for this effect were considered⁴⁴.

The direction of elimination leading to the olefin with the greater number of alkyl substituents on the double bond is known as Saytzeff-oriented elimination. For more highly substituted alkyl halides, pyrolysis of alkyl halides tends to yield predominantly the Saytzeff product¹²⁻¹⁴.

OBJECT OF PRESENT STUDY

It has been described previously that apart from the charge distribution in the transition states, little is known about the geometry of elimination for the pyrolysis of alkyl halides. Such information could be obtained from a study of isomeric products whose geometry may reflect that of the transition state. Sec-butyl halides, pyrolyzing by simple elimination of halogen acid to produce three isomers of n-butene, have been studied intensively by several groups of workers^{8,40-41,44;10,42-44;45}. However, their studies do not throw any satisfactory light on the geometry of the elimination reaction because there were certain experimental problems in determining the true ratios of the n-butene isomers, originating from a purely homogeneous unimolecular elimination. This has been discussed in detail in the previous section. In the present work, two straight chain sec-pentyl chlorides, 3-chloropentane and 2-chloropentane were chosen to study the geometry of the transition state in gas phase pyrolysis. 3-chloropentane pyrolyses by simple elimination of hydrochloric acid.

Trans- and cis-isomers of pent-2-ene are produced. 2-chloropentane however, pyrolyses to produce the three isomers of n-pentenes, that is, pent-1-ene, trans- and cis-pent-2-ene. The following steps were taken to overcome the experimental difficulties mentioned in the previous sections: (A) Various amounts of decompositions of the alkyl chlorides were performed from 0 to 60%. These will serve two purposes. Firstly, at low percentage of decomposition, from 0 to 10%, the amount of hydrochloric acid produced in the reaction is insufficient to cause any isomerization of n-pentenes produced. Thus the true ratio of the n-pentene isomers can be determined. Secondly, at high percentage of decomposition, from 10 to 60%, the degree of catalyzed isomerization of the n-pentenes, if any, can be determined. (B) Cis-but-2-ene carbon coating was used for the pyrolysis. It is the least active coating in isomerizing the n-butenes. It was assumed that this will also be true in n-pentenes.

The temperature range employed in pyrolysis of 3-chloropentane was from 293 to 350°C and that of 2-chloropentane from 317 to 376°C.

CHAPTER 2

APPARATUS AND EXPERIMENTAL TECHNIQUE(A) The vacuum system

It was a conventional static vacuum system made of Pyrex glass. A single manifold connecting all parts of the apparatus is shown in a schematic diagram in Figure 1. In the evacuation unit, a trap T_1 , a mercury diffusion pump D, a by-pass, another trap T_2 , and a rotary oil pump were connected in series. Four 1-litre bulbs to store the n-pentenes, hydrochloric acid gas and a small storage vessel for liquids which was used for trap to trap distillation, were connected to the main vacuum line. To check the vacuum in the system, a McLeod gauge G and a manometer M for handling the gases in the system were also connected to the main line.

Another vacuum line connected by two taps to the main line, consisted of two liquid sample tubes, and a gas burette leading to the reaction vessel (R.V.). Between the reaction vessel and the tap there was put a side arm with a small bulb B at the end to condense the sample before decomposition of the alkyl halide.

Dow-Corning silicone high vacuum grease was used in all the taps and the traps in the system. The entire system was evacuated down to 10^{-5} mm of mercury using the mercury diffusion pump and the rotary oil pump. The outlets L_1 and L_2 were used to introduce the gas sample in the storage bulbs or in the system.

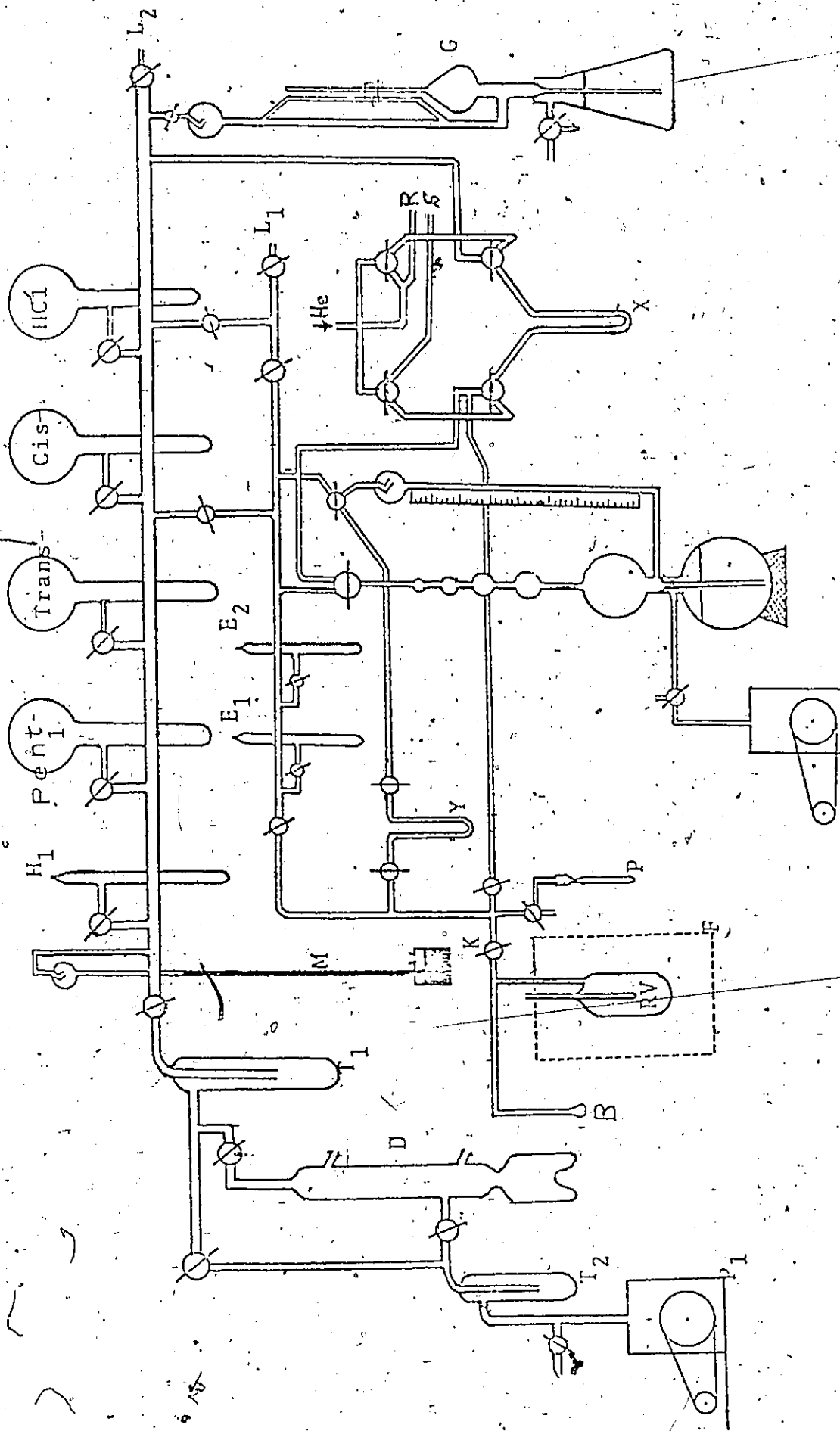


Fig. 1. A schematic diagram of a conventional static vacuum system.

(B) The reaction vessel and the thermostat

The reaction vessel was made of Pyrex glass tubing with a volume of 150 ml. giving a surface:volume ratio 1:1 approximately. The reaction vessel had one capillary tube joined to the vacuum line and a thermocouple well in its center. The reaction vessel was fitted evenly in a thermostat which was placed in a transite sheet box of dimensions 30x30x40 cm. The thermostat consisted of two concentric electrically heated tubes each of 30 cm. in length. The ceramic outer tube had a diameter of 10 cm. and was 1 cm. thick, while the thickness and diameter of the steel inner pipe was 1 cm. and 8 cm. respectively. The inner portion of the steel pipe was lagged with thick, uniformly moulded asbestos to fit the reaction vessel and make the latter free of any strain. The exterior of the ceramic cylinder was wound with nichrome heating ribbon in three separate coils connected to powerstats and the voltage was so adjusted in the three to get a temperature gradient of less than 0.2°C along the reaction vessel. The temperature was controlled by a thermoelectronic temperature regulator connected in series with the central heating coil. A chromel-alumel thermocouple was employed in the regulator, the one junction of which was placed near the bottom of the reaction vessel. A mercury plunger relay was also placed in series with the central heating coil.

Another chromel-alumel thermocouple was used to record the temperature in the reaction vessel and other end was kept at 0°C in ice-water mixture to serve as a standard reference. A portable Doran thermocouple potentiometer was put in series to measure the temperature.

The side arm of the reaction vessel was heated by a separate heating coil attached to a heated cup to warm the bulb B when needed.

(C) The chromatographic apparatus

A schematic diagram of the chromatographic unit, used to resolve the three n-pentene isomers produced in the pyrolysis is shown as Fig. 2. The sample to be analyzed was collected in the U tube X at -193°C . After warming the sample to room temperature it was passed through the chromatograph column at 0°C using helium as the carrier gas at a rate of 80 ml. per minute in both the sample and the reference column. The columns were made from 10 meter copper tubing of 0.5 cm. diameter and were packed with 25% (w/w) 2,4-dimethylsulfolane on Chromosorb P non-acid-washed, 60-80 mesh. The column when used at 0°C resolved the three isomers satisfactorily as shown in Fig. 3.

A 'GowMac' thermal conductivity cell in a standard Wheatstone bridge circuit was used as a detector and a Sargent recorder model SRG was employed to record the signals from the detector.

(D) Calibration of the n-pentenes

After evacuating the system to about 10^{-5} mm of Hg, pent-1-ene was admitted through the tap H_1 and was condensed in one storage bulb with liquid nitrogen. The pent-1-ene was degassed three or four times till it showed no impurity on chromatographic analysis. Similarly trans-pent-2-ene and cis-pent-2-ene were introduced in their respectively storage bulbs.

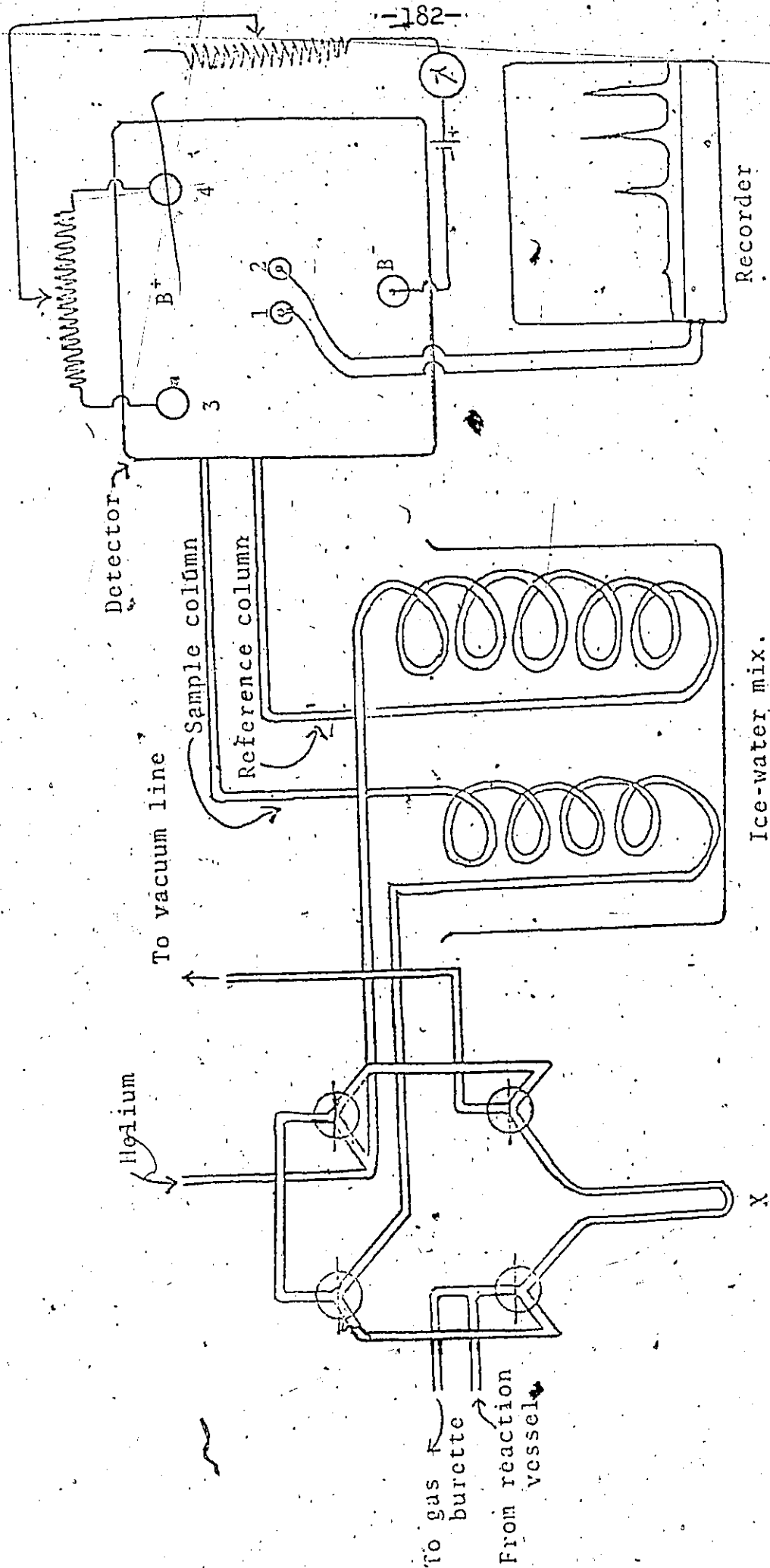


Fig. 2. A schematic diagram of the gas chromatographic unit.

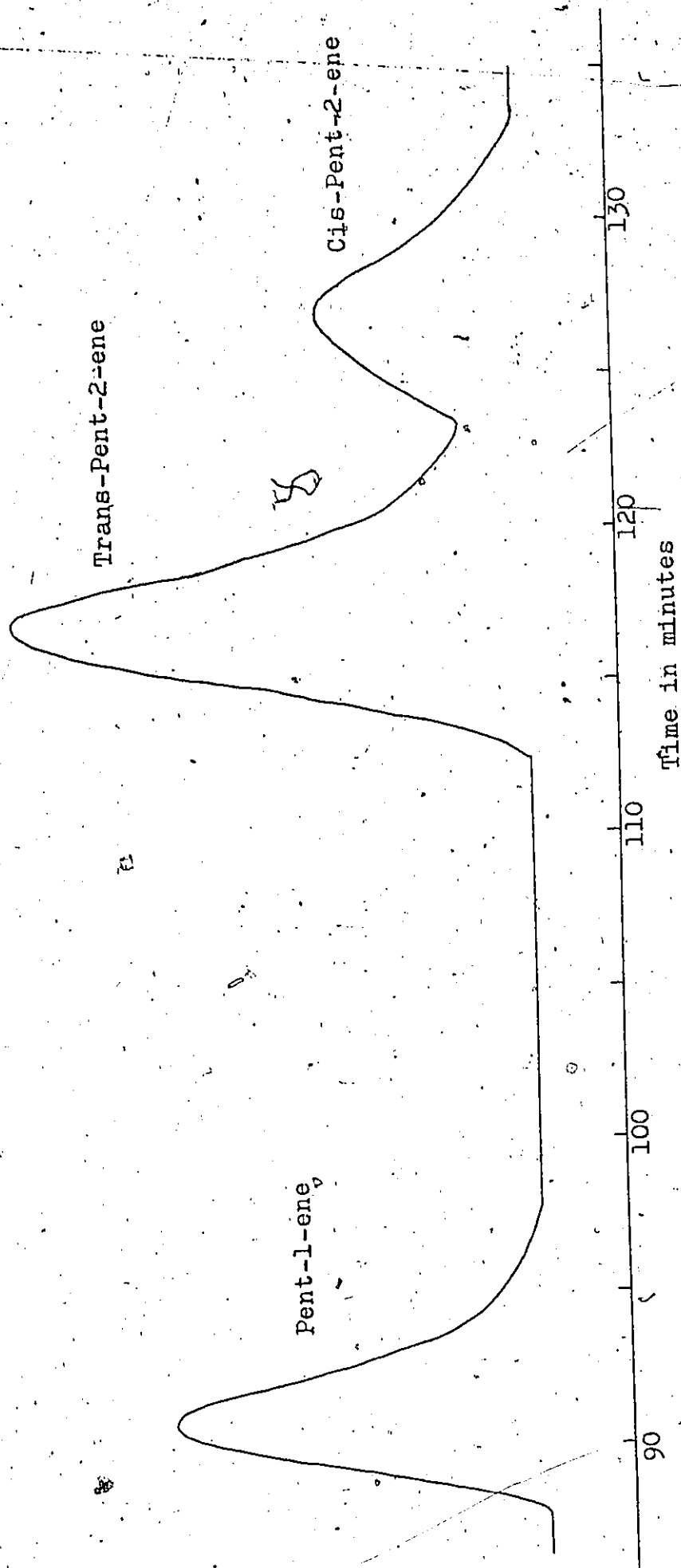


Fig. 3. A gas chromatogram of the three n-pentene isomers.

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A known amount of pent-1-ene in μ moles (calculated from the formula:

$$n = PV/RT$$

where n = number of moles

P = pressure

V = volume

R = gas constant

T = absolute temperature)

was condensed in the U tube X and the trapped sample was passed through the column at 0°C. After a retention time of 50 minutes a peak was recorded on the chart paper. Taking different amounts of pent-1-ene, different peak heights were recorded and a graph was plotted with μ moles against peak height. In the same manner, graphs were plotted with trans-pent-2-ene and cis-pent-2-ene, as shown in Fig. 4.

(E) Treatment of the reaction vessel

About 50 cm. of Hg pressure of pure cis-but-2-ene were decomposed at 480°C for 15 hours in the reaction vessel. A light carbonaceous film was deposited on the surface of the vessel.

(F) Procedure of a typical run

The vapor of well degassed 2-chloropentane from tube E₂ were admitted in the gas burette at a known volume level. Pressure and temperature were recorded and the number of moles were calculated for that volume of vapor. This measured amount of 2-chloropentane was condensed in the bulb B of the reaction vessel with liquid nitrogen and the tap K was closed. The condensed chloride was

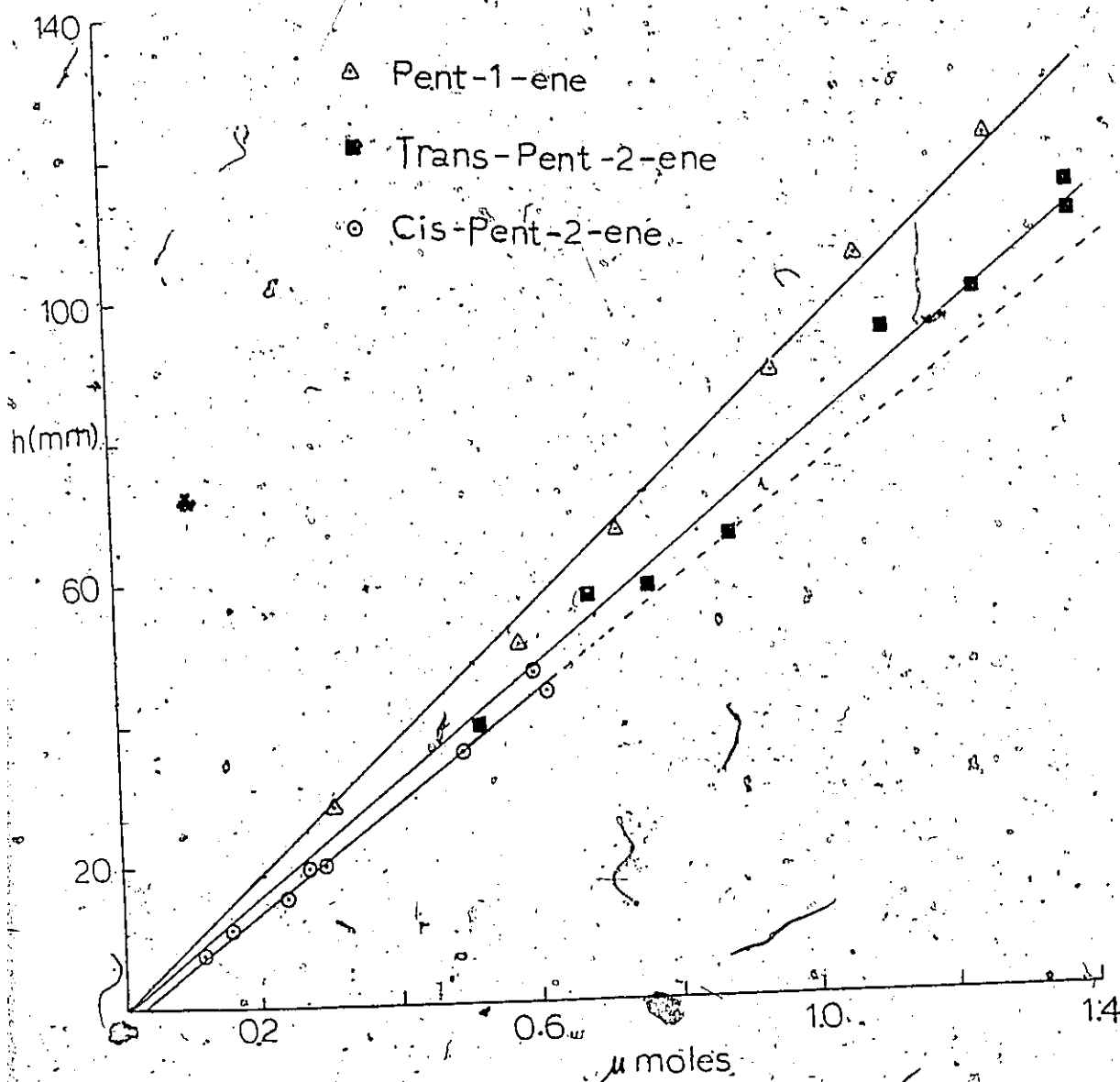


Fig. 4. Calibration curves (peak height vs μ moles) for the three n-pentene isomers.

rapidly vaporized into the reaction vessel by putting a hot glass cup around the bulb B. The dead space volume was approximately 1 ml.

After decomposing the 2-chloropentane for a certain time the products and the undecomposed reactant were condensed in the U tube X in liquid nitrogen. The trapped sample was passed through the column at 0°C. Only the three n-pentenenes' signals showed on the recorder whereas the 2-chloropentane and the hydrochloric acid stayed in the column (due to their long retention times). After ten runs, the columns were cleaned by passing helium and keeping the columns in water bath at 50°C for about eight hours. From the height of each n-pentene peak, the corresponding amount of the individual olefin was found from the calibration curves (Fig. 4) and their rates of production were calculated.

(G) Purification and storage of materials

(1) Chloropentanes

2-chloropentane and 3-chloropentane were obtained from K & K Laboratories, Inc., and Columbia Organic Chemical, Co., Inc., respectively. They were of analytical grade which were first distilled using an 18 inch fractionating column and then trap to trap distillations were carried out under vacuum. In the first distillation, the fraction of 2-chloropentane was collected at 95°C/755 mm of Hg, $^{24}n_D$ 1.4070 (reported 97°C/770 mm of Hg, $^{24}n_D$ 1.4079).

The fraction of 3-chloropentane was collected at 98°C/754 mm of Hg, $^{24}n_D$ 1.4074 (reported 98°C/760 mm Hg, $^{20}n_D$ 1.4082).

After these distillations, each chloropentane was subjected to gas phase chromatographic analysis. Only one peak was found in each case. Therefore, these two chlorides were taken as satisfactorily pure for the pyrolytic work.

(2) n-Pentenenes

Pent-1-ene and pent-2-ene (mixed cis- and trans-isomers) were obtained from Baker Chemical Co., Pent-1-ene (b.p. 30-33°C) and pent-2-ene (b.p. 35-37°C) were of "Baker grade" of high purity. Cis-pent-2-ene (b.p. 37°C, $^{20}n_D$ 1.3819) of high purity was supplied by Aldrich Chemical Co., Inc., Each isomer (or mixed cis- and trans-isomers) was well degassed before use, by condensing in liquid nitrogen and evacuating any condensed impurities such as air. The process was repeated at least three times. On gas chromatography, each isomer (except the mixed trans- and cis-pent-2-ene) was found to contain only one component. These three isomers were used for experimental and calibration purposes.

(3) Hydrochloric acid

Hydrochloric acid was obtained from the Matheson Co. It was degassed in the same manner before use.

CHAPTER 3

EXPERIMENTAL DATA

List of Abbreviations

- k_1 = Rate of production of pent-1-ene
 k_t = Rate of production of trans-pent-2-ene
 k_c = Rate of production of cis-pent-2-ene
 K = Rate of production of total pentenes

All the pentenes produced in the reaction, are reported in micromoles (μ moles).

Table 5

Pyrolysis of 3-Chloropentane at 350°C

<u>μmoles</u>	<u>Time</u>	<u>Trans-Pent-2-ene</u>	<u>Cis-Pent-2-ene</u>	<u>Total</u>
7.54	300 sec.	0.450	0.200	0.650
7.42	300	0.500	0.212	0.712
3.54	600	0.415	0.195	0.610
7.65	720	1.040	0.460	1.500
4.45	1200	0.985	0.420	1.405
2.28	1500	0.650	0.305	0.955

$$k_t = .213 \times 10^{-6} \text{ sec}^{-1}$$

$$k_c = 90.8 \times 10^{-6} \text{ sec}^{-1}$$

$$K = 321 \times 10^{-6} \text{ sec}^{-1}$$

Table 6

Pyrolysis of 3-Chloropentane at 340°C

4.10 μ moles at 340°C

<u>Time</u>	<u>Trans-Pent-2-ene</u>	<u>Cis-Pent-2-ene</u>	<u>Total</u>
5 min.	0.168	0.086	0.254
10	0.310	0.146	0.456
20	0.460	0.213	0.673
30	0.758	0.379	1.137
40	1.010	0.499	1.509
50	1.070	0.527	1.597
60	1.400	0.675	2.075

$$k_t = 117 \times 10^{-6} \text{sec}^{-1}$$

$$k_c = 50 \times 10^{-6} \text{sec}^{-1}$$

$$K = 186 \times 10^{-6} \text{sec}^{-1}$$

8.00 μ moles at 340°C

<u>Time</u>	<u>Trans-Pent-2-ene</u>	<u>Cis-Pent-2-ene</u>	<u>Total</u>
5 min.	0.391	0.203	0.594
10	0.585	0.282	0.867
20	1.190	0.582	1.772
30	1.690	0.855	2.545

$$k_t = 137 \times 10^{-6} \text{sec}^{-1}$$

$$k_c = 60.5 \times 10^{-6} \text{sec}^{-1}$$

$$K = 211 \times 10^{-6} \text{sec}^{-1}$$

Table 7

Pyrolysis of 3-Chloropentane at 332°C

<u>moles</u>	<u>Time</u>	<u>Trans-Pent-2-ene</u>	<u>Cis-Pent-2-ene</u>	<u>Total</u>
8.10	780. sec.	0.350	0.165	0.515
11.79	780	0.550	0.260	0.810
9.30	1500.	0.840	0.395	1.235
5.35	2000	0.570	0.280	0.850
3.60	3600	0.615	0.297	0.912
3.29	5100	0.830	0.383	1.213

$$k_t = 57.7 \times 10^{-6} \text{sec}^{-1}$$

$$k_c = 26.2 \times 10^{-6} \text{sec}^{-1}$$

$$K = 88.0 \times 10^{-6} \text{sec}^{-1}$$

Table 8

Pyrolysis of 3-Chloropentane at 321°C

R

<u>μ moles</u>	<u>Time</u>	<u>TransPent-2-ene</u>	<u>CisPent-2-ene</u>	<u>Total</u>
13.1	1000 sec.	0.345	0.155	0.500
11.0	1560	0.450	0.211	0.661
4.11	2400	0.250	0.110	0.360
6.15	3000	0.475	0.225	0.700
3.56	3300	0.305	0.138	0.443
7.97	3720	0.715	0.372	1.147
3.52	6780	0.555	0.270	0.825

$$k_t = 26.3 \times 10^{-6} \text{ sec.}^{-1}$$

$$k_c = 12.3 \times 10^{-6} \text{ sec.}^{-1}$$

$$K = 40.0 \times 10^{-6} \text{ sec.}^{-1}$$

Table 9

Pyrolysis of 3-Chloropentane at 312°C8.00 μ moles at 312°C

<u>Time</u>	<u>TransPent-2-ene</u>	<u>CisPent-2-ene</u>	<u>Total</u>
30 min.	0.372	0.190	0.562
60	0.573	0.282	0.855
90	0.832	0.421	1.252
120	0.969	0.467	1.438
150	1.285	0.655	1.940

$$k_t = 18.1 \times 10^{-6} \text{ sec.}^{-1}$$

$$k_c = 7.94 \times 10^{-6} \text{ sec.}^{-1}$$

$$K = 28.5 \times 10^{-6} \text{ sec.}^{-1}$$

12.0 μ moles at 312°C

<u>Time</u>	<u>TransPent-2-ene</u>	<u>CisPent-2-ene</u>	<u>Total</u>
30 min.	0.316	0.150	0.466
60	0.705	0.339	1.040
90	0.954	0.467	1.421
120	1.100	0.550	1.650

$$k_t = 15.0 \times 10^{-6} \text{ sec.}^{-1}$$

$$k_c = 7.37 \times 10^{-6} \text{ sec.}^{-1}$$

$$K = 22.2 \times 10^{-6} \text{ sec.}^{-1}$$

Table 10

Pyrolysis of 3-Chloropentane at 302°C7.00 μ moles at 302°C

<u>Time</u>	<u>TransPent-2-ene</u>	<u>CisPent-2-ene</u>	<u>Total</u>
90 min.	0.348	0.179	0.527
192	0.740	0.380	1.120
270	0.840	0.440	1.280

$$k_t = 8.50 \times 10^{-6} \text{ sec.}^{-1}$$

$$k_c = 4.50 \times 10^{-6} \text{ sec.}^{-1}$$

$$K = 13.7 \times 10^{-6} \text{ sec.}^{-1}$$

14.0 μ moles at 302°C

<u>Time</u>	<u>TransPent-2-ene</u>	<u>CisPent-2-ene</u>	<u>Total</u>
60 min.	0.424	0.222	0.646
120	0.727	0.363	1.090
180	1.080	0.570	1.640
252	1.460	0.745	2.105

$$k_t = 7.30 \times 10^{-6} \text{ sec.}^{-1}$$

$$k_c = 3.64 \times 10^{-6} \text{ sec.}^{-1}$$

$$K = 10.8 \times 10^{-6} \text{ sec.}^{-1}$$

Table 11

Pyrolysis of 3-Chloropentane at 293°C

14.00 μ moles At 293°C

<u>Time</u>	<u>TransPent-2-ene</u>	<u>CisPent-2-ene</u>	<u>Total</u>
126 min.	0.367	0.184	0.550
240	0.676	0.350	1.030
300	0.792	0.416	1.118
390	0.995	0.513	1.508

$$k_t = 3.34 \times 10^{-6} \text{ sec.}^{-1}$$

$$k_c = 1.67 \times 10^{-6} \text{ sec.}^{-1}$$

$$K = 5.00 \times 10^{-6} \text{ sec.}^{-1}$$

Table 12

Pyrolysis of 2-Chloropentane at 376°C

4.00 μ moles at 376°C

<u>Time</u>	<u>Pent-1-ene</u>	<u>Trans-Pent-2-ene</u>	<u>Cis-Pent-2-ene</u>	<u>Total</u>
600 sec.	0.300	0.540	0.230	1.070
600	0.330	0.670	0.260	1.260
900	0.410	0.700	0.340	1.450
1200	0.520	0.870	0.430	1.820

$$k_1 = 125 \times 10^{-6} \text{ sec}^{-1}$$

$$k_t = 238 \times 10^{-6} \text{ sec}^{-1}$$

$$k_c = 92.1 \times 10^{-6} \text{ sec}^{-1}$$

$$K = 475 \times 10^{-6} \text{ set}^{-1}$$

Table 13

Pyrolysis of 2-chloropentane at 352°C

55.0 μ moles at 352°C

<u>Time</u>	<u>Pent-1-ene</u>	<u>TransPent-2-ene</u>	<u>CisPent-2-ene</u>	<u>Total</u>
5 min.	0.260	0.480	0.230	0.970
10	0.440	0.960	0.480	1.880
20	0.930	1.770	0.900	3.600
30	1.370	2.530	1.300	5.200
40	1.660	3.050	1.580	6.290

$$k_1 = 21.7 \times 10^{-6} \text{sec.}^{-1}$$

$$k_t = 41.4 \times 10^{-6} \text{sec.}^{-1}$$

$$k_c = 22.9 \times 10^{-6} \text{sec.}^{-1}$$

$$K = 86.0 \times 10^{-6} \text{sec.}^{-1}$$

Table 14

Pyrolysis of 2-chloropentane at 350°C

12.0 μ moles at 350°C

<u>Time</u>	<u>Pent-1-ene</u>	<u>TransPent-2-ene</u>	<u>CisPent-2-ene</u>	<u>Total</u>
25 min.	0.420	0.830	0.410	1.660
40	0.620	1.130	0.510	2.260
60	0.740	1.380	0.690	2.810
75	0.900	1.600	0.810	3.310
90	1.140	2.040	1.080	4.260

$$k_1 = 19.1 \times 10^{-6} \text{ sec.}^{-1}$$

$$k_2 = 36.2 \times 10^{-6} \text{ sec.}^{-1}$$

$$k_c = 17.6 \times 10^{-6} \text{ sec.}^{-1}$$

$$K = 79.5 \times 10^{-6} \text{ sec.}^{-1}$$

Table 15

Pyrolysis of 2-Chloropentane at 326°C70.0 μ moles at 326°C

<u>Time</u>	<u>Pent-1-ene</u>	<u>Trans-Pent-2-ene</u>	<u>Cis-Pent-2-ene</u>	<u>Total</u>
15 min.	0.340	0.700	0.330	1.380
20	0.450	0.920	0.450	1.820
30	0.670	1.350	0.680	2.700
60	1.330	2.470	1.130	4.930

$$k_1 = 5.28 \times 10^{-6} \text{ sec}^{-1}$$

$$k_t = 10.3 \times 10^{-6} \text{ sec}^{-1}$$

$$k_c = 5.28 \times 10^{-6} \text{ sec}^{-1}$$

$$K = 21.0 \times 10^{-6} \text{ sec}^{-1}$$

Table 16

Pyrolysis of 2-Chloropentane at 317°C70.0 μ moles at 317°C

<u>Time</u>	<u>Pent-1-ene</u>	<u>Trans-Pent-2-ene</u>	<u>Cis-Pent-2-ene</u>	<u>Total</u>
15 min.	0.130	0.280	0.140	0.550
30	0.220	0.510	0.260	0.990
45	0.380	0.740	0.400	1.520
60	0.500	0.980	0.500	1.980
90	0.730	1.470	0.780	2.980
105	0.810	1.650	0.870	3.330

$$k_1 = 2.00 \times 10^{-6} \text{ sec}^{-1}$$

$$k_t = 4.00 \times 10^{-6} \text{ sec}^{-1}$$

$$k_c = 2.00 \times 10^{-6} \text{ sec}^{-1}$$

$$K = 7.94 \times 10^{-6} \text{ sec}^{-1}$$

<u>μ moles</u>	<u>Time</u>	<u>Pent-1-ene</u>	<u>Trans-Pent-2-ene</u>	<u>Cis-Pent-2-ene</u>	<u>Total</u>
324	15 min.	0.630	1.290	0.660	2.580
386	15	0.680	1.350	0.720	2.750

$$k_1 = 2.06 \times 10^{-6} \text{ sec}^{-1}$$

$$k_t = 4.19 \times 10^{-6} \text{ sec}^{-1}$$

$$k_c = 2.11 \times 10^{-6} \text{ sec}^{-1}$$

$$K = 8.36 \times 10^{-6} \text{ sec}^{-1}$$

CHAPTER 4

RESULTS3-Chloropentane

3-Chloropentane was decomposed at several temperatures from 293 to 350°C. At certain temperatures, different pressures of the chloride were decomposed to see if there was any concentration effect. It was found that the decomposition was of first order. The rate constants were independent of concentration, and percentage decomposition within experimental error.

The individual rates of the production of n-pentenes and the rates of total n-pentene production have been calculated and are shown in Tables 5-11. Their average rate constants are given in Table 17a.

Arrhenius plots for each n-pentene and the total n-pentene production were drawn and are shown in Fig. 5.

2-Chloropentane

2-Chloropentane was decomposed at five temperatures, from 317 to 376°C. At 317°C, different pressures of the chloride were decomposed to see if there was any concentration effect. It was found that the decomposition was of first order. The rate constants were independent of concentration within experimental errors. The following rates of decomposition were calculated from the data given in the Tables 12-16, and are given in Table 17b.

The Arrhenius plots for the individual n-pentene and the total n-pentene production are shown in Fig. 6.

Table 17(a)

Effect of Temperature on Average Rate Constants
for 3-Chloropentane Pyrolysis

	350°C	340	332	321	312	302	293
$10^6 k_t (\text{sec}^{-1})$	213	127	57.7	26.3	16.6	7.90	3.34
$10^6 k_c (\text{sec}^{-1})$	90.5	55.0	26.2	12.3	7.66	4.07	1.67
$10^6 K (\text{sec}^{-1})$	321	199	88.0	40.0	25.9	12.8	5.00

Table 17(b)

Effect of Temperature on Average Rate Constants
for 2-Chloropentane Pyrolysis

	376°C	352	350	326	317
$10^6 k_1 (\text{sec}^{-1})$	125	21.7	19.1	5.28	2.00
$10^6 k_t (\text{sec}^{-1})$	238	41.4	36.2	10.3	4.00
$10^6 k_c (\text{sec}^{-1})$	92.1	22.9	17.6	5.28	2.00
$10^6 K (\text{sec}^{-1})$	475	86.0	79.5	21.0	7.94

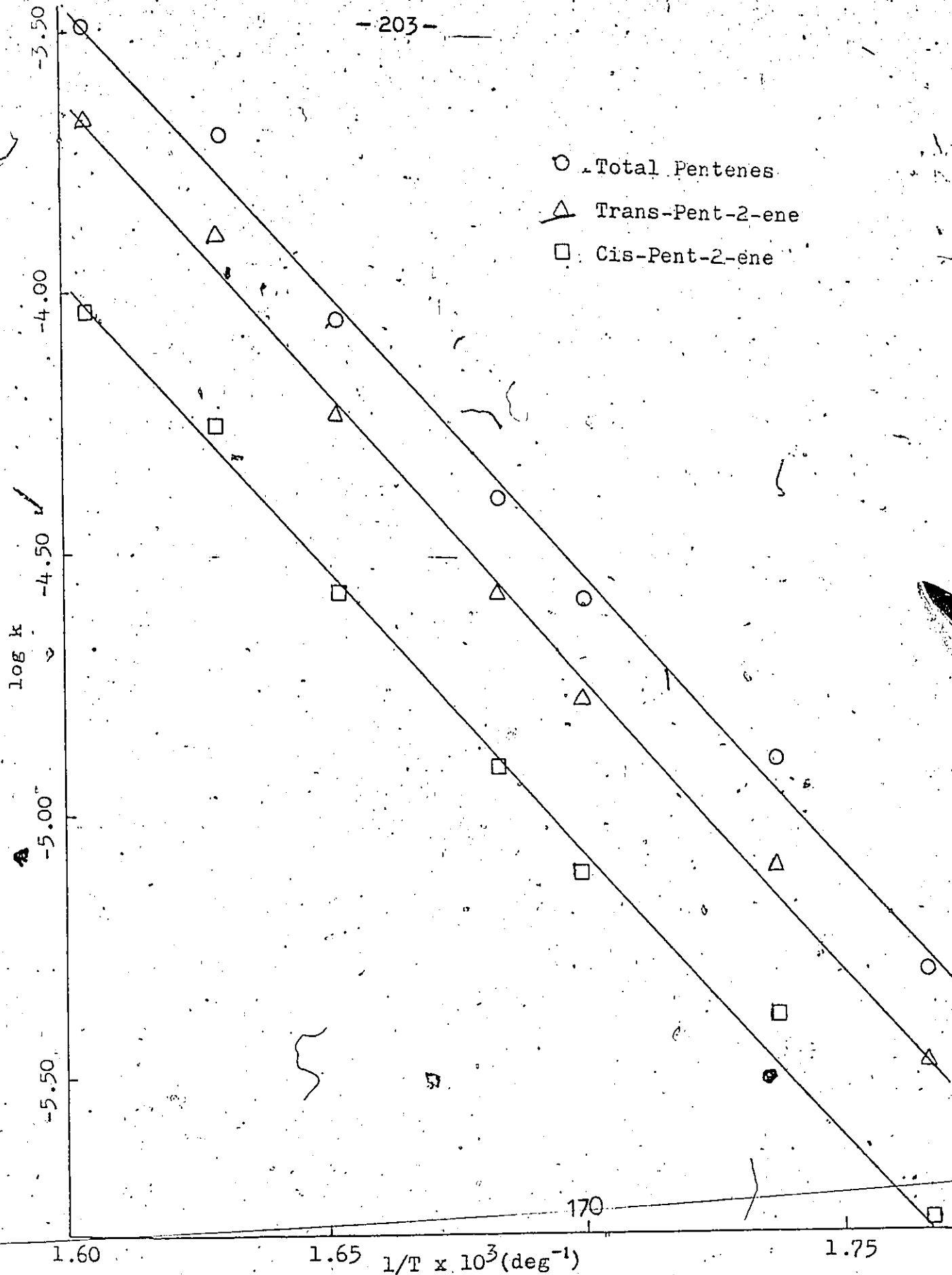


Fig. 5. The Arrhenius plots for the pyrolysis of 3-chloropentane for each n-pentene and the total n-pentene production.

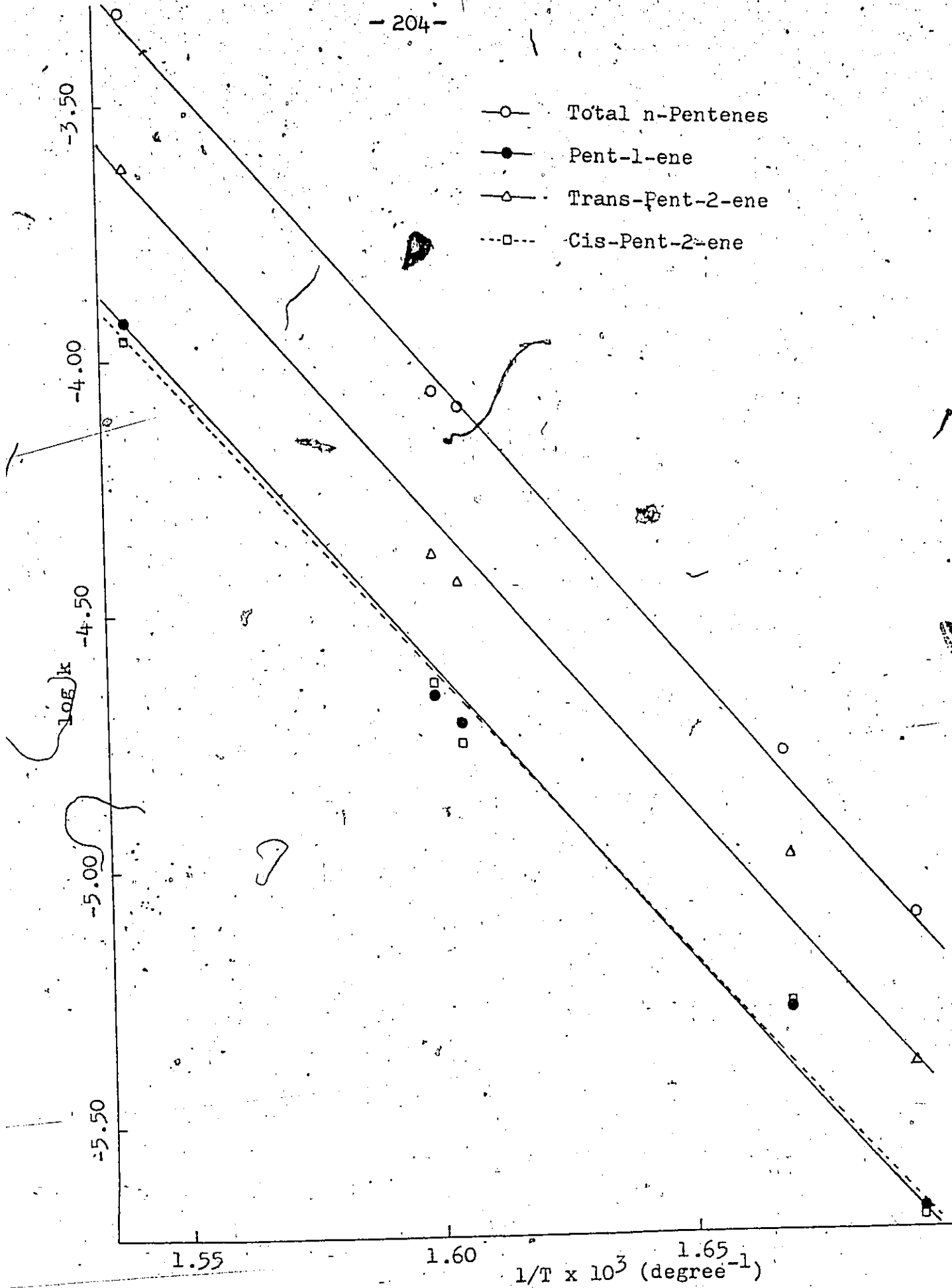


Fig. 6. The Arrhenius plots for the pyrolysis of 2-chloropentane for each n-pentene and the total n-pentene production.

CHAPTER 5

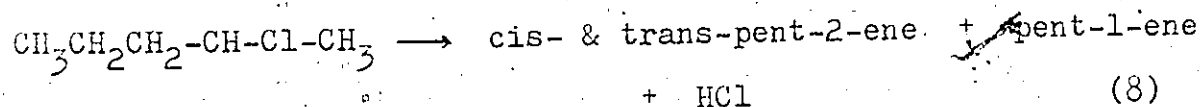
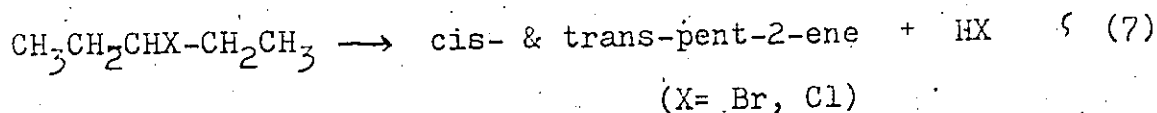
DISCUSSION

In the pyrolysis of 3-chloropentane and 2-chloropentane the stoichiometry of the reactions can be represented by equation 6:



This followed from two pieces of evidence. First, no permanent gas or hydrocarbons other than the n-pentenes were observed in the products⁷. Secondly, the ratios of the final to the initial pressures approached the theoretical value of two^{7, 11}. Also, the values of pressure determined manometrically and analytically (by titrating the hydrochloric acid produced) did not differ significantly⁷.

The results indicate that the stoichiometry of pyrolysis of 3-chloropentane and 3-bromopentane, and 2-chloropentane can be represented by equations 7 and 8 respectively:



Moreover, the rates of decomposition were independent of the initial pressures of the halides^{7, 11}. These were observed here. The first-order log plots were satisfactory to 65%, and 75% for 3-chloropentane and 2-chloropentane respectively⁷ and

several half-lives for 3-bromopentane¹¹. Thus it was concluded that the pyrolyses were first order reactions. The reactions showed no induction period^{7, 11}. The addition of cyclohexene as chain inhibitor resulted in no significant change in the reaction rate within experimental error^{7, 11}. Since no inhibition was observed, by accepted criteria, the reactions were unimolecular.

Capon, Maccoll and Ross¹¹ checked the homogeneity of the pyrolysis of 3-bromopentane. They carried out the pyrolysis in a reaction vessel packed with glass tubing to give a surface: volume ratio increased by a factor of 5. No increase was found in the mean rate constant of the unpacked reaction vessel. In view of the large increase in surface:volume ratio, it was concluded that the reaction was homogeneous and followed a first order law.

In the present work, the decomposition of 3-chloropentane and 2-chloropentane in a reaction vessel coated with cis-but-2-ene carbon was studied between 295-350°C and 317-376°C ranges respectively. The relative ratios of n-pentene production did not change very much within the temperature ranges as shown in Tables 18a and 18b, for 3-chloropentane and 2-chloropentane pyrolyses respectively. No previous work on individual n-pentene production measurement for the pyrolyses of 2-chloropentane and 3-chloropentane has been reported.

As discussed earlier, the pyrolysis of sec-butyl chloride and bromide using different coatings for the reaction vessel has been studied by Maccoll and Stone⁴⁰, Heydtmann and Rinck^{8, 41}, Holbrook and Rooney³⁸ and Capoor⁴⁴. The ratios of n-butenes from the pyrolysis at different temperatures by different workers and that of their equilibrium values by different methods are

Table 18(a)

Trans:cis-pent-2-ene-ratio for 3-chloropentane pyrolysis

	350°C	340	332	321	312	302	293
Trans-pent-2-ene	2.20	2.04	2.11	2.16	2.00	1.95	1.95
Cis-pent-2-ene	1.00	1.00	1.00	1.00	1.00	1.00	1.00

Table 18(b)

Trans:cis:pent-1-ene-ratio for
2-chloropentane pyrolysis

	376°C	352	350 ^b	326.	317
Trans-pent-2-ene	2.34	1.99	2.01	2.09	1.93
Cis-pent-2-ene	1.00	1.00	1.00	1.00	1.00
Pent-1-ene	1.25	1.02	1.08	1.05	0.94

summarized in Tables 19a and b respectively. The differences in n-butene isomers production among the four groups of workers for the pyrolysis of sec-butyl halides can be attributed to three reasons. These are discussed as below:

(A) Isomerization of olefinic products by carbon coatings

Maccoll and Stone⁴⁰ decomposed the halide using a reaction vessel coated with allyl bromide carbon. Heydtmann and Rinck^{8, 41} and Holbrook and Rooney³⁸ used a potassium chloride and ethyl chloride coated vessel respectively. Capoor⁴⁴ employed a carbon coating produced from cis-but-2-ene pyrolysis. Holbrook and Rooney, and Heydtmann and Rinck reported that isomerization of n-butenes by ethyl chloride and potassium chloride coating respectively was unimportant. The former also claimed that cis-but-2-ene and allyl bromide coatings promoted cis- and trans-but-2-ene isomerization.

It has recently been shown however, by Holmes and Ruoff³⁹ that the cis-but-2-ene coating was less active towards isomerization of cis-but-2-ene than the carbon coatings produced from allyl bromide and ethyl bromide. Their results suggested that the greater activity of allyl bromide and ethyl bromide carbons was due to their bromine content. ~~This was supported by observations that cis-but-2-ene carbon could be activated by exposure to the n-propyl bromide pyrolysis, in which bromine atoms were thought to be the chain carriers. Also, treatment with molecular bromine raised its activity close to that of allyl bromide carbon.~~ It was proposed that the electronegative halogen atom could lessen delocalization of the odd electrons giving rise to regions of

Table 19(a)

But-1-ene:trans-but-2-ene:cis-but-2-ene product
ratios for the pyrolysis of 2-chlorobutane

<u>Workers</u>	<u>Temp. (°C)</u>	<u>But-1-ene</u>	<u>Trans-But-2-ene</u>	<u>Cis-But-2-ene</u>	<u>Coating</u>
Heydtman & Rinck (8, 41)	299	2.14	1.95	1.00	KCl
	395	2.03	1.79	1.00	
Holbrook & Rooney (38)	348	1.95	1.80-1.90	1.00	Ethyl chloride
Maccoll & Stone (40)	330	1.91	1.72	1.00	Allyl bromide
	343	1.55	1.60	1.00	
	357	2.11	1.81	1.00	
	360	1.52	1.47	1.00	
	364	1.75	1.58	1.00	
	372	1.19	1.75	1.00	
	391	1.91	1.67	1.00	
Capoor (44)	302	1.32	1.34	1.00	cis-but- 2-ene
	318	1.43	1.43	1.00	
	335	1.55	1.54	1.00	
	350	1.76	1.74	1.00	

Table 19(b)

Average values of K_{lt}^* and K_{ct}^* for n-butenes
at different temperatures^a

Temperature, °C	K_{lt}	K_{ct}
300	2.49	1.60
325	2.25	1.56
350	2.06	1.52
375	1.89	1.49
400	1.75	1.46

* But-1-ene $\xrightleftharpoons{K_{lt}}$ Trans-But-2-ene

Cis-But-2-ene $\xrightleftharpoons{K_{ct}}$ Trans-But-2-ene

a. Average values calculated from references 46-54.

higher spin density. Thus Holmes and Ruo³⁹ suggested that if reaction vessel seasoning had to be undertaken, pyrolytic carbon from a hydrocarbon pyrolysis (e.g. cis-but-2-ene) was to be preferred over other types of coatings.

(B) The halogen acid catalyzed isomerization of olefins

The second reason could be the isomerization of n-butenes catalyzed by the halogen acid produced in the reaction.

The effect of hydrobromic acid catalysis on the isomerization of n-butenes has been studied extensively by Ross and Maccoll⁷¹, and Holmes and Ruo⁵⁴. Both workers showed that the rate of isomerization depended upon the concentration of butene and hydrobromic acid, i.e.,

$$\text{Rate} = k_2 (\text{Butene})x(\text{HBr})$$

Holmes and Ruo⁵⁴ studied the isomerization of cis-but-2-ene with hydrochloric acid. They found that the rate of isomerization was:

$$\begin{aligned} \text{Rate} &= k_2 (\text{cis-but-2-ene})x(\text{HX}) \quad (\text{X}=\text{Br}, \text{Cl}) \\ &= k_{ct} (\text{cis-but-2-ene}) \end{aligned}$$

Thus for equimolar initial concentrations of cis-but-2-ene and hydrochloric acid at 400°C, the rate constants k_{c-l} and k_{c-t} were 0.61×10^{-6} and $2.74 \times 10^{-6} \text{ sec}^{-1}$ respectively. k_{c-l} and k_{c-t} represent the rate constants for the isomerization of cis-but-2-ene to but-1-ene and trans-but-2-ene respectively. Similarly, at 400°C, $k_{t-l} = 1.46 \times 10^{-6} \text{ sec}^{-1}$ and $k_{t-c} = 1.48 \times 10^{-6} \text{ sec}^{-1}$, and $k_{l-t} = 2.84 \times 10^{-6} \text{ sec}^{-1}$ and $k_{l-c} = 2.06 \times 10^{-6} \text{ sec}^{-1}$ were obtained

for the hydrochloric acid isomerization of trans-but-2-ene and but-1-ene respectively, to their appropriate isomers. Thus, in the presence of hydrochloric acid, the rates of isomerization of but-1-ene to its trans- and cis-isomers were about the same (i.e. $k_{1-t} = 2.84 \times 10^{-6} \text{ sec}^{-1}$ and $k_{1-c} = 2.06 \times 10^{-6} \text{ sec}^{-1}$). Similarly, the cis-isomer had the tendency to isomerize more readily to its trans-isomer (i.e. $k_{c-t} = 2.74 \times 10^{-6} \text{ sec}^{-1} > k_{t-c} = 1.48 \times 10^{-6} \text{ sec}^{-1}$), but not vice versa.

Heydtmann and Rinck^{8, 41} pyrolyzed the chloride to nearly 100% conversion and Maccoll and Stone⁴⁰ to about 50%. The acid produced was thought to be enough to cause isomerization of the n-butenes produced. Holbrook and Rooney³⁸ studied the pyrolysis of sec-butyl chloride in an ethyl chloride coated vessel (with or without hydrochloric acid present initially). They found that the n-butene product distribution agreed with Heydtmann and Rinck's results using potassium chloride coating. In Capoor's work⁴⁴, the decomposition was never allowed to exceed 15%. The amount of halogen acid produced was certainly insufficient to cause any isomerization. It is interesting that Capoor's result had a low trans:cis-ratio range (1.34-1.74). The others, however, had a much higher ratio range (1.79-1.95). If isomerization of the n-butene product by halogen acid did occur in Heydtmann and Rinck, Maccoll and Stone and Holbrook and Rooney's studies, the cis-product would tend to isomerize to the trans-form, but not vice versa. This could indicate a lack of isomerization of n-butenes by hydrochloric acid in Capoor's work and the presence of some isomerization in the latter case. Although the equilibrium value,

K_{c-t} , is not known accurately, experimental values by various workers (Table 19b) seems to indicate that $K_{c-t} = 1.55 \pm 0.05$ at 350°C . Heydtmann and Rinck, and Holbrook and Rooney's results (trans:cis but-2-ene ratio, about 1.9 at 350°C) might suggest that though the amount of halogen acid produced was appreciable, the rate of isomerization by the acid could still be too slow to be significant. Thus the true amounts of n-butenes produced from the elimination reaction could be measured.

(C) Catalytic elimination of halogen acid by carbon coatings

As discussed above, there seems to be no significant isomerization of n-butenes by halogen acid that was produced. Holbrook and Rooney³⁸ reported that a cis-but-2-ene carbon coating could be active in the elimination of hydrochloric acid in sec-butyl chloride decomposition. This was possible, since the trans: cis ratios and but-1-ene percentages obtained were much lower than those found in ethyl chloride and potassium chloride-coated vessels. However, the heterogeneous reaction yielding a higher cis-but-2-ene production was corrected for in Capoor's work. It was found to be very small in the temperature range studied ($300-350^\circ\text{C}$). Thus it is likely that in the pyrolysis of sec-butyl halides, there could exist at least two types of carbon coatings which might eliminate halogen acid catalytically, but in an opposite direction. The cis-but-2-ene carbon coating favored cis-elimination. Thus a low trans:cis but-2-ene ratio range (1.43-1.74) was obtained. The ethyl chloride or the potassium chloride carbon coating, on the other hand, favored trans-elimination, which gave a high trans:cis but-2-ene ratio

range (1.79-1.95). The equilibrium constant was found to be 1.55 ± 0.05 . A catalytic elimination reaction favoring cis-product formation³⁸ will be discussed latter.

Cis-but-2-ene carbon coating was used in the present study of pyrolyses of 3-chloropentane and 2-chloropentane. The results are different in two aspects from those of Capoor's work on the pyrolysis of sec-butyl chloride⁴⁴ using the same carbon coating. Firstly, the trans:cis pent-2-ene ratio (Table 18a and Table 18b; 1.93-2.20; 293-376°C) in 2-chloropentane and 3-chloropentane is larger than the trans:cis but-2-ene ratio (Table 19a; 1.34-1.74; 302-350°C) in Capoor's results. Secondly, in the present work, the product distribution did not change with percentage decomposition in the range 0 to 60%. This is shown in Tables 18a and 18b for the pyrolysis of 3-chloropentane and 2-chloropentane respectively. This indicates that the hydrochloric acid produced (up to 60%) was insufficient to cause any isomerization. Thus the true amounts of n-pentenenes produced from the homogeneous elimination reactions were measured. This was further checked by performing a series of experiments on the hydrochloric acid catalyzed isomerization of cis-pent-2-ene in the cis-but-2-ene carbon coated vessel. At 350°C, pent-1-ene and trans-pent-2-ene were not observed when equimolar amounts of cis-pent-2-ene and hydrochloric acid were introduced into the reaction vessel for periods comparable to the reaction time for the pyrolyses of the pentyl chlorides. Similar experiments were done for mixed trans, and cis-pent-2-ene in a known ratio and pure pent-1-ene respectively. Gas chromatographic analyses showed that the trans:cis

pent-2-ene ratio did not change in the former case. Neither trans- nor cis-pent-2-ene isomer was observed in the latter case.

From these true amounts of n-pentenes produced in the pyrolyses of 3-chloropentane and 2-chloropentane, the following Arrhenius parameters were calculated from the Arrhenius plots in Figs. 5 and 6 respectively (Tables 20 and 21).

The activation energies for individual n-pentene production are similar to within 2.2 kcal/mole. The Arrhenius parameters for the total pentene production from 3-chloropentane and 2-chloropentane on pyrolysis, found by Chytrý and his co-workers⁷ are shown in parentheses in Tables 20 and 21. The values are in good agreement with those of the present work. Arrhenius plots for 3-chloropentane and 2-chloropentane studied by Chytrý and his co-workers together with the present study are shown in Figs. 7 and 8 respectively.

Capoor⁴⁴ found in his study, the following Arrhenius parameters for 2-chlorobutane pyrolysis. He used cis-but-2-ene carbon coating as in the present study.

2-Chlorobutane

	E_a kcal/mole	$\log A$ (A in sec^{-1})
But-1-ene	53.3	14.21
Trans-But-2-ene	52.3	13.81
Cis-But-2-ene	50.0	12.80
Total butenes production	53.1	14.26

Cis-but-2-ene production had a significantly lower activation energy than that of the other two isomers⁴⁴. This

Table 20

Arrhenius Parameters for 3-Chloropentane Pyrolysis*

<u>n-Pentene</u>	<u>E_a (kcal/mole)</u>	<u>$\log A$ (A in sec^{-1})</u>
Trans-Pent-2-ene	50.7 ± 1.2	14.13 ± 0.37
Cis-Pent-2-ene	48.5 ± 1.1	12.96 ± 0.34
Total n-pentene production	50.5 ± 1.2 $(51.0)^7$	14.24 ± 0.37 $(14.4)^7$

Table 21

Arrhenius Parameters for 2-Chloropentane Pyrolysis*

<u>n-Pentene</u>	<u>E_a (kcal/mole)</u>	<u>$\log A$ (A in sec^{-1})</u>
Pent-1-ene	50.7 ± 1.2	13.11 ± 0.34
Trans-Pent-2-ene	49.9 ± 1.2	13.14 ± 0.34
Cis-Pent-2-ene	47.3 ± 1.1	11.90 ± 0.31
Total n-Pentene production	50.3 ± 1.2 $(50.7)^7$	13.58 ± 0.35 $(14.1)^7$

* Calculated by the "method of least squares" (see Appendix 1, p. 234a).

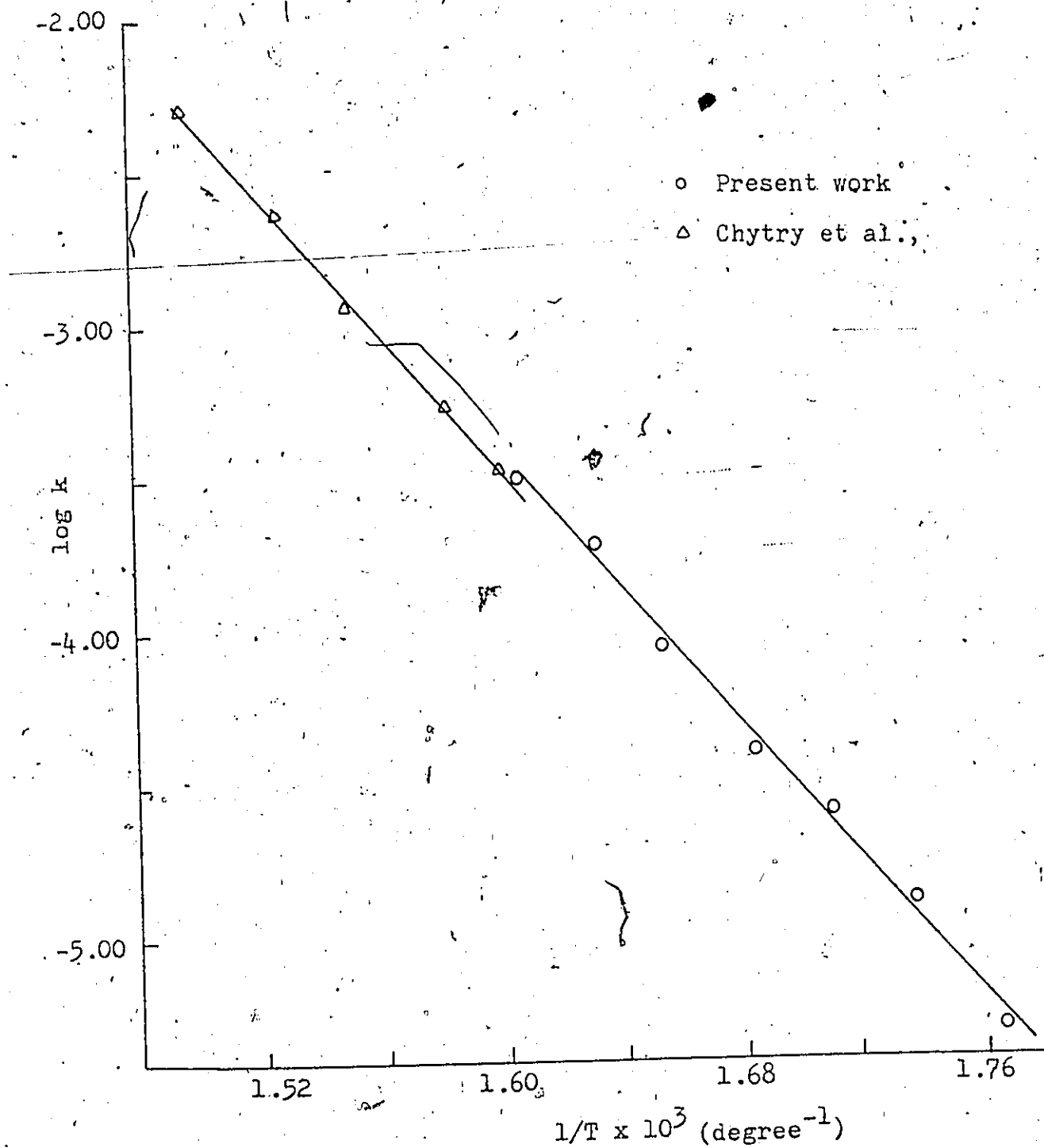


Fig. 7. The Arrhenius plot for the pyrolysis of 3-chloropentane.

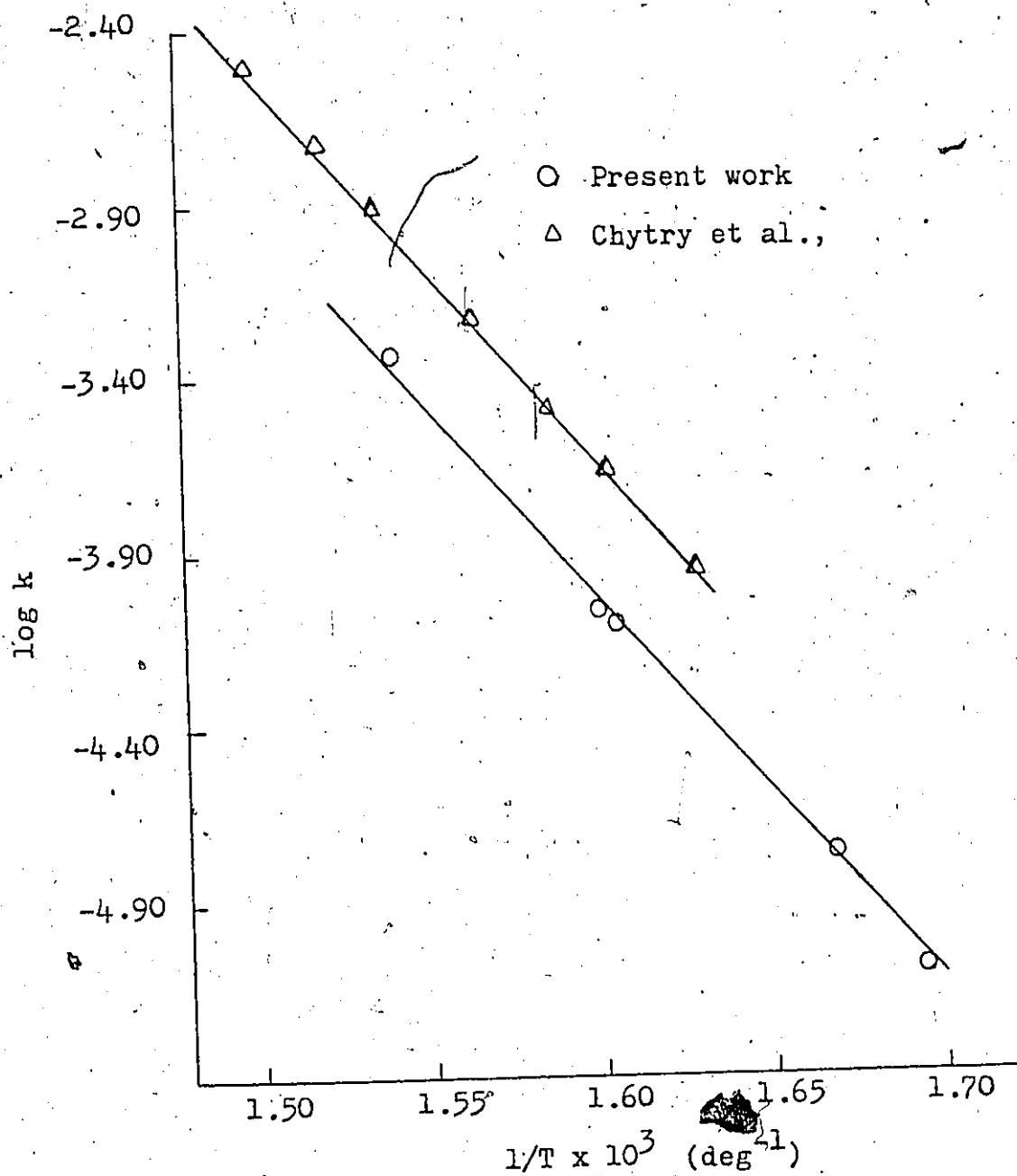


Fig. 8. The Arrhenius plot for the pyrolysis of 2-chloropentane.

suggests that 2-chloropentane and 3-chloropentane might have lower activation energies for cis-isomer production as compared with the other two isomers, produced in the gas phase elimination process. In the present study, the activation energies for cis-pent-2-ene production are from 2.2 to 2.6 kcal/mole lower than those for the trans-isomer.

It is apparent from the above discussion that so far as the Arrhenius parameters are concerned, a cis-but-2-ene carbon coating has the same effect on the pyrolyses of 2-chloropentane, 3-chloropentane and 2-chlorobutane.

(D) Trans:cis ratio observed for olefinic products

Interpretation of the present sets of results, as in the case of pyrolysis of sec-butyl chloride, obviously requires very careful assessment of the equilibrium values for the three n-pentene isomers. Unfortunately the published data for the n-pentenés showed some divergence (see Table 22). Different workers' values for K_{lt} were in fair agreement^{50, 53, 55-58}. There was however, considerable uncertainty as to the value of K_{ct} and its temperature dependence. The spread of values for K_{ct} was wide, particularly at 600°K. The mean values from the references cited in Table 22, were $K_{lt} = 4.36$ and $K_{c-t} = 1.97$.

The trans:cis ratios observed for the present study are compared with values for previous work on similar compounds shown in Table 23. In general, the product ratios for the unpacked vessel or coated vessel were close to the equilibrium values or else slightly in favor of the trans-product. It should be emphasized that under these conditions, with the exception of

Table 22

Values for K_{ct}^* and K_{lt}^* for n-pentenes at 300 and 600°K

$K_{ct}(300^{\circ}\text{K})$	$K_{ct}(600^{\circ}\text{K})$	$K_{lt}(300^{\circ}\text{K})$	$K_{lt}(600^{\circ}\text{K})$	Ref.
2.73	1.61	45.0	4.30	53,55
4.27	1.82	----	----	56
4.14	2.25	37.8	4.37	57
4.37	2.43	42.4	4.41	58
4.64	1.74	----	----	50

* $\text{Cis-Pent-2-ene} \xrightleftharpoons{K_{ct}} \text{Trans-pent-2-ene}$

$\text{Pent-1-ene} \xrightleftharpoons{K_{lt}} \text{Trans-Pent-2-ene}$

Table 25. Trans:cis ratio observed for olefinic products

Olefin	Pyrolytic source	Temperature, °C	Trans:cis product ratio	Equilibrium value, K_{ct}
But-2-ene	2-chlorobutane (8,40 41, 44)	a ₃₅₀ °C	1.63	1.52
		b ₃₉₃	1.80	1.47
		b ₂₉₉	1.95	1.60
		c ₃₅₀	1.62	1.52
		c ₂₃₁	0.80	1.75
Pent-2-ene	3-chloropentane (present study)	d ₃₅₀	1.89	1.52
		e ₂₁₀	0.68	1.80
		c ₂₉₃ 350	2.10	1.97(327°C)
		c ₃₁₅ 376	2.10	1.97(327°C)
		f ₄₅₇	0.55	0.53
1-chloropropene	1,2-Dichloropropane (59-60)	g ₃₇₈	0.36	0.48
		h ₅₀₀	0.59	0.56
		i ₄₅₆	0.83	0.53
		e ₃₇₀	0.40	0.56
		i ₄₅₀	1.00	0.63
1-chlorobutene	1,1-Dichlorobutane (61)	e ₃₇₀	0.40	0.56
2-chlorobut-ene	2,2-Dichlorobutane (62)	a ₃₅₀	2.20	--

Table 23: (continued)

Vessel conditions:

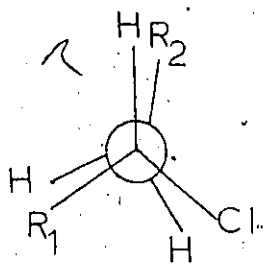
- a. Allyl bromide carbon coating.
- b. Potassium chloride coating.
- c. Cis-but-2-ene carbon coating.
- d. Ethyl chloride carbon coating.
- e. Packed pyrex.
- f. Unpacked silica.
- g. Silica packed with silica wool or pyrex packed with pyrex helices.
- h. Seasoned with 1,2-dichloropropane.
- i. Unpacked pyrex.

an allyl bromide carbon coating, no trans:cis isomerization occurred. At the temperatures used for the pyrolyses in packed reaction vessels and at temperatures well below 300°C using cis-but-2-ene carbon coating in the pyrolysis of 2-chlorobutane⁴⁴, the homogeneous reactions contribute little (usually < 10%) towards the total rate. As direct cis-trans isomerization of products did not occur, the trans:cis ratios obtained therefore could reflect the nature of the activated complexes for the heterogeneous pyrolyses of the chloro-compounds concerned. Table 23 shows that the cis-product was clearly favored in every case irrespective of whether thermodynamic equilibrium favors the cis- or trans-olefin. High yields of cis-olefins have been previously reported for many heterogeneous reactions. It is likely that there may be a common explanation for this phenomenon. One such possible explanation³⁸ was the formation of π -complexed intermediates at the surface. Several conclusions can be drawn from these data (Table 23).

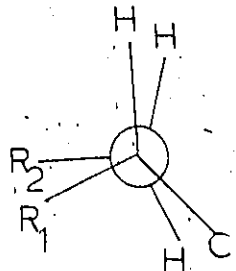
(1) The trans:cis:pent-1-ene ratio (2.1:1:1) indicates that the concentrations of pent-1-ene and trans-pent-2-ene were always higher than their respectively equilibrium concentrations. The trans:cis:pent-1-ene ratio was 1.97:1.00:0.45 at 350°C at equilibrium. This further confirms that the elimination reaction catalyzed by cis-but-2-ene carbon coating was not important in the sec-pentyl chloride system.

(2) Maccoll¹ suggested in his review that if coplanarity was a requirement of the transition state in elimination reaction, then the trans-product should predominate over the cis-product.

This can be seen from the projections III and IV, where R_1 and R_2 are alkyl groups or halogen atoms.



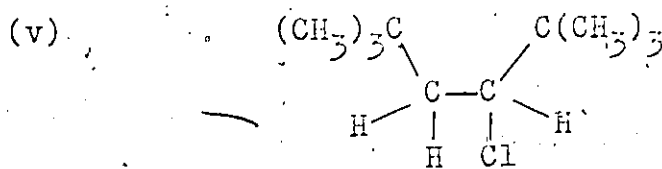
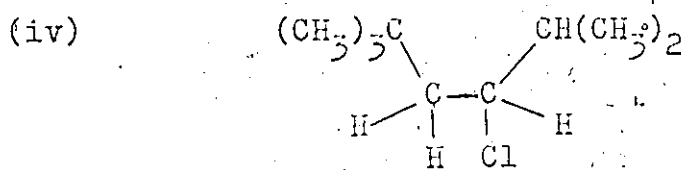
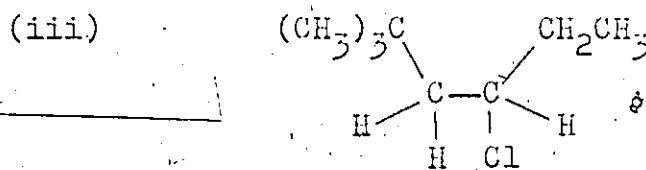
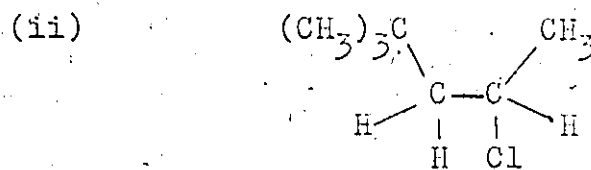
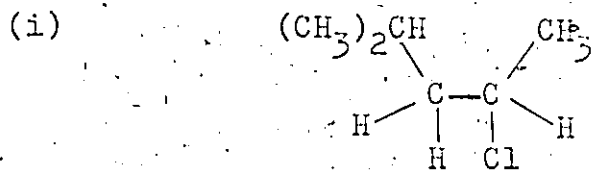
(III)



(IV)

(III) which leads to the trans-olefin is less sterically hindered than (IV) which leads to the cis-product. The trans-form is also favored by thermodynamic stability. It has been mentioned that trans:cis ratio in the pyrolysis of sec-butyl chloride ($R_1 = R_2 = \text{CH}_3$) was from 1.4 to 1.95 at temperature range 300 to 400°C. In the present study of 2-chloropentane and 3-chloropentane pyrolyses ($R_1 = \text{CH}_2\text{CH}_3$, $R_2 = \text{CH}_3$), both the ratios were 2.1 ± 0.1 (293-376°C). This supports Maccoll's point of view as it is obvious from projections (III) and (IV) that the trans:cis ratio should be larger in the sec-pentyl chloride pyrolysis. Furthermore since 2-chloropentane and 3-chloropentane have the same stability in both projections, the trans:cis pent-2-ene ratio has to be equal to each other.

This model can further be tested by investigating similar secondary halide systems with larger alkyl groups, R_1 and R_2 . Such molecules which might suffice are shown below:



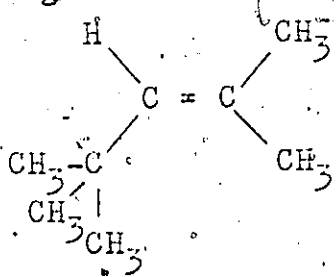
Based upon the results of this work, one would expect the trans:cis product ratio produced in the gas phase elimination process to be increasing in the order from (i) to (v). It should be emphasized, of course, that the trans-product is also favored by thermodynamic stability.

Maccoll in his recent review¹ has stated that "there is a close similarity between gas phase eliminations and polar substitutions (S_N1) and elimination reactions (E1) in polar solvents".

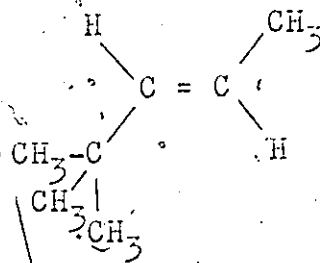
It was found, for example, that in the elimination reaction of secondary alkyl brosylate series, $\text{RCH}_2\text{CH}(\text{OBS})\text{CH}_3$, in polar solvents⁶⁵, the 2-olefin was predominantly the trans-form. This represented a very sharp range for $\text{R} = t\text{-butyl}$, as compared to $\text{R} = \text{CH}_3$, CH_2CH_3 , and isopropyl.

$\text{CH}_3\text{CH}_2\text{CH}(\text{OTs})\text{CH}_3$	trans:cis = 1.08
$\text{C}_2\text{H}_5\text{CH}_2\text{CH}(\text{OBS})\text{CH}_3$	trans:cis = 1.39
$(\text{CH}_3)_2\text{CHCH}_2\text{CH}(\text{OBS})\text{CH}_3$	trans:cis = 1.94
$(\text{CH}_3)_3\text{CCH}_2\text{CH}(\text{OBS})\text{CH}_3$	trans:cis = 85

This observation is similar to the present study. Brown and Nakasawa⁶³ suggested that this behaviour was in excellent agreement with the steric strain interpretation for the 2-olefinic products. For example, in 2,4,4-trimethyl-2-pentene (V), the $t\text{-butyl}$ group cannot avoid being cis to the methyl group. In the 2-olefin,



(V)



(VI)

from $(\text{CH}_3)_3\text{CH}_2\text{CH}(\text{OBS})\text{CH}_3$, the $t\text{-butyl}$ group can avoid steric interactions with the methyl group by assuming the trans-conformation (VI). In other words, in 2,4,4-trimethyl-pent-2-ene (V), the olefin can benefit from the hyperconjugative stabilization

afforded by the 2-olefin only at the cost of large steric strains resulting from the steric interactions of the *cis*-*t*-butyl and methyl groups. On the other hand, in *trans*-4,4-dimethyl-pent-2-ene, the molecule can benefit from the hyperconjugative stabilization of the 2-olefin without suffering from the steric disadvantages of the *cis*-*t*-butyl-methyl arrangement.

(3) The *trans*:*cis* ratios for 1-chloropropene and 1-chlorobutene were less than and equal to unity respectively, in pyrolysis of dichlorides using unpacked or carbon coating vessels⁵⁹⁻⁶². These ratios were slightly larger than their respective equilibrium values. No isomerization of *cis*- to *trans*-1-chloro-olefin or vice versa was found to occur at the temperatures studied either alone or in the presence of added hydrochloric acid. If coplanarity was a requirement of the transition state, the reverse would be expected since the configuration of the dichloride compounds, as discussed previously, leading to the *trans*-isomer was less sterically hindered. Holbrook⁶⁰ suggested that dipole-dipole interactions between the $\text{CH}_3^{\delta+}$ and $\text{Cl}^{\delta-}$ groups which were postulated to explain the thermodynamic preference for *cis*-1-chloropropene over *trans*-1-chloropropene⁶⁴ were also operative in the transition state leading to the formation of the *cis*-isomer. The observed *trans*:*cis* ratios were in fact larger or close to the observed equilibrium value due to these two effects operating in the opposite direction. Furthermore, 1-chloropropene was produced both by the pyrolysis of 1,1- and 1,2-dichloropropene^{61, 59-60}. The latter compound⁵⁹⁻⁶⁰ was β -chlorinated and pyrolyzed to this product was slower than that originated from the pyrolysis of the α -chlorinated

1,1-dichloropropane⁶¹. This behaviour was explained if the chlorine atom not undergoing elimination was involved in lone-pair donation in the case of 1,1-dichloropropane and inductive withdrawal in the case of 1,2-dichloropropane⁶⁵. The factor would tend to make this chlorine atom more negatively charged in the case of 1,2-dichloropropane than in the case of 1,1-dichloropropane. Since the increased stability of cis- over trans-1-chloropropene has been attributed to electrostatic attraction between $\text{CH}_3^{\delta+}$ and $\text{Cl}^{\delta-}$ groups, it could be argued that more-cis-olefin would be expected from 1,2-dichloropropane than from 1,1-dichloropropane. This was supported by the observed trans:cis ratios of 0.56 and 0.83 respectively for the pyrolysis of the compounds.

It is also of interest to compare the trans:cis ratios of chloro-olefin produced from 1,1-dichlorobutane⁶¹ and 2,2-dichlorobutane⁶². The products of interest were 1-chlorobutenes (trans:cis ratio = 1.00 in unpacked vessel at 450°C) and 2-chlorobut-2-enes (trans:cis ratio = 2.20 at 350°C using allyl bromide carbon coating) respectively. In the former case, coplanarity and dipole/dipole interaction between the $\text{CH}_3^{\delta+}$ and $\text{Cl}^{\delta-}$ counterbalanced each other. Thus a low trans:cis ratio, but greater than the equilibrium value was obtained. In the latter case however, only coplanarity operated. So the trans-olefinic product was formed in excess of the cis-form, giving a large trans:cis ratio (2.2) considerably greater than the equilibrium proportion. This observation was similar to that obtained from the pyrolysis of 2-chlorobutane.

(E) Common mechanism for the pyrolysis of secondary chlorides

In the present study, pyrolysis of 2-chloropentane (315-376°C)

and 3-chloropentane (293-350°C) are homogeneous and of the first order. There were no induction periods, and the addition of cyclohexene caused no appreciable change in the products or in the reaction velocity⁷. These results are consistent with a unimolecular mechanism for the elimination of hydrochloric acid. Further evidence in support of this mechanism is provided by the agreement between the estimated values for the Arrhenius parameters for other secondary chlorides that have been studied as shown in Table 24. Values for 2-chloropentane and 3-chloropentane are in line with those for other chlorides.

(F) The relative rates of secondary halides of the form
 $R_1-CHX-R_2$ (X= Cl and Br)

It is of interest to compare the relative rates for the pyrolysis of secondary chlorides and bromides of the form $R_1-CHX-R_2$ at 550°C where R_1 and R_2 are alkyl groups (Table 25). The rates for 2-propyl chloride and bromide were taken as unity. Data for 2-pentyl and 2-octyl bromides are not available. In calculating rate ratios, it was thought better to use the single set of results obtained by one worker rather than the average values for the secondary halides¹. Thus Chytrý and his co-workers' work⁷ on pyrolysis of 2-propyl, 2-pentyl and 3-pentyl chlorides, and Maccoll and his co-workers' work on 2-butyl⁴⁰ and 2-octyl³ chlorides, and 2-propyl⁹, 2-butyl¹⁰ and 3-pentyl¹¹ bromides were quoted for comparison. The close agreement between the data for the two sets of compounds is strongly indicative of a common mechanism.

Table 24
Arrhenius Parameters for Secondary Chloride Pyrolysis

Chloride	logA (A in sec. ⁻¹)	E _a (kcal/m.)	Ref.,
2-Propyl	13.40	50.5	66
	13.64	51.1	67
	13.40	50.3	7
2-Butyl	13.62	49.6	40
	14.00	50.6	8,41
	14.07	50.8	8,41
	14.56	53.2	44
2-Pentyl	13.58	50.3	present study
	14.10	50.7	7
3-Pentyl	14.24	50.5	present study
	14.40	51.0	7
2-Octyl	13.53	48.7	3
Cyclopentyl	13.47	48.3	68
Cyclohexyl	13.77	50.0	34
	13.88	50.2	69,70

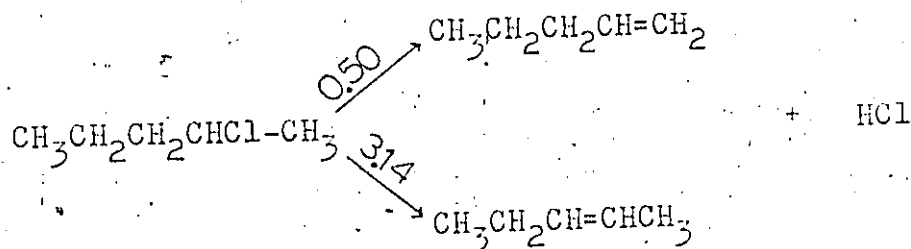
Table 25

Relative rates of pyrolysis of secondary
chlorides and bromides (350°C)

	2-Propyl ($R_1=R_2=CH_3$)	2-butyl ($R_1=CH_3$, $R_2=C_2H_5$)	2-pentyl ($R_1=CH_3$, $R_2=n-C_3H_7$)	3-pentyl ($R_1=R_2=C_2H_5$)	2-octyl ($R_1=CH_3$, $R_2=n-C_6H_{11}$)
Chloride	1.00 ⁷	2.91 ⁴⁰	3.64 ⁷	5.70 ⁷	4.87 ³
Bromide	1.00 ⁹	2.52 ¹⁰	----	5.12 ¹¹	----

(C) Direction of elimination for secondary halides

An interesting point arises as to the effect of β -ethylation (or β -alkylation and β -methylation). This may either be a first-order effect on the β -carbon-hydrogen bond, or a second-order effect on the α -carbon-chlorine bond. If the former was true, the increase in rate from 2-propyl to 2-pentyl chloride should be due to elimination towards the center of the molecule, resulting in pent-2-ene. Thus at 350°C, if 2-propyl chloride⁷ was assigned a rate of 1, that of 2-pentyl chloride⁷ would be 3.64 (see Table 25). This would imply:



The ratio of pent-1-ene to pent-2-ene should be 1:6.3, giving 86% of pent-2-ene. Analysis of the product mixture gave about 75% of pent-2-ene. The effect of the β -methyl group (or β -alkyl group) thus appears to be predominantly a second-order effect on the carbon-halogen bond, rather than a first-order effect on the carbon-hydrogen bond. Similar analysis can be made of β -methyl substitution.

The effect can be analyzed in a different fashion as shown in Table 26. It shows that the added methyl or ethyl group not only increases the rate of elimination in the branch to which it was added but also in the branch which was unchanged. Here 60% of the pyrolytic product in the 2-butyl halide was but-2-ene, and 75% of the product in 2-pentyl chloride was pent-2-ene. Thus

Table 26

Direction of reaction, at 350°C

Rel. rate per hydrogen	Rel. rate per changed branch	Halide used	Rel. rate per unchanged branch	Rel. rate per hydrogen
0.17 (1.0)	0.5 (1.0)	${}^7\text{CH}_3\text{CHClCH}_3$	0.5 (1.0)	
0.88 (5.2)	1.75 (3.5)	${}^4\text{CH}_3\text{CH}_2\text{CHClCH}_3$	1.15 (2.3)	
1.57 (8.1)	2.73 (5.5)	${}^7\text{CH}_3\text{CH}_2\text{CH}_2\text{CHClCH}_3$	0.91 (1.8)	
1.45 (8.4)	2.85 (5.7)	${}^7\text{CH}_3\text{CH}_2\text{CHClCH}_2\text{CH}_3$	a -----	
0.17 (1.0)	0.50 (1.0)	${}^9\text{CH}_3\text{CHBrCH}_3$	0.50 (1.0)	
0.76 (4.5)	1.51 (3.0)	${}^{10}\text{CH}_3\text{CH}_2\text{CHBrCH}_3$	1.01 (2.0)	
a -----	a -----	${}^a\text{CH}_3\text{CH}_2\text{CH}_2\text{CHBrCH}_3$	a -----	
1.28 (7.5)	2.56 (5.1)	${}^{11}\text{CH}_3\text{CH}_2\text{CHBrCH}_2\text{CH}_3$	a -----	

a. Data not available.

according to Table 26, the added methyl and ethyl group increased the rate of elimination in the "changed" branch of the chlorides by 3.5 and 5.5 to 5.7 respectively. The rate of elimination in the branch of 2-propyl chloride⁷ was assigned to be unity. In the branch which was "unchanged", the elimination in that branch only increased by a factor of about two (1.8 and 2.3). In fact, since there are three primary β -hydrogen in each branch of 2-propyl chloride, and only two secondary β -hydrogen atoms in the β -methylated or β -ethylated branch, it is more appropriate to compare the relative rate per hydrogen atom in those "changed" branches. This is found to be 1:5.2:8.1:8.4 for 2-propyl⁷, 2-butyl⁴⁰, 2-pentyl⁷ and 3-pentyl chlorides respectively (Table 26). Similar interpretation can be made of the bromide analogs (Table 26).

These results confirm the low sensitivity of the pyrolysis of secondary alkyl halides to β -alkyl substitutions, and also emphasize the analogy between gas phase elimination and unimolecular solvolyses in polar solvents¹.

Further evidence of the second-order nature of the effect of β -methylation came from work by Wong and Maccoll¹² on the series $(CH_3)_2CClR$, with $R = CH_3$, CH_2CH_3 , isopropyl and *t*-butyl. The rate of elimination progressively increased with β -methylation, despite the fact that in the last compound elimination was of necessity entirely in the short branch (Table 4).

Appendix 1

Calculation of the Arrhenius Parameters

by the "Method of Least Squares"

Experimentally, the activation energy (E_a) and frequency factor ($\log A$) are determined by plotting the common logarithm of the rate constant ($\log k$) against the reciprocal of the absolute temperature ($1/T$). The slope of the line/ of is then equal to minus the activation energy divided by $2.303R$ according to the Arrhenius equation:

$$\log k = \log A - E_a/2.303 (1/T) \dots\dots\dots(1)$$

where R is the gas constant.

The best line is not always easily discerned by eye, but can readily be obtained by a calculation which eliminates personal error. The "method of least squares" is generally used, in which the sum of the squares of the deviations of the experimental points from the chosen line is a minimum.

The equation to a straight line may be expressed in the form:

$$y = a + bx \dots\dots\dots(2)$$

where a and b are the constants to be determined, and y and x are dependent and independent variables respectively. If N readings have been made then:

$$\Sigma y = Na + b \Sigma x$$

Further

$$\Sigma xy = a \Sigma x + b \Sigma x^2$$

It can then be shown that:

$$a = \frac{\Sigma x \cdot \Sigma xy - \Sigma x^2 \cdot \Sigma y}{(\Sigma x)^2 - N \Sigma x^2} \dots\dots\dots (3)$$

and

$$b = \frac{\Sigma x \cdot \Sigma y - N \cdot \Sigma xy}{(\Sigma x)^2 - N \Sigma x^2} \dots\dots\dots (4)$$

In the case of the Arrhenius equation (1) given above, the linear equation (2) is obtained by substituting $\log k = y$, $1/T = x$, $a = \log A$ and $b = -E_a/2.303R$. The values of $\log A$ and E_a can then be determined from equations (3) and (4).

CLAIMS TO ORIGINAL RESEARCH

(1) The mass spectra of neopentyl alcohol, bromide and chloride have been studied. Based on the appropriate labelling experiments and the presence of metastable ion peaks, fragmentation schemes for their dissociations are proposed.

(2) Isomeric $C_4H_8X^+$ ions ($X = OH, OD, Br$ and Cl) have been generated in the mass spectrometer from various sources. The structures of the decomposing ions, and the mechanisms of decomposition have been investigated by extensive 2H and ^{13}C -labelling experiments.

(3) The losses of HCl and H_2O from the molecular ions of the homologous series of chlorohydrins, $OHCH_2C(CH_2)_nCH_2Cl$ ($n=0$ to 5) and $ClCH_2(CH_2)_2CH_2OH$ were found to arise from chlorine-hydroxyl and hydroxyl-methylene interaction respectively. Similar trends were also observed for the mass spectra of some chloroacids briefly investigated.

(4) The mass spectra of methylcyclopentene and cyclohexene; and 4-methylcyclohexene and cycloheptene have been studied. Fragmentation of each pair of these isomers for the most part proceeds via common intermediates in which hydrogen atoms have lost their positional identity. The loss of methyl radical from methylcyclopentene and 4-methylcyclohexene molecular ions involves, to a great extent, simple direct bond cleavage.

(5) The pyrolyses of 3-chloropentane and 2-chloropentane were first studied in a reaction vessel coated with carbon produced

by cis-but-2-ene pyrolysis. The n-pentenenes, produced in the reactions were analyzed by gas-liquid chromatography. Their individual rate constants for their production and the corresponding Arrhenius parameters were calculated.

(6) It was found that trans- and cis-pent-2-ene product ratio from both pyrolyses reflects that coplanarity is a requirement of the transition state in elimination reactions. That is, the trans-product predominated over the cis-form.

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