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# MASS SPECTRA AND MOLECULAR STRUCTURE OF HYDROCARBONS

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## I. INTRODUCTION

Modern ideas on the molecular structure of organic compounds are to a large extent linked with the study of physical properties, such as absorption spectra in all regions from the ultraviolet to the microwave, dipole moments, atomic and electronic polarisation, etc. In the last two decades a new method for investigating organic compounds — molecular mass spectrometry — has been developed; this deals with the interaction of molecules and electrons. The overall relative probability of the formation of various ions that arise when a molecule is bombarded with slow (20–70 eV) electrons is characteristic of the stability of the molecule, and, what is very important for the organic chemist, of its structure, since the possible rupture of a given bond depends mainly on the distribution of electron density.

The formation of mass spectra is generally considered from the point of view of the Franck–Condon principle[1], according to which the first act in any inelastic collision between an electron and a molecule is electronic excitation of the latter, which occurs as an electronic transition while the distance between nuclei remains unchanged. In the inelastic collision of an ionising electron with a molecule, one of the valence electrons is removed and a molecular ion corresponding to the molecular weight and empirical formula of the compound is formed. Electrons acting on the molecule in the ion source of the mass spectrometer usually possess energy of several tens of electron volts; therefore, in the bombardment of polyatomic molecules, in addition to ionisation, decomposition of molecular ions occurs with rupture of C–C and C–H bonds and the formation of ionic fragments, which may also decompose in turn. This multiplicity of processes is responsible for the complexity of the mass spectra of polyatomic molecules with their multiplicity of lines.

The stability of organic molecules to electron impact is characterised by the probability of decomposition of molecular ions[2], $W_Z$, and is determined by the ratio of the number of molecular ions ($I_{mol}$) to the number of fragmentation ions ($\Sigma I_{frag}$): $W_Z = \Sigma I_{frag}/(I_{mol} + \Sigma I_{frag})$. The value of $W_M = (1 - W_Z)$ determines the stability of the molecule to electron impact.

This ratio, in turn, reflects the rate of decomposition of the molecular ion; since the time between the formation of ions and their detection is usually $10^{-5}$ s, the absence of particular molecular-ion peaks in the mass spectrum indicates that these ions have a short life. The rate of decomposition of the molecular ion is a function of the energy acquired by the ion during its formation; when the energy of the ionising electrons falls to a value close to the ionisation potential of the molecule, the proportion of molecular ions is increased in relation to that of fragmentation ions.

The ionisability of molecules and radicals formed in the rupture of chemical bonds is characterised by what is termed complete ionisation, which represents the quantity of ions formed by unit quantity of the compound[3]. It is determined by the sum of the intensities of all the peaks in the spectrum multiplied by the coefficient of sensitivity of the strongest peak; the latter is expressed in units of ion current referred to unit pressure.

In addition to the ions formed by simple rupture of bonds, the mass spectra of nearly all molecules containing more than two carbon atoms show the presence of ions that are produced as a result of rearrangement of atoms at the moment of dissociation. Rearrangements with migration of a hydrogen atom are observed very frequently[4]. The activation energy of rearrangements in ions is low and commensurable with the activation energy of rearrangements in neutral molecules; accordingly, rearrangements in the molecular ion proceed comparatively easily[3]. With hydrocarbons the difference in activation energies of various rearrangements is very small, and therefore competing reactions lead to the formation of diverse fragments.

Although the number of carbon and hydrogen atoms in the ion can be readily established, the question as to which of the hydrogen atoms has separated with a given fragment can only be decided by a study of the mass spectra of isotopically "labelled" compounds[6,7]. Information on the structure of ionised fragments can also be obtained by measuring the energy changes in the reactions that occur and by studying metastable transitions.

All the ions formed in the primary step of interaction of the electrons with the molecule† may be divided into three groups: (1) stable ions, with insufficient excitation energy for decomposition before detection; (2) unstable ions, with sufficient energy for decomposition before they leave the ion source; and (3) metastable ions of intermediate energy[8]. The latter, which decompose after acceleration (but before deflection by the magnetic field), are generally focussed with the production of "false" peaks corresponding to ions of "non-integral" mass. The relationship between the apparent mass of the metastable ion, $m^*$, the mass of the initial ion before dissociation, $m_0$, and the mass of the fragmentation ion is expressed by the equation $m^* = m^2/m_0$. The metastable ions are "witnesses" of a given stage of the decomposition process, and they can be used to decide the question of the probable routes of dissociative ionisation.

Temperature is one of the other factors that affect the distribution of intensities in mass spectra. An increase in the temperature of a gas increases the vibrational energy of the molecules and in this way changes the probability of formation of various ions in the mass spectrum of the compound under examination. The most reliable studies on the temperature dependence of mass spectra indicate that there are different changes in intensity of the peaks of various ions[9-12]. The intensity of a molecular-ion peak always decreases with increase in temperature; the peaks of fragmentation ions can increase, decrease, or pass through a maximum; the intensity of ion peaks due to the end products of dissociative ionisation increases with increasing temperature. The value of the complete ionisation depends little, or not at all, on change of temperature.

The variety of phenomena that occur on the interaction of complex molecules with electrons is not limited to those mentioned above. We thought it expedient to consider only those phenomena and characteristics that reflect the specific features of dissociative ionisation processes.

Any examination of the present state of the theory of molecular mass spectrometry from the point of view of the organic chemist must take into account the fact that none of the current views allows quantitative predication of the intensity distribution in the mass spectrum of a complex organic compound of known formula. Therefore, in addition to work designed to set up a quantitative theory of the formation of mass spectra, based on studies of primary and secondary acts in the ionisation of complex molecules, research work is also needed to establish correlations between the structures of organic compounds and their mass spectra. The study of regularities in the mass spectra of organic compounds, and of the relationship between structure and intensity distribution, brings us nearer a solution of the problem of determining a structure from the results of mass-spectrometric analysis. The establishment of different kinds of empirical rules will provide the basis for the development of methods of identification and of qualitative and quantitative analysis.

The methods of molecular mass spectrometry are widely used to study various classes of organic compounds, but their greatest analytical use has been in the hydrocarbon field. However, despite the large number of published papers on the subject, up to now there has been no general systematic summary of the regularities in the mass spectra of hydrocarbons with different degrees of unsaturation. The present review is an attempt, in some measure, to fill this gap.

## II. PARAFFIN HYDROCARBONS

The most intense peaks in the mass spectra of hydrocarbons correspond to ions of odd mass number[13] with an even number of electrons, $C_2H_5^+$, $C_3H_7^+$, $C_4H_7^+$, $C_4H_9^+$, etc. The absence from paraffin molecules of groupings that either are stable to electron impact, or produce considerable weakening of certain single bonds, makes it difficult to establish correlations; usually, the primary decomposition process is clear only for branched molecules.

Bloom and coworkers[14], and also Mohler and coworkers[15], studied the mass spectra of octane and nonane isomers and extended the regularities they discovered to all paraffin hydrocarbons. They showed that the most probable processes are those in which the fragmentation ions $C_3H_7^+$ and $C_4H_9^+$ are formed. Molecules with ethyl, propyl, and isopropyl groups readily eliminate these ions, the ion produced corresponding to the mass of the remaining part of the molecule. In most instances, hydrocarbons with a terminal tertiary butyl group give similar spectra, the maximum peak corresponding to $C_4H_9^+$ ions.

In many instances the configuration of the carbon atoms in the hydrocarbon ions can be determined by examining the energetics of the process without the use of labelled compounds[16]. A study of the potentials at which the $C_2H_5^+$, $C_3H_7^+$, and $C_5H_{11}^+$ ions appear‡ in the mass spectra of the normal paraffin hydrocarbons[17] $C_5H_{12}$ and $C_8H_{18}$ has shown that propyl, butyl, and pentyl ions have the secondary structure, but the free radicals formed with them usually have the primary structure, and only sometimes the secondary. The stability of the $C_3H_7^+$ ion, which is encountered in considerable quantities in the mass spectra of all paraffin hydrocarbons, appears to be associated with its cyclopropenyl structure, that is, with the presence of a protonated cyclopropane ring[18]. This conclusion was further supported by the work of Stevenson[7], who established that, in the mass spectra of [1-$^{13}$C]propane and [2-$^{13}$C]propane, the relative intensities of the peaks for the fragmentation ions $C_1H_x^+$ and $C_2H_x^+$ are identical; this indicates that the carbon atoms are indistinguishable in the molecular ion $C_3H_8^+$, from which these fragments are formed. Urch also showed that with ionisation by electron impact there is a change in the symmetry of the neutral molecule[19].

Of 80 mass spectra of alicyclic $C_2$–$C_{12}$ hydrocarbons presented in the catalogue of the American Petroleum Institute[20], only two (those of ethane and 3,4-dimethylhexane) show the formation of more intense peaks of the

† The primary processes also include electron capture and the formation of negative ions. However, since these processes are not typical of hydrocarbons, we shall not consider them here.

‡ The adiabatic ionisation potential of a molecule or atom is theoretically defined as the energy required for the removal of an electron from a neutral particle in the ground state with the formation of a molecular or atomic ion, also in the ground state. The ionisation potential determined by the electron-impact method is, in most instances, the so-called "vertical potential", which exceeds the adiabatic potential by the energy of vibration at excitation of the ion; this is due to the difference in the equilibrium configurations of the nuclei in the molecule and in the molecular ion. The term "appearance potential" applies to those instances of ion formation in which dissociation accompanies ionisation; the appearance potential corresponds to the minimal energy for the production of fragmentation ions.

fragmentation ions $C_2H_4^+$ and $C_4H_8^+$, with an odd number of electrons. Intense peaks of $C_nH_{2n}^+$ ions, the formation of which was related to the elimination of groups with tertiary carbon atoms and the migration of hydrogen, have also been observed in the mass spectra of some dodecanes[21].

The formation of ions which isomerise is not generally typical of paraffin hydrocarbons, but in some instances, for example, in the dissociative ionisation of neohexane, the formation of $C_3H_7^+$ ions must entail rupture of two C–C bonds and migration of a hydrogen atom. These considerations are also valid for the $C_2H_5^+$ ion in the spectrum[22] of isobutane $(CH_3)_3CH$. Analysis of the mass spectra of deuterated hydrocarbons also indicates that migration occurs. For example, $(CH_2D)^+$ and $(CHD_2)^+$ ions are present in the mass spectrum of 1,1,1-trideuteroethane[17].

Several hypotheses have been advanced to explain the specificity of decomposition of complex molecules, including hydrocarbon molecules. An attempt to solve this problem based on the concept of the distribution of the electron density of single bonds[23] led to disagreement with the experimentally observed distribution of intensities, particularly for $C_3$ and $C_4$ ions of long-chain molecules[24,25]. Nor were positive results obtained when bond energies for the initial molecule were used to calculate mass spectra; the appearance of very high peaks coreesponding to ions with a small number of carbon atoms could not be explained[26,27].

The quasi-equilibrium theory of mass spectra[28,29] allows the calculation of intensities in the mass spectra of paraffin hydrocarbons containing not more than five carbon atoms. Satisfactory results were obtained in the calculation of mass spectra of low-molecular ethers, alcohols, etc.[30–34] In the investigation of large molecules, a discordance was observed between theory and experiment, particularly in the region where the ionising electrons have low energies; most of the fragments are then formed by direct dissociation on electron impact. The normal paraffins $C_nH_{2n+2}$ from $C_6$ to $C_{30}$ have been used as models to explain the factors which give rise to the anomalous (from the standpoint of statistical theory) decomposition of molecules on electron impact[35]. Treatment of the mass spectra of these compounds showed that the yield of heavy ions (with the number of carbon atoms in the ion $m \geq 15$) does not depend on $m$ and $n$ as such, but is determined only by $(n - m)$, that is, by the size of the neutral fragment. For low values (3–15) of $m$, the yield of ions depends on both $n$ and $m$.

Ryhage and coworkers[36] examined the mass spectra of the labelled paraffin hydrocarbon $CD_3-[CH_2]_{24}-CD_3$ and concluded that fragmentation ions are formed from the central portion of a saturated chain, since the $C_2-C_5$ fragmentation ions contained no deuterium. Theoretical investigation of the dissociation of molecular ions of normal paraffins has shown[37] that fragmentation ions are formed as a result of competing successive decomposition steps; each ion decomposes in such a way that no charged fragments are formed with less than half the initial number of carbon atoms.

Gur'ev and coworkers[38,39], who studied the mass spectra of [5-$^{13}$C]-n-nonane, suggested that fragmentation ions are formed by "shedding" of a charged part of the molecule in the region of electron impact, the C–C bonds being ruptured at equal distances from the point of impact. The complete set of probabilities of the mass spectra of an infinitely large molecule appear at each point of collision (independently of the size of the molecule); if the rupture of one of the bonds should take place "outside the limits" of the molecule, only one bond is broken and a smaller fragment is formed. Potapov and coworkers[40,41] studied the probability curves for the appearance of various ions, which give an indication of the mechanism by which ions are formed, and they showed that $C_nH_{2n+1}$ ions are formed from n-octane and n-nonane by simple rupture of one C–C bond to give an ion and a radical. The formation of ions accompanied by the production of many neutral fragments is less favoured energetically. Examination of the mechanism of formation of $C_nH_{2n}^+$ ions, in particular $C_3H_6^+$ ions, led to the conclusion that rupture of two C–C bonds and union of the terminal parts of the hydrocarbon chain take place in a synchronous step. Comparison of the mass spectra obtained in electron and ion collisions[42] showed that dissociation of the ions occurs some time after the moment of excitation, and the relative decomposition probabilities depend to a small extent on mass and type of neutral particle with which collision occurs[43].

To establish the role of different mechanisms for the formation of the commonest ions, $C_3H_7^+$ and $C_4H_9^+$, in the mass spectra of long-chain paraffins, Beynon and coworkers studied [4-$^{13}$C]-n-eicosane and [1-$^{13}$C]-n-heptadecane and examined the degree of enrichment of fragmentation ions with heavy carbon[44]. The following hypothetical routes of formation of ions were considered: (1) simple rupture of one carbon–carbon bond in the molecular ion with the formation of an ion and a neutral fragment; (2) rearrangement of the molecular ion to a protonated ring structure; (3) complete "disintegration" of the carbon–carbon skeleton before the formation of fragments; (4) removal of any given number of adjacent carbon atoms from a (linear) molecular ion; (5) decomposition of a molecular ion with simple rupture of the carbon–carbon double bond, followed by rearrangement of the fragmentation ion to a ring structure and further fragmentation by Scheme (2); (6) simple bond rupture with subsequent removal of $C_2H_4$ fragments.

The validity of these hypotheses was tested by comparing experimental and calculated curves reflecting the proportion of unlabelled and labelled fragmentation ions with a different number of carbon atoms. The results showed that ions with a small number of carbon atoms are generally not formed by simple rupture of the carbon chain. On the other hand, rupture of one C–C bond is characteristic for larger ions. Further decomposition occurs mainly by successive removal of $C_2$ ions. The hypothesis that a ring structure is formed directly from a molecular ion is not in agreement with experimental results obtained with heavy fragments. The best agreement between the experimental and theoretical curves was obtained with mechanism (5); it was assumed, from steric considerations, that the rings usually contain five or six carbon atoms.

The specificity of dissociative ionisation of paraffins with a normal, or not too branched, chain is reflected in the nature of the distribution curve: the maximum corresponds to $C_3H_x^+$ ions, which are formed with the highest probability, irrespective of the length of the paraffin chain (Fig. 1). When the chain contains quaternary carbon atoms, a second maximum appears. Thus, investigation of the mass spectra of isomeric tetradecanes with the methyl side group in different positions showed that secondary maxima appear, owing to the rupture of a bond at the tertiary carbon atom[45,46].

The degree of decomposition of the paraffin molecule that occurs when it interacts with ionising electrons depends

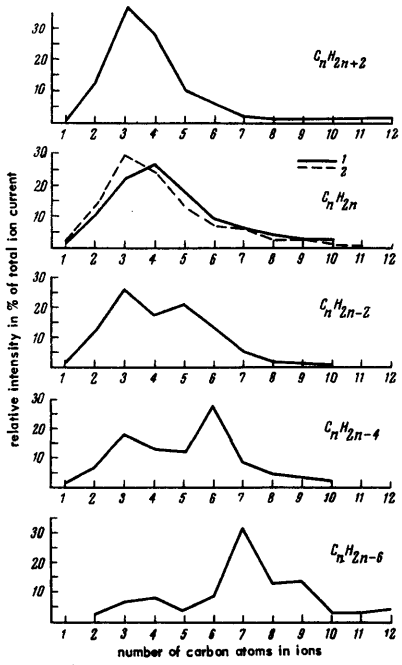



Fig. 1. Distribution curves of intensities against number of carbon atoms in ions for different hydrocarbon groups
1) naphthene; 2) monoalkene.

on the branching of the carbon skeleton: Bloom and coworkers analysed the spectra of 18 octane isomers and showed that the most intense molecular-ion peak is observed in the mass spectrum of the normal isomer[14]. Examination of the spectra of the tetradecanes[45,46] and the hexadecanes[47] showed a similar picture. The intensity of the molecular-ion peak decreases with increase in molecular weight; a more rapid rate of decrease is shown by branched paraffins than by the normal isomers. The peak intensities of the molecular ions of $C_6$–$C_{12}$ hydrocarbons are, with some exceptions, 3–6% of the maximum. Further increase in molecular weight leads to virtually complete disappearance of the molecular-ion peaks in the spectra of branched paraffins[48]. Gur'ev examined the mass spectra of normal paraffins and showed that the dependence of the fraction of molecular ions on molecular size is well represented by an exponential curve[49]. Polyakova and coworkers[50] studied the mass spectra of normal paraffins on different instruments, and showed that, in all instances, the sensitivity coefficients of the molecular-ion peaks are a function of molecular weight. However, the nature of the dependence, which is represented by an interpolation formula, varies somewhat from one instrument to another.

## III. NAPHTHENE HYDROCARBONS

In many ways the dissociative ionisation of naphthene hydrocarbons is similar to the process observed when electrons interact with paraffin molecules.

Unlike paraffins, naphthene hydrocarbons have intense molecular-ion peaks; for $C_6$–$C_{11}$ isomers, the mean intensity of the molecular-ion peaks is 18.5% of the maximum.

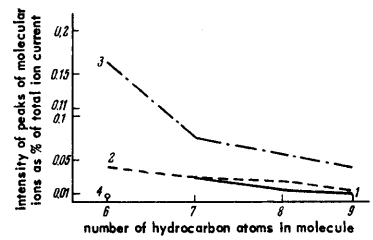



Fig. 2. Stability of $C_nH_{2n}^+$ molecular ions to electron impact:
1) monoalkenes; 2) five-membered naphthenes; 3) six-membered naphthenes; 4) ethylcyclobutane.

The stability of naphthene hydrocarbons to electron impact is greater than that of paraffins, and it does not change so sharply as the number of carbon atoms in the molecule increases. However, hydrocarbons with the empirical formula $C_nH_{2n}$ differ in their resistance to electron impact. Fig. 2 shows the intensities of the molecular-ion peaks relative to the complete ion current in the mass spectra of monoalkenes and naphthene hydrocarbons with five- and six-membered rings. The figures representing the degree of decomposition of monoalkenes and cyclopentane hydrocarbons are very close (curves *1* and *2*), but the figures for cyclohexane hydrocarbons (curve *3*) indicate that these are much more stable to electron impact.

Several qualitative relationships between the structure of the initial molecule and the intensity of the molecular-ion peaks in the mass spectra of naphthene hydrocarbons can be established: (1) the molecular peaks of hydrocarbons with a five-membered ring are, as a rule, less intense than the corresponding peaks of naphthenes with a six-membered ring; (2) *gem*-disubstituted hydrocarbons have the lowest molecular peaks; (3) with few exceptions, hydrocarbons with a branched group attached to the ring have a lower molecular peak than hydrocarbons with an unbranched group having the same number of carbon atoms.

In comparison with paraffins the dissociative ionisation of naphthene hydrocarbons is associated with a much greater probability of processes in which a hydrogen atom migrates. As a result, so-called "pseudomolecular" fragmentation ions are produced with the same mass as true molecular ions from a homologue of lower molecular weight.

Stevenson[51], who studied the mass spectra of five-membered naphthene hydrocarbons, showed that, under electron impact, the excited molecular ion rearranges to the corresponding alkene ion, which undergoes further dissociation. For example, when methylcyclopentane labelled with $^{13}C$ dissociates, the methyl group is not removed directly, but a number of successive reactions occur that lead to the formation of methyl and other, heavier fragmentation ions. Energy calculations also show that $C_5H_9^+$ ions, which are formed by the decomposition of cyclopentane hydrocarbons, correspond to alkenes with some excess energy[52]. Analysis of the mass spectra of labelled cyclohexane, methylcyclohexane, ethylcyclopentane, and methylcyclopentane[53] has shown that, for methylcyclopentane, the $^{13}C$ atom may appear on the $C_5H_9^+$ or the $CH_3^+$ ions with equal probability; consequently, on ionisation the ring is ruptured at the substituent and the open chain then dissociates.

With methylcyclohexane, the $CH_3$ group is removed only from the side-chain. $CH_3$ and $C_2H_5$ groups removed from molecular ions of ethylcyclopentane and methylcyclopentane are only partly derived from the side-chain. With methylcyclohexane and methylcyclopentane, $C_2H_4$ groups are detached mainly from the ring, and with ethylcyclopentane exclusively from the ring. The heats of formation of $C_6H_{11}^+$ ions from cyclohexane and methylcyclohexane undoubtedly show that dissociative ionisation of hydrocarbons of this type gives an ion with a cyclic and not the alkene structure which occurs with cyclopentane hydrocarbons. The differences in behaviour of cyclopentane and cyclohexane hydrocarbons on electron impact is in accord with the stereochemistry of alicyclic compounds[54]. The presence of $CH_3^+$ ions in the mass spectrum of cyclobutane also points to the possibility of isomerisation to a structure of the type $(CH_3-CH-CH_2-CH_2)^+$,[55] the formation of which is associated with ring cleavage and migration of a hydrogen atom to one of the end carbon atoms. The likelihood of this process has been confirmed by a study of deuterated cyclobutane. Isomerisation of the molecular ion of naphthene hydrocarbons competes with the process in which two bonds of the naphthene ring are ruptured and a stable radical or molecule is formed, and possibly also with the process in which a group attached to the ring is removed. The probability of these processes depends on the structure of the ring and on the nature of the substituent[56-58].

The effect of stereoisomerism on the distribution of intensities in mass spectra was observed in a study of 1,2-, 1,3-, and 1,4-dimethyl cyclohexanes[59,60]. The spectra of the *cis*- and *trans*-isomers differed materially in the number of $(M - 15)^+$ ions§. Thus, the probability of removal of a methyl group from 1,2-dimethylcyclohexane was 35% greater for the *trans*-isomers; with 1,3-dimethylcyclohexane, it was 20% greater for the *cis*-isomer; and with 1,4-dimethylcyclohexane, it was 7% greater for the *trans*-isomer.

Special features in the molecular structure of naphthene hydrocarbons are also reflected in the distribution curve of ion intensities according to the number of carbon atoms[61]. In the dissociative ionisation of five- and six-membered naphthene hydrocarbons, roughly equal amounts of $C_3H_x^+$ and $C_4H_x^+$ ions are formed, but the amount of $C_5H_x^+$ ions formed differs significantly; the proportion of these ions formed from cyclopentane hydrocarbons is 2 to 2.4 times that formed from cyclohexane hydrocarbons

## IV. MONOALKENE HYDROCARBONS

The interpretation of the mass spectra of monoalkene hydrocarbons is very complicated. The probability of the decomposition of paraffin hydrocarbons is mainly determined by the size of the molecule and the nature of the branching, but the direction of dissociative ionisation of monoalkene hydrocarbons is affected by the position of the double bond and by its interaction with nucleophilic methyl groups.

The increased resistance to electron impact of monoalkene molecules compared with alkanes means that in the mass spectra of monoalkenes the molecular ions give fairly intense peaks. The intensities for $C_6-C_{12}$ hydrocarbons vary, as a rule, between 20% and 30% of the maximal peak, and sometimes they may even exceed 40%; only a small number of isomers have molecular-ion peaks with intensities less than 10% of the maximal.

The most intense peaks of fragmentation ions in the spectra of monoalkenes are formed, as a rule, by the rupture of the bond in the $\beta$-position to the double bond. The probability of this process increases when one or two methyl groups are attached to the carbon atom in the $\alpha$--position to the double bond, and when a hydrogen atom migrates. Rupture of the bond in the $\alpha$-position to the double bond, which is frequently accompanied by migration of a hydrogen atom, competes with this process. A double bond nearer the centre of the molecule is more likely to undergo decomposition[62]. However, in this case decomposition also occurs at the $\beta$-bond; two decomposition routes are therefore possible, and the predominance of one over the other is determined by the presence or absence of branching and by the position of the branching when it is present.

The migration of hydrogen is of great importance in the dissociative ionisation of monoalkenes; this migration leads to the formation of "pseudomolecular" ions, which are identical with molecular ions of lower members of the homologous series.

The formation of $(M - 15)^+$ ions is also typical, particularly in those instances in which the methyl group is attached at the $\beta$-position to the multiple bond. Thus, this process leads to the formation of an intense $C_5H_9^+$ peak (91.3% of the maximal) in the spectrum of 4-methylpent-2--ene. The probability of removing a methyl group is increased when several methyl groups are in the $\beta$-position to the double bond.

The intensity of ion peaks associated with rupture of the $\beta$-bond largely depends on the structure of the alkyl group and can be evaluated quantitatively in some instances. The results of calculations presented in Fig. 3 show that the probability of forming ions of mass 57 is about 6 times as great for the tertiary butyl group as for the normal butyl group. When the butyl group is in the $\alpha$-position to the double bond, the peak intensity of ions of mass 57 sharply decreases. However, as for $\beta$-bond rupture, the greatest intensity is shown by the ion peak corresponding to a charged group with a tertiary carbon atom.

The same regularities have been established (less clearly, however) for hydrocarbons containing propyl and isopropyl groups. The maximal peaks corresponding to removal and formation of the $C_3H_7^+$ ion are associated with a structure containing this ion in the $\beta$-position to the double bond. The dependence of the intensity of ions of mass 43 on the structure of the propyl group and its position relative to the double bond is illustrated by the graph in Fig. 3. Normal alk-1-enes that form "paraffin-type" fragments in considerable quantity, and in particular, fragments corresponding to ions of mass 43, have not been considered.

The selectivity of dissociative ionisation of monoalkenes is reflected not only in the preferential formation of $C_nH_{2n-1}^+$ ions but also in the distribution of intensities according to the number of carbon atoms in the ions. The nature of the distribution curves is related to differences in the molecular structure of the isomers and depends on the position of the double bond in the structure of the carbon skeleton[63]. Alkenes with a normal carbon chain (Fig. 4) have one maximum on the distribution curve, corresponding to $C_3H_x^+$ ions for alk-1-enes and -3-enes, and to $C_4H_x^+$ ions for alk-2-enes and -4-enes. The shape of

§ $M$ denotes the mass of the molecular ion.

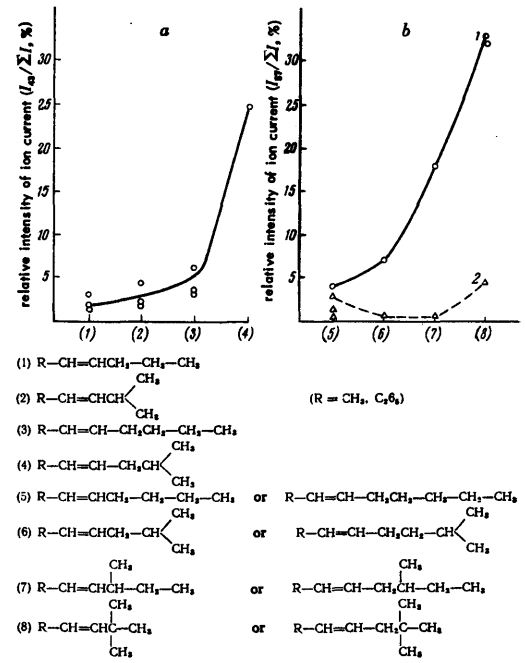



Fig. 3. Effect of structure and position of alkyl group on intensity of formation of ions of mass 43 (*a*) and 57 (*b*):
1) rupture of β-bond; 2) rupture of α-bond.

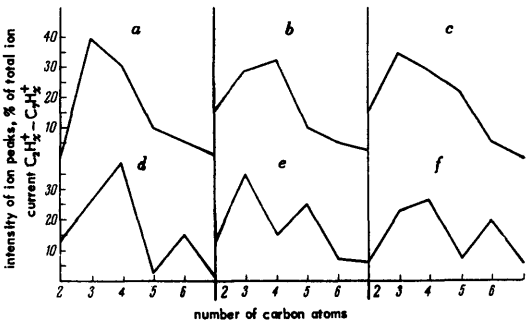



Fig. 4. Distribution of intensities against number of carbon atoms in ions for different types of monoalkenes.

the distribution curve changes as the degree of branching of the carbon skeleton increases; the formation of about equal amounts of $C_3H_x^+$, $C_4H_x^+$, and $C_5H_x^+$ ions is characteristic of mono- and di-substituted alk-1-enes (Fig. 4*c*). In addition to a maximum for $C_4H_x^+$ ions, the distribution curves of trimethylalk-1-enes show a second maximum, corresponding to $C_6H_x^+$ ions. Monomethylalk-2-enes and -3-enes show two maxima, $C_3H_x^+$ and $C_5H_x^+$. The maxima of dimethyl- and trimethylalk-2-enes correspond to $C_4H_x^+$ and $C_6H_x^+$ ions.

For a long time it was accepted that geometric isomerism of monoalkenes had no effect on the nature of the mass spectrum[64,65]. Later work showed the possibility of identifying *cis*- and *trans*-butylenes[66]. Investigation of geometric isomers showed that the differences in the mass spectra of isomers become more marked as the ionising energy of the electrons decreases, because near the ionisation threshold the greater internal energy of the *cis*-isomers compared with the *trans*-isomers facilitates dissociation[67]. This is confirmed by the values of the ionisation potentials, which are lower for the *trans*-isomers than for the *cis*-isomers[68]. Similar conclusions can be drawn from the work of Natalis[69], who showed that, when monoalkenes of the type R–CH=CHR′ (where R and R′ are methyl, ethyl, secondary propyl, or t-butyl groups), the ratio of the intensities of the molecular-ion peaks for *trans*- and *cis*-isomers increases as the size of the group increases[69]. This effect is due to liberation of excess energy on isomerisation of the *cis*-isomer with a larger alkyl radical, which promotes more rapid decomposition of the ion formed.

Arbuzov and coworkers[70] studied the mass spectra of $\Delta^3$-carene oxide (α- and β-forms), camphene oxide, and β-pinene oxide at electron-ionising energies of 50 and 9 eV, and showed that stereoisomerism has an important effect on the course of dissociative isomerisation of these molecules, changing the probability of even very "energy-consuming" processes.

Using an MX1304 mass spectrometer, the authors studied the mass spectra of the *cis*- and *trans*-isomers of pent-2-ene: at 70 eV the distribution curves for both isomers are virtually identical; at 20 eV the quantity of ions containing five carbon atoms is about 20% greater for *trans*-pent-2-ene than for *cis*-pent-2-ene, which allows identification of these isomers.

The problem of the probability of rupture of the C–H bond has been considered[71,72]. When ethylene is ionised by monochromatised electrons, $C_2H_3^+$ ions are formed; the considerable yield of ions in this process is due to the relatively low ionisation potential of the $C_2H_3$ radical (9.55 eV). Study of the mass spectra of molecules of propene and its deuterated derivatives, $CH_2CHCH_3$, $CH_3CDCH_2$, $CH_3CHCD_2$, and $CD_3CHCH_2$, has shown that $C_3H_5^+$ ions are formed with equal probability from propene and from $CH_3CDCH_2$. Thus, in dissociative ionisation the C–H (or C–D) bond is ruptured at the central carbon atom. To elucidate the mechanism of dissociative ionisation of ethylene, the mass spectra of this compound were investigated at electron energies of 10–70 eV; tetrafluoroethylene was examined in the same way[73]. It is suggested that a number of peculiarities in the mass spectra may be explained by a difference in charge distribution in molecular ions.

## V. UNSATURATED $C_nH_{2n-2}$ HYDROCARBONS

All hydrocarbons of this group with a normal carbon skeleton readily ionise on electron impact. Conjugated diene hydrocarbons are somewhat more stable. Complete ionisation is little affected by the mutual arrangement of the multiple bonds; different isomers form about the same number of ions per unit quantity of compound[14].

The structure of the carbon skeleton, in combination with the position of the multiple bonds, has a much greater effect on the character of the distribution of the ion intensities in the mass spectrum.

### 1. 2,3- and 3,4-Diene Hydrocarbons

In the mass spectra of 3,4-dienes (octa-3,4-diene, 7-methylocta-3,4-diene, deca-3,4-diene[74]), the greatest

intensity is shown by the peak of $C_5H_7^+$ ions, which are formed on rupture of the bond in the $\alpha$-position to the allene group, accompanied by elimination of a larger group. In addition, the excited molecular ion decomposes simultaneously at two C–C bonds with the formation of $C_3H_x^+$ ions. Of the ions of this type, the most intense are $C_3H_3^+$ and $C_3H_5^+$, that is, those ions with a conjugated or a cyclopropenyl structure[22].

The general nature of mass spectra of 2,3-dienes is similar to that of 3,4-dienes; the curve showing the distribution of intensity against the number of carbon atoms in the ions also has two maxima, corresponding to the $C_3H_x^+$ and $C_5H_x^+$ ions. However, the maximal intensity in the spectrum is shown not by the peak of $C_5H_7^+$ ions but by the peak of $C_5H_8^+$ ions, which are formed by decomposition of a molecular ion at the $\beta$-bond, accompanied by migration of hydrogen.

Some information on the mechanism of formation of the most intense ions in the spectrum can be obtained by examining the curves showing the effectiveness of ionisation¶. Curves for the probability of appearance of ions of mass 67, which are of maximal intensity in the spectrum of 3,4-dienes, show that changes in the intensity of the ion current as a function of electron energy can be represented virtually by a single general curve[74]; this appears to indicate that this ion is formed by the same mechanism from different 3,4-dienes. For octa-3,4-diene, 7-methylocta-3,4-diene, and deca-3,4-diene, the appearance potentials are within the range 11.6–11.9 eV. The appearance potentials of ions of mass 68, corresponding to the maximal peaks in the spectra of octa-2,3-diene and 7-methylocta-2,3-diene, are 9.2 and 9.9 eV respectively. The appearance potentials of ions of mass 67 are considerably higher, at 13.8 and 12.7 eV.[74] It would appear that the penta-1,3-diene structure can be ascribed to $C_5H_8^+$ ions formed by rupture of a $\beta$-bond accompanied by migration of hydrogen. This hypothesis is confirmed by the values of the heats of formation — 9.64 eV for the penta-1,3-diene molecular ion, and 9.68 eV for $C_5H_8^+$ ions.

The mass spectrum of 7,7-dimethylocta-3,4-diene differs markedly from the spectra of other representatives of this series[74]; its intensity distribution curve shows only one maximum, corresponding to $C_4H_x^+$ ions. The peak of $C_4H_9^+$ ions shows the maximal intensity. An explanation of the anomalous dissociation of 7,7-dimethylocta-3,4-diene is probably to be sought in the different ways various atomic groupings can affect the electron-density distribution in the molecule. The ease with which the $C_4H_9^+$ ion is formed may be due to polarisation of the C–C bond on interaction with electrons of a molecule containing a tertiary butyl group. The formation of a tertiary butyl ion is favoured by energy considerations, since the corresponding decomposition of the initial molecular ion is either exothermic or thermoneutral. Similar specificity in the decomposition of 7,7-dimethylocta-3,4-diene is in agreement with the known relationship[75], according to which the extent of removal of alkyl groups on electron impact increases linearly in the sequence: normal, iso-, and tertiary alkyl groups. This tendency, which is more pronounced in compounds with a permanent dipole, can also be traced in the

¶ In determinations on the mass spectrometer of ionisation and appearance potentials, the change in ion current is recorded as a function of the energy of the ionising electrons; what is termed an ionisation effectiveness or probability curve is then obtained, from which the ionisation potential is determined by some method.

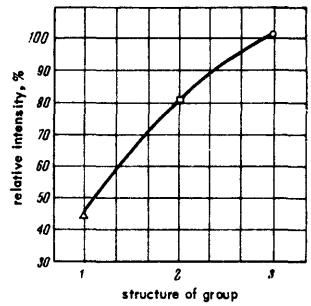



Fig. 5. Probability of decomposition at $\beta$-bond in 3,4-diene hydrocarbons:
1) normal structure; 2) iso-structure;
3) tertiary.

3,4-diene series. When a $\beta$-bond in 7,7-dimethylocta-3,4-diene is broken, $C_4H_x^+$ ions are formed. When the same bond is broken in 7-methylocta-3,4-diene, $C_3H_x^+$ and $C_2H_x^+$ ions are formed. Fig. 5 shows how the decomposition probability changes from the normal to the tertiary alkyl group. The $C_4H_9^+$ ion, which has the greatest probability of formation in the mass spectrum of 7,7-dimethylocta-3,4-diene shows the lowest appearance potential, 11.7 eV, in comparison with the ions $C_3H_5^+$, $C_3H_7^+$, and $C_5H_8^+$, for which the potentials are 15.0, 13.5, and 12.6 eV respectively.

Investigation of the mass spectra of 2,2-dimethyldeca-3,4-diene, 2,2,7,7-tetramethylocta-3,4-diene, and 4,4-dimethylpent-1-ene has permitted elucidation of the effect on dissociative ionisation of the structure of the butyl group at the $\beta$-carbon atom[76]. In the mass spectra of these hydrocarbons, the greatest intensity is shown by ion peaks formed by decomposition of a molecular ion into a butyl radical and a fragmentation ion containing multiple bonds. For 2,2-dimethyldeca-3,4-diene and 2,2,7,7-tetramethylocta-3,4-diene, the relevant ions are $C_4H_9^+$ and $C_8H_{13}^+$; for 7,7-dimethylocta-3,4-diene, $C_4H_9^+$ and $C_6H_9^+$; and for 4,4-dimethylpent-1-ene, $C_4H_9^+$ and $C_3H_7^+$. The $C_4H_9^+$ ion evidently corresponds to the butyl group in the $\beta$-position to the double bond. The probability of forming this ion, which is determined by the structure of the group, can be characterised by the ratio of the height of the $C_4H_9^+$-ion peak to the full ion current and by the dependence of this quantity on the relative weight of the tertiary butyl group in the molecule (Fig. 6). The intensity of formation of the $C_4H_9^+$ ion is a linear function of the relative weight of the t-butyl group (in the $\beta$-position to the double bond) in the molecule. It is noteworthy that the monoalkenes are also subject to this relationship (point *4* on Fig. 6). The probability that a positive charge will be found on one of the two fragments formed when the molecular ion decomposes is determined by the structure of the butyl group. The greater the relative weight of the tertiary butyl group, the greater will be the intensity of the peak of the $C_4H_9^+$ ion in comparison with the $(M - 57)^+$ ion. Thus, for 2,2,7,7-tetramethylocta-3,4-diene and 7,7-dimethylocta-3,4-diene, dissociative ionisation proceeds mainly with rupture of the $\beta$-bond between the t-butyl group and the allene grouping to give the ions $C_4H_9^+$, $C_8H_{13}^+$, and $C_6H_9^+$ respectively. The two latter ions appear to serve as sources of ions of mass 95, 81, 67, and 39, which are formed by elimination of methylene radicals. In the mass spectra of 2,2-dimethyldeca-3,4-diene, successive decomposition processes, together with rearrangements, play a much more important part than does rupture

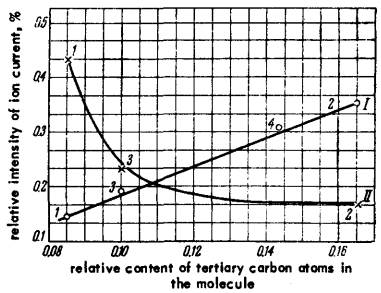



Fig. 6. Relationship between the structure of the butyl groups and the probability of formation of $C_4H_9^+$ ions. I) $I_{57}/\Sigma I_j$; II) $I_{57}/I$ ($M = 57$): 1) 2,2-dimethyldeca-3,4-diene; 2) 2,2,7,7-tetramethylocta-3,4-diene; 3) 7,7-dimethylocta-3,4-diene; 4) dimethylpent-1-ene.

of the $C_4H_9-C_8H_{13}$ bond. The peaks of rearrangement ions of empirical formula $C_nH_{2n-2}$ are very intense; the ions $C_5H_8^+$, $C_6H_{10}^+$ and $C_8H_{14}^+$ are stabilised with the migration of hydrogen. When the electron-ionising energy is reduced from 70 to 20 eV, the selectivity of decomposition greatly increases, and the quantitative ratio of the characteristic ions changes somewhat. In the mass spectrum of 2,2-dimethyldeca-3,4-diene, at electron energies of 70 eV, the probability of finding a positive charge on the $C_4H_x^+$ ions was 2.6 times greater than that for $C_8H_x^+$ ions. At 50 eV these values are fairly close, and at 20 eV the intensity of $C_8H_x^+$ ions is 1.6 times that of $C_4H_x^+$ ions. For 2,2,7,7-tetramethylocta-3,4-diene, reduction of the electron-ionising energy from 70 to 30 eV leads to a relative increase in the number of $C_8H_x^+$ ions compared with the number of $C_4H_x^+$ ions, but the intensity of the latter changes very little.

The structure of the $C_4H_9^+$ ions formed in the dissociative ionisation of the $\beta$-bond in 2,2-dimethyldeca-3,4-diene and 2,2,7,7-tetramethylocta-3,4-diene can be deduced by comparing the heats of formation of these compounds[76]. The $C_4H_9^+$ ions must obviously have a different structure, while the $C_8H_{13}$ radicals are probably identical.

The heats of formation† of $C_8H_{13}^+$ ions were 9.10 and 9.00 eV. This suggested that the $C_8H_{13}$ radicals produced when $C_4H_9^+$ ions are formed have the same heats of formation. It thus become possible to evaluate the difference in heats of formation of $C_4H_9^+$ ions, which was found to be 0.55 eV. A similar difference (0.56 eV) was observed in the heats of formation of the $C_4H_9^+$ ions produced by dissociative ionisation of iso- and n-butanes[78]. The existence of this difference shows that the $C_4H_9^+$ ions formed by electron impact differ in structure from one another in the same way as the groups forming part of the molecule under examination.

### 2. Conjugated Dienes

On electron impact, conjugated diene hydrocarbons with a normal or slightly branched chain of carbon atoms behave in the same way as alkenes and mainly from $C_3H_x^+$ and $C_5H_x^+$ ions. The mass spectra of conjugated diene hydrocarbons with a t-alkyl group at the double bond, such as:

| | |
|---|---|
| $(CH_3)_3C-CH=CH-CH=CH_2$ | ($C_8H_{14}$) |
| $(CH_3)_2(C_2H_5)C-CH=CH-CH=CH_2$ | ($C_9H_{16}$) |
| $(CH_3)(C_2H_5)_2C-CH=CH-CH=CH_2$ | ($C_{10}H_{18}$) |
| $(C_2H_5)_3C-CH=CH-CH=CH_2$ | ($C_{11}H_{20}$) |

are different[79].

In this series of compounds, stability to electron impact decreases with increase in molecular weight; the intensity of the molecular-ion peak decreases by a factor of 5 when the number of carbon atoms in the molecule increases from 8 to 11. Complete ionisation is also a function of molecular weight and increases from 1.18 for $C_8H_{14}$ to 2.74 for $C_{11}H_{20}$‡. A similar dependence was also observed with other types of hydrocarbons[80].

The main decomposition routes of molecular ions are similar for the hydrocarbons that have been examined, but the intensity of fragmentation ions depends on the ratio of methyl and ethyl groups near the tertiary carbon atom. In dissociative ionisation, alkyl or alkenyl groups, or ethylene molecules, are successively eliminated. At first, a methyl group (from $C_8H_{14}$), or an ethyl group (from other hydrocarbons) appears to be removed from the molecular ion. The maximal intensity in the mass spectra of the hydrocarbons $C_8H_{14}$, $C_9H_{16}$, and $C_{10}H_{18}$ is shown by the peaks of ions of mass 95, 109, and 123, that is, $(M-15)^+$ and $(M-29)^+$. These ions can decompose in turn to form smaller fragments. In the dissociation of $C_{11}H_{20}^+$, an ethyl group is eliminated and an ion of mass 123 is formed, which on further decomposition gives an ion of mass 81, corresponding to the maximal peak in the spectrum. The scheme in Fig. 7 illustrates the suggested routes of dissociative ionisation. This sequence of decomposition reactions has been confirmed by the presence of metastable ions.

## VI. UNSATURATED $C_nH_{2n-4}$ HYDROCARBONS

This homologous series includes enyne and triene hydrocarbons containing conjugates and unconjugated double and triple bonds[81,82].

The first member of the enyne series, vinylacetylene, is highly resistant to electron impact. The molecular-ion peak shows the greatest intensity in the mass spectrum of this compound. The most abundant fragmentation ions are formed by rupture of the C–H bond. Fragmentation ions produced by decomposition at the carbon–carbon bond are not characteristic of vinylacetylene. Appreciable decomposition at this bond only occurs when an ion of mass 26 is formed.

The introduction of a methyl group into the vinylacetylene molecule at any position somewhat lowers the stability of the molecular ion, but this ion retains its maximal intensity. Thus, the probability of decomposition of vinylacetylene is 60%, compared with 80% for methylvinylacetylene, isopropenylacetylene, and n-propenylacetylene. The probability of rupture of the molecule at a C–H bond is very high and about equal for all isomers, probably because of the formation of ions of mass 65, stabilised by conjugation. Normal hydrocarbons differ from isopropenylacetylene in showing a much more intense peak for ions of

† The heats of formation of allene hydrocarbons were calculated on the basis of the additivity of the thermodynamic functions of the structural groupings that make up the molecule[77].

‡ Complete ionisation was determined relative to benzene.

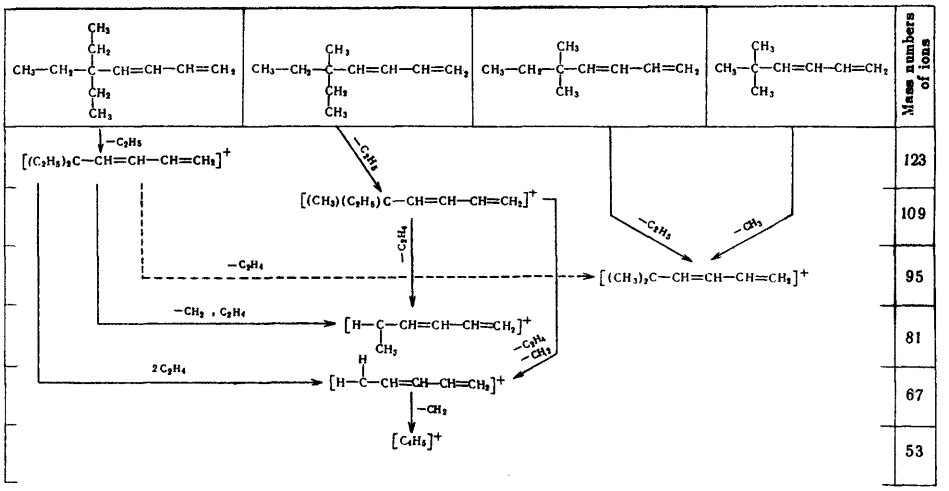



Fig. 7. Scheme of dissociative ionisation of diene hydrocarbons with a tertiary alkyl group at the multiple bond. The dotted line indicates decomposition routes not confirmed by metastable transitions. The figures correspond to the masses of the fragmentation ions.

mass 63. These ions may be produced by the following scheme:

$$C_5H_6^+ \rightarrow C_5H_5^+ \rightarrow C_3H_3^+ + (H_2).$$

Decomposition of the molecule at the bond between the methyl group and the vinylacetylene system occurs to a small extent (15–25%) with all isomers except propynylacetylene. The spectra of all the isomers show a very intense ion of mass 39, the appearance of which is due to rupture of a single C–C bond and loss of hydrogen:

$$C_5H_6^+ \rightarrow C_3H_5^+ \rightarrow C_3H_3^+.$$

The $C_3H_3^+$ ion may also be produced when a molecule decomposes at the triple bond, but its appearance in the spectrum of the branched-chain isomer, and also in the spectra of piperylene and isoprene, indicates that the first hypothesis is more likely to be correct. Examination of the spectra of the methyl derivatives of vinylacetylene shows that introduction of a methyl group adjacent to the triple bond is the factor that has the greatest effect on the stability of the molecular ion.

Investigation of the mass spectra of alkyl derivatives of vinylacetylene of higher molecular weight(pent-1-en-3-yne, hex-1-en-3-yne, oct-1-en-3-yne, and dec-1-en-3-yne) shows[82] that, as the size of the alkyl group increases, the intensity of the molecular-ion peak falls to 1.9% (in the spectrum of dec-1-en-3-yne), but the probability of decomposition increases to 99.5%. The preferential formation of two types of ions, $C_3H_x^+$ and $C_6H_x^+$ is characteristic of all the representatives of the alkylvinylacetylenes studies; these ions correspond to two maxima on the intensity distribution curves of the ions. The $C_3H_3^+$ ions appear to be formed by different mechanisms; in vinylmethylacetylene the ion of mass 39 is produced by simple rupture of a C–C bond, but for other homologues the formation of this ion is associated with the rupture of other carbon–carbon bonds of different stability and with the migration of hydrogen. This hypothesis is confirmed by the values of the appearance potential of the $C_3H_3^+$ ion[82], which are directly proportional to the size of the alkyl radical and vary from 13.0 for vinylmethylacetylene to 18.4 eV for vinylhexylacetylene. The mass spectra of vinylacetylene shows considerable abundance of ions of the type $C_nH_{2n-5}^+$, $C_nH_{2n-7}^+$, and $C_nH_{2n-4}^+$; these are produced by rearrangements in which hydrogen migrates. A specific feature of dissociation, due to the presence of conjugated bonds in the molecule, is that the carbon–carbon bond in the $\gamma$-position to the conjugated system in molecules of higher vinylacetylene homologues is the most stable to electron impact. In thermal conversions the $\beta$-bond is the least stable.

The introduction of the t-butyl group as a substituent at the double or triple bond in enyne hydrocarbons(2,2-dimethylhex-5-en-3-yne, 2-t-butylbut-1-en-3-yne, 2,2,5-trimethylhex-5-en-3-yne, 2,2-dimethylhept-6-en-3-yne, and 2-t-butylhex-1-en-3-yne)[83] materially alters the intensity distribution of the ions in the mass spectra.

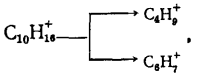
The maximum for $C_3H_x^+$ ions is less sharp because of more intense formation of $C_4H_x^+$ ions, and the maximum for $C_6H_x^+$ ions is affected by the intense formation of $C_7H_x^+$ ions. The maximal peaks in the mass spectra of $C_8H_{12}$ and $C_9H_{14}$ hydrocarbons correspond to ions that are produced by elimination of one methyl group from the molecular ion. This process leads to the formation of $C_7H_9^+$ ions from $C_8H_{12}$ hydrocarbons, and $C_8H_{11}^+$ ions from $C_9H_{14}$ hydrocarbons. In addition, an important part is played by reactions in which hydrogen and methylene groups are eliminated; as a result, the ions $C_7H_7^+$, $C_8H_8^+$, $C_6H_5^+$, etc. appear in the spectra.

The observed analogies suggest the existence of a general mechanism for the formation of fragmentation ions; this may be represented by the following scheme, which includes all ions with an intensity greater than 20% of the maximal:

$$C_8H_{12}^+ \xrightarrow{-CH_3} C_7H_9^+(100\%) \xrightarrow{-2H} C_7H_7^+(50\%) \xrightarrow{-C_2H_2} C_5H_5^+(20\%) \xrightarrow{-C_2H_2} C_3H_3^+(40\text{–}90\%),$$
$$C_7H_7^+ \xrightarrow{-CH_2} C_6H_5^+(75\%) \xrightarrow{-C_2H_2} C_4H_3^+(30\%)$$

$$C_9H_{14}^+ \xrightarrow{-CH_3} C_8H_{11}^+(100\%) \xrightarrow{-2H} C_8H_9^+(25\%) \xrightarrow{-CH_2} C_7H_7^+(30\text{–}90\%) \xrightarrow{-C_2H_2} C_5H_5^+(25\%),$$
$$C_7H_7^+ \xrightarrow{-CH_2} C_6H_5^+(25\text{–}45\%)$$

It follows from this scheme that the formation of $C_4H_9^+$ ions plays an important part only for compounds containing a t-butyl group at the double bond in the β-position to the triple bond; elimination of the t-butyl group is then favoured by the presence of an alkyl substituent in the acetylene grouping. The intensities of the peaks of $C_4H_9^+$ ions in the spectrum of 2-t-butylbut-1-en-3-yne ($C_8H_{12}$) and 2-t-butylhex-1-en-3-yne ($C_{10}H_{16}$) are 38.2 and 99.6% respectively. Decomposition of the latter compound may be represented as follows:



Any of the fragments formed may carry a positive charge with equal probability. Some stages of the hypothetical successive reactions have been confirmed by the presence of metastable ions in the peaks of the mass spectra. Thus, the mass spectrum of

$$(CH_3)_3C{-}C \equiv C{-}CH_2{-}CH{=}CH_2,$$

indicates the presence of an ion with an apparent mass of 46.6; this corresponds to the following reaction:

$$C_7H_7^+ \rightarrow C_5H_5^+ + C_2H_2.$$

Similar processes have also been observed in the dissociative ionisation of alkylbenzenes[84,85,86], cycloheptatriene[87], and spiro[2,4]cycloheptadiene[88]. Ions of mass 91 have been assigned the cyclic tropylium structure, the decomposition of which has been shown by mass spectra of samples labelled with $^{13}C$ and by energy calculations, to occur by the successive elimination of acetylene molecules.

Definite conclusions on the reactivity of organic compounds can be drawn from a comparison of the ionisation potentials for molecular ion formation. Vinylacetylene (9.9 eV) and isopropenylacetylene (10.1 eV) are the most difficult to ionise. Lengthening of the normal carbon chain adjacent to the triple bond reduces the ionisation potential to 9.4 eV (vinylmethylacetylene), and adjacent to the double bond, to 8.5 eV (propenylacetylene). Thus, the ionisation potentials of molecules change according to the position of the methyl group. It would be interesting to compare these results with those on the kinetics of reactions of vinylacetylenes that proceed by an ionic mechanism. However, information of this kind is not available in the literature.

## VII. HYDROCARBONS OF THE GENERAL FORMULA $C_nH_{2n-6}$

This group includes hydrocarbons with an open chain containing conjugated and unconjugated double and triple bond, cyclic dienes with an unsaturated alkyl group in the side-chain, as well as benzene and its homologues.

Generally, isomeric hydrocarbons show a similar distribution of intensities in their mass spectra. However, the spectra of initial representatives of homologous series of highly unsaturated hydrocarbons, such as the $C_nH_{2n-6}$ series, show considerable differences, which are associated with structural features[89]. In the first place, the stability of the molecule to electron impact varies in the same way as do, for example, the stabilities of the isomeric $C_5H_6$ enyne hydrocarbons. In the mass spectra of hexa-1,3-diyne, hexa-2,4-diyne, hexa-1,5-dien-3-yne, and benzene, the relative stability of the molecule, in the same way as the full ion current, depends largely on the structure of the initial $C_6H_6$ hydrocarbon. The benzene molecule is the most stable. Ethyldiacetylene is 20% less stable than benzene and 30% less stable than the isomeric dimethyldiacetylene. However, the molecular-ion peak is the maximal peak in the spectrum of all four compounds.

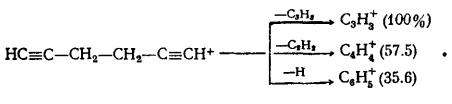
The ion-intensity distribution curves of all the $C_6H_6$ hydrocarbons investigated have two maxima, corresponding to the $C_6H_x^+$ and $C_4H_x^+$ ions[89]. The $C_6H_x^+$ group includes fragmentation ions from $(M-1)^+$ to $(M-5)^+$ in addition to molecular ions. The $(M-1)^+$ and $(M-4)^+$ ions are the most intense ions in the ethyldiacetylene spectrum. The $C_4H_x^+$ group includes ions formed from the parent ion by removal of two carbon atoms and different numbers of hydrogen atoms. Most of the ions of this group are capable of rearranging and are formed by the rupture of more than one C–C bond.

The removal on electron impact of one carbon atom with the formation of $C_5H_x^+$ ions is a process characteristic only of ethyldiacetylene. The peak of rearrangement ions of mass 64, corresponding in empirical formula to methyldiacetylene, shows the highest intensity in this group. The ability of the ethyldiacetylene molecular ion to dissociate with the formation of $C_5H_x^+$ ions appears to be related to the fact that this is the only hydrocarbon of those considered that can give fragments with rupture of a (less stable) bond in the β-position to the conjugated system.

Reduction of the energy of ionising electrons seriously affects the distribution of intensities only at energies lower than 30 eV. Near the ionisation threshold, differences in the spectra of ethyldiacetylene, divinylacetylene, and benzene are levelled out. It has been shown that the ionisation potentials of ethylacetylene, divinylacetylene, and benzene are quite similar.

### 1. 1,5-Unconjugated Diynes

Because of the absence of conjugation, hexa-1,5-diyne, hepta-1,5-diyne, and octa-1,5-diyne are relatively unstable to electron impact[90]. The main decomposition route, the formation of fragmentation ions by cleavage of the molecular ion at the bond in the β-position to the acetylene grouping, may be represented by the following schemes:




In the mass spectra of methyl- and ethyl-dipropargyl, the maximum intensity is shown by peaks of $C_7H_7^+$ fragmentation ions. The molecular-ion peaks are low (8.2 and 2.6% of the maximum). The $C_7H_7^+$ ions appear to be produced by rupture of an outer β-bond, with elimination of hydrogen or a methyl group. These ions may have a cyclic "tropylium" structure. They decompose further according to the general scheme (with elimination of acetylene molecules). In this respect, the mass spectra of 1,5-diynes

are very similar to the spectra of the isomeric $C_nH_{2n-6}$ hydrocarbons with conjugated multiple bonds.

$$[CH_3{-}C{\equiv}C{-}CH_2{-}CH_2{-}C{\equiv}CH]^+ (8\%) \xrightarrow{-C_3H_3} C_4H_5^+ (36\%)$$
$$\xrightarrow{-H} C_7H_7^+ (100\%) \xrightarrow{-C_2H_2} C_5H_5^+ (21\%) \xrightarrow{-C_2H_2} C_3H_3^+ (25\%)$$

$$[CH_3{-}CH_2{-}C{\equiv}C{-}CH_2{-}CH_2{-}C{\equiv}CH]^+ (3\%) \xrightarrow{-CH_3} C_7H_7^+ (100\%)$$
$$\xrightarrow{-H} C_8H_9^+ (21\%) \xrightarrow{-C_2H_2} C_5H_7^+ (8\%) \xrightarrow{-C_2H_2} C_3H_3^+ (45\%)$$

The decomposition of molecular ions of methyl- and ethyl-dipropargyl hydrocarbons at an inner $\beta$-bond occurs to only a slight extent, if at all. The spectrum of methyldipropargyl shows a peak corresponding to the $C_4H_5^+$ ion, which may in fact be produced in this way, but the presence of a peak of a metastable ion of mass 30.8 (0.2%) indicates that this ion is formed, at least partly, by the reaction $C_7H_7^+ \rightarrow C_4H_5^+ + C_2H_2$. The relative content of the analogous $C_5H_7^+$ ion in the ethyldipropargyl spectrum is small. The $C_5H_5^+$ ion in the ethyldipropargyl spectrum is formed mainly by the transition $C_8H_9^+ \rightarrow C_5H_5^+$ as is indicated by the presence of a metastable ion of mass 40.3. As a result of these reactions, the curves for the distribution of intensities show three maxima for hexa-1,5-diyne (corresponding to the ions $C_3H_x^+$, $C_4H_x^+$, and $C_6H_x^+$), two maxima for hepta-1,5-diyne ($C_4H_x^+$ and $C_7H_x^+$), and three maxima for octa-1,5-diyne ($C_3H_x^+$, $C_5H_x^+$, and $C_7H_x^+$). The low intensity of rearrangement ions in comparison with isomers containing conjugated bonds is a particular feature of the spectra of 1,5-diynes.

## 2. 2,4-Conjugated Diynes

The effect of conjugation on the behaviour of molecules under electron impact can be studied on the mass spectra of 2,4-diyne hydrocarbons[91] and of the alkenylvinylacetylenes[92]. It has been shown above that, in the spectra of hexa-2,4-diyne and in the spectra of the remaining isomers, the maximal intensity is exhibited by the peak of the molecular ion, which is inferior only to the benzene ion in its stability. With 6-methyl- and 6,6-dimethyl-hepta-3,4--diyne, decomposition of the molecular ion begins to play a much greater part; stability to electron impact decreases steadily from 30.9% for hexa-2,4-diyne to 5.9% for 6,6-dimethylhepta-2,4-diyne. The diversity of dissociative ionisation processes is reflected in the distribution of intensities. The curve of intensity distribution has two maxima, corresponding to the $C_4H_x^+$ and $C_6H_x^+$ ions. The maxima of the hydrocarbons $C_8H_{10}$ and $C_9H_{12}$ are displaced by one carbon atom.

The relatively low proportion of $C_3H_3^+$ ions is noteworthy and indicates that the probability of rupture of the central bond (A) in hexa-2,4-diyne is 3.7%:

$$CH_3{-}C{\equiv}C\overset{(A)}{\}}C{\equiv}CH_3.$$

In the spectra of hexa-2,4-diyne homologues, the $C_3H_3^+$ ion can be formed in a different way, namely, by rupture of the bond (B) and removal of hydrogen atoms from the propyl group.

$$CH_3{-}C{\equiv}C{-}C{\equiv}C\overset{(B)}{\}}\underset{CH_3}{CH}{-}CH_3.$$

This process results in some increase in the probability of the formation of the $C_3H_3^+$ ion; the peak intensity of ions of mass 39 becomes 7.9% of the full ion current; the proportion of $C_3H_3^+$ ions in the spectrum of 6,6-dimethylhepta--2,4-diyne relative to the full ion current is the same (7.4%). Removal of a methyl group, which is necessary for this process, meets with no difficulties, in so far as it is associated with rupture of a carbon–carbon bond in the $\beta$-position to the multiple bond.

It is very difficult to interpret the mechanism of formation of $C_4H_x^+$ ions, which are probably formed by removal of two methyl groups and migration of hydrogen atoms to a fragment with conjugated bonds. The ions $C_5H_x^+$, $C_7H_x^+$, $C_6H_x^+$, and $C_8H_x^+$ also appear to be formed by processes in which extensive isomerisation occurs. The first stage is probably effected by rupture of a bond in the $\beta$-position to the triple bond, and removal from the molecular ion of a methyl group derived from an isopropyl or t-butyl group, with the formation of $C_7H_x^+$ and $C_8H_x^+$ ions.

## 3. Alkenylvinylacetylenes

The mass spectra of the isomeric alkenylvinylacetylenes ($C_7H_8$), propenyl-, isopropenyl-, and allyl-vinylacetylene, show a similar distribution of intensities[92]. The maximal peak corresponds to the $C_7H_7^+$ ion; ions of mass 65 and 63 are also formed in large quantities. The probability, $W_Z$, of decomposition of the parent ions depends on the structure of the alkenyl group (Fig. 8). Isopropenylvinylacetylene ($W_M$ = 16.4%) is the most stable to electron impact. The intensity of the $C_7H_7^+$ ion peak is 18.3%, and the total proportion of fragmentation ions is 84.6%. The allylvinylacetylene molecular ion undergoes somewhat more extensive conversion ($W_Z$ = 81.2%); the proportion of $C_7H_7^+$ ions is 32.1%. Of the three isomers studied, propenylvinylacetylene undergoes the most extensive decomposition ($W_Z$ = 92.3%), but the quantity of ions of mass 91 and 65 is 1.9 and 2.4 times greater respectively than for isopropenylvinylacetylene.

Crotylvinylacetylene and its isomer, allylisopropenylacetylene, mainly dissociate in the same way as $C_7H_8$ hydrocarbons; the maximal intensity in their spectra is shown by the $C_7H_7^+$ ion peak; the stabilities of the parent ions are 9.8 and 7.7% respectively.

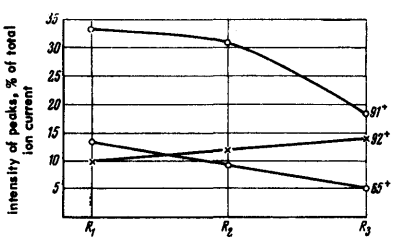
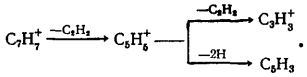



Fig. 8. Effect of structure of alkenyl group on probability of formation of molecular and fragmentation ions: $R_1$ = ($CH_3$–CH=CH–); $R_2$ = ($CH_2$=$CH_2$–$CH_2$–); $R_3$ = = (–C=$CH_2$).
|
$CH_3$

Comparison of the mass spectra of dienyne hydrocarbons with the spectra of aromatic hydrocarbons, cycloheptadiene[84,87], and alkyl vinylacetylenes[81], not only indicates certain analogies in the distribution of ion intensities, but also suggests the existence of a general mechanism for the formation of separate typical ions. Evidently, in many instances in which the hydrocarbon molecule contains seven or more carbon atoms, the carbon skeleton rearranges to a seven-membered ring, and this excited ion acts as the main source of other fragmentation ions.

It may be assumed that when dienyne hydrocarbons dissociate the $C_7H_7^+$ ion formed acquires the structure of the tropylium ion, which may then undergo cleavage according to the following scheme:



Since all seven hydrocarbon atoms of the tropylium ion are equivalent, acetylene may be eliminated in several ways, which considerably increases the probability of this process. The above-mentioned scheme for the decomposition of the $C_7H_7^+$ ion formed by the dienyne hydrocarbons $C_7H_8$ and $C_8H_{10}$ is confirmed by the presence in the spectra of these hydrocarbons of a metastable ion of mass 46.6 (intensity 0.5%).

The general scheme of dissociative ionisation becomes somewhat more complicated in higher members of the series (Fig. 9). At the first stage of decomposition, a methyl group is removed, and the most intense peak in the spectrum is formed ($C_8H_9^+$ ion); the position of the methyl group does not materially affect the peak intensity of these ions. Other fragmentation ions appear to be formed by removal of acetylene molecules, methylene groups, and hydrogen from the $C_8H_9^+$ ion.

Since fragmentation ions in the mass spectra of $C_7$–$C_9$--dienyne hydrocarbons are formed by a common mechanism, it may be that in the dissociation of $C_8H_9^+$ ions the carbon skeleton also rearranges to a seven-membered ring. These conclusions are in good agreement with the results of a study of the mass spectrum of tetrahydronaphthalene[93], in which the ions $C_8H_8^+$ and $C_7H_7^+$ are formed from the molecular ion $C_{10}H_{12}^+$ by elimination of $C_2H_4$ and $C_3H_5$ respectively. A cyclic structure can be ascribed to the ions $C_8H_8^+$ and $C_7H_7^+$ — that of cyclo-octatetraene to the first, and that of tropylium to the second.

The cyclic structure of ions in the gas phase, particularly of the tropylium ion, may explain the absence of material differences in the mass spectra of the isomers of dienyne

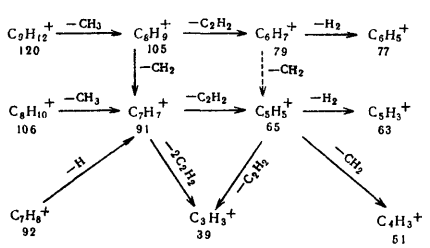


Fig. 9. Scheme of dissociative ionisation of dienyne hydrocarbons.

hydrocarbons and the similarities of these spectra to the spectra of hydrocarbons of other groups, such as alkylbenzenes, cycloheptatriene, and styrene, and also to the spectra of compounds other than hydrocarbons.

## 4. Alkylbenzenes

The most marked effects of conjugation on dissociative ionisation are shown by benzene and its homologues.

Benzene and its homologues are highly resistant to electron impact; the stability, which is 33% for benzene, decreases somewhat with increasing molecular weight, but it remains fairly high, averaging about 10% of the total ion current.

The alkylbenzenes dissociate mainly by rupture of the bond in the $\beta$-position to the benzene ring. The process includes the removal of a hydrogen atom from toluene, or from the alkyl group of other homologues, and the formation of a phenylalkyl ion. Sometimes, rupture of the $\beta$-bond is accompanied by migration of hydrogen with the formation of an alkylbenzene ion and an alkene.

Other things being equal, the mode of decomposition of the alkylbenzene molecule depends on the size and chain length of the alkyl groups attached to the benzene nucleus[84]. The main dissociation products of monoalkylbenzenes are ions formed by rupture of the side-chain at the $\beta$-bond. The size and chain length of the substituents at the $\alpha$-carbon atom also affect the distribution of intensities.

Alkylbenzenes with the structure PhC(X)(Y)Z have been used in studies on the main modes of decomposition[84]. If X and Y = H, and Z is a group larger than the methyl group, rupture of the Y–C bond is accompanied by migration of hydrogen to the ion containing the ring. The probability of this migration, which is measured by the ratio of the heights of the ion peaks for masses 91 and 92, increases with increasing chain length. If X = H, and Y and Z are groups larger than the methyl group, appreciable peaks corresponding to the rupture of single bonds appear, and, for normal groups, the intensity of these peaks is directly proportional to the number of carbon atoms in the groups lost. If X and Y are methyl groups and Z is any alkyl group, significant peaks corresponding to ions of mass 91 are observed.

The probability of dissociation at an $\alpha$-bond also varies with the substituent groups at the $\alpha$-carbon atom. Branching at the $\alpha$-carbon atom favours rupture at the $\alpha$-bond.

Rylander and Meyerson[85], and also Hanuš[87], showed that the formation of the most intense ions in the mass spectra of alkylbenzenes is associated not only with migration of hydrogen, but also in many instances with rearrangement of the carbon skeleton. Detailed study of the mass spectra of deuterated toluenes shows the the probability of removing any of the hydrogen atoms from the molecule is the same. It may therefore be assumed that the carbon skeleton of the molecular ion rearranges, and all the carbon atoms become equivalent[94,95]. Various phenomena observed when alkylbenzenes interact with electrons, and not hitherto explained, become clear if it is assumed that in dissociative ionisation one of the most intense ions in the spectra of these compounds ($C_7H_7^+$) isomerises to the highly stable tropylium ion[96]. This hypothesis explains the stabilisation of the phenyl ion when the first methyl group is introduced into benzene by rearrangement of the benzenoid ion to the symmetrical, stable tropylium ion.

The introduction of a second methyl group does not change the fundamental structure of the ion and therefore has no effect on its stability. The existence of the tropylium ion also explains the identical distribution of intensities in the mass spectra of *o*-, *m*-, and *p*-dialkylbenzene isomers.

In the dissociation of polyalkylbenzenes, most of the ions are formed by rupture of a β-bond (with the exception of examples in which the side-chains consist of methyl or ethyl groups). As the number of side-chains increases, so does the number of bonds and therefore the number of possible characteristic peaks. Rupture at the β-bond in some chains, and at the α-bond in others, can lead to appreciable formation of peaks of ions of mass 91. Dialkylbenzenes with two groups larger than the methyl group behave differently. Dissociation occurs preferentially at the centre of the longest side chain with the greatest amount of branching at the α-carbon atom. If all the side-chains are short (for example, methyl groups), rupture at the α-bond predominates over β-rupture. The maximal peak for the polymethylbenzenes usually corresponds to $(M - 15)^+$ ions. With polyethylbenzenes, two competing processes that depend on structure are observed; these lead to the formation of about equal amounts of $(M - 15)^+$ and $(M - 29)^+$ ions.

The isomeric polyalkylbenzenes, which differ only in the position of the side-chains in the ring, generally have similar spectra. The intensity distribution of the ions obtained by electron bombardment does not permit the *ortho*-, *para*-, and *meta*-positions to be distinguished.

Notwithstanding some differences in the behaviour of the polyalkylbenzenes, their mass spectra have much in common, in particular these spectra show the preferential formation of ions of mass 77, 78, 91, 92, 105, 106, 119, 120, 133, 134, 147, 148, 161, and 162; on an average these ions make up 60% of the total ion current. The spectra of all polyalkylbenzenes show the presence of ions of mass 77, 78, and 79, and also of ions of mass 91, 92, 93, 105, 106, and 107, which are formed by rupture of the side chains at α- and β-bonds. The peaks of these ions are the most specific for establishing a relationship between structure and spectra. A clearly-defined system for the identification of 34 alkylbenzenes containing up to 24 carbon atoms in the side-chain has been worked out on the basis of mass spectra[84].

We shall not deal with polycyclic aromatic hydrocarbons. It should be noted, however, that as the number of condensed rings in the molecule increases the stability to electron impact increases, and $W_M$ is a linear function of the ratio of the numbers of carbon and hydrogen atoms in compounds with different numbers of rings[97].

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Examination of the mass spectra of hydrocarbons of different homologous series has shown that, as the degree of unsaturation increases, large fragmentation ions tend to be stabilised, and this is reflected in the distribution of ion intensities (Fig. 1).[98] The distribution curve of alkanes and monoalkenes shows a single well-defined maximum, corresponding to $C_3H_x^+$ ions. A study by Coggeshall[99] of the mass spectra of alkane and alk-1-ene hydrocarbons showed that the proportion of ions containing the same number of carbon atoms ($m$) in relation to the full ion current has a maximum in the region where $m = 3-4$, the maximum of the alkene curve being displaced towards larger values of $m$.

One maximum, corresponding to $C_5H_x^+$ ions, also appears on the distribution curve of $C_nH_{2n-2}$ ions. For enyne hydrocarbons ($C_nH_{2n-4}$), the second maximum is displaced in the direction of ions of greater mass ($C_6H_x^+$). $C_7H_x^+$ ions show a high intensity in the spectra of the alkenylvinylacetylene hydrocarbons ($C_nH_{2n-6}$). Fig. 10 illustrates this tendency towards reduced formation of ions of relatively low mass as the degree of unsaturation of the hydrocarbons increases.

This tendency is not confined to hydrocarbons; it is also shown by a number of cyclic fluoro-compounds[100].

The observed displacement of maxima on the distribution curves towards heavier ions appears to be related to the possibility of stabilisation of these ions as conjugated or cyclic structures, and it is no doubt also associated with processes in which rearrangements occur[98]. $C_3H_3^+$ ions play the main part in the formation of the first maximum, corresponding to $C_3H_x^+$ ions; in the formation of the second maximum in the spectrum of $C_nH_{2n-2}$ hydrocarbons, corresponding to $C_5H_x^+$ ions, the main part is played by $C_5H_5^+$ and $C_5H_7^+$ ions and by $C_5H_8$. In dissociative ionisation of 3,4-dienes, the $C_5H_7^+$ ion may acquire the stable structure of the cyclopentyl ion, but in the case of 2,3-dienes stabilisation occurs by transfer of hydrogen to give the $C_5H_8^+$ ion. Curves showing the effectiveness of ionisation indicate that the processes that lead to the formation of $C_5H_7^+$ and $C_5H_8^+$ ions are quite general[74].

The main $C_6H_x^+$ ions in the mass spectra of $C_nH_{2n-4}$ hydrocarbons are $C_6H_5^+$ and $C_6H_7^+$. These ions are also characteristic of the first members of homologous series of the general formula $C_nH_{2n-6}$.

Attempts have been made to obtain an idea of the structure of the $C_6H_x^+$ ion from an examination of the mass spectra of benzene and its open-chain isomers[89,90,101]. The appearance potentials of fragmentation ions and their enthalpies of formation indicate isomerisation of the excited molecular ion of benzene to a structure of the type:

$$(CH_2{=}CH{-}CH{=}CH{-}C{=}CH)^+.$$

The heat of isomerisation corresponds to the excited electronic state of the benzene ion (10.3 eV) observed by the photoionisation method. The molecular ion $C_6H_6^+$, which has a linear structure with a conjugated system of multiple bonds, dissociates in turn to form the fragmentation ions $C_6H_5^+$ and $C_6H_4^+$, which are also linear in their ground states. The high degree of unsaturation of the ions $C_6H_6^+$, $C_6H_5^+$, and $C_6H_4^+$ is responsible for the high probability of processes in which hydrogen migrates and $C_6H_7^+$ ions are formed; these

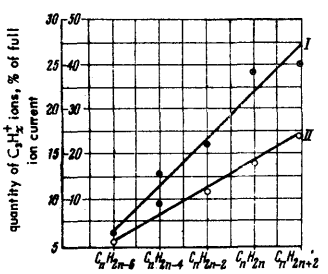



Fig. 10. Selectivity of dissociation of different types of hydrocarbons $C_8$ (*I*) and $C_{10}$ (*II*).

ions are present in the spectra of vinylalkylacetylenes to the extent of 30–40% of the total ion current. Similar processes probably give rise to the formation of ions of mass 77, 78, and 79 in the mass spectra of some alkylbenzenes[102].

Dienynes and the isomeric alkylbenzenes show maxima on the distribution curves corresponding to $C_3H_x^+$ and $C_5H_x^+$ ions that are characteristic of highly unsaturated compounds; moreover, the isomeric $C_7H_8$ and $C_8H_{10}$ hydrocarbons, such as toluene, ethylbenzene, and xylene, have a third maximum for $C_7H_x^+$ ions. For $C_9H_{12}$ hydrocarbons, this maximum is displaced in the direction of the heavier $C_8H_x^+$ ions.

To obtain a more precise idea of the structure of rearranged ions produced in the dissociative ionisation of highly unsaturated compounds, the authors determined the potentials at which $C_3H_3^+$, $C_5H_5^+$, and $C_7H_7^+$ ions were produced from alkyl- and alkenyl-vinylacetylenes. Using these potentials and the known heats of formation of the molecules, they were able to calculate the heats of formation of the ions, decide between different possible ionic structures, and establish the mechanism by which these are formed. The heats of formation of $C_3H_3^+$ ions obtained from different hydrocarbons are close to one another (292–294 kcal mole$^{-1}$); it is possible that $C_3H_3^+$ ions acquire a cyclic structure, which can be assigned to them in the same way as to quasiaromatic systems[95]. Within the limits of experimental error, the heats of formation obtained for $C_7H_7^+$ ions coincide with the heat of formation of the tropylium ion (238–240 kcal mole$^{-1}$)[86], which undoubtedly indicates that these ions have a cyclic structure.

Study of the mass spectra of toluene and its isomers, cycloheptatriene, spiro[2,4]hepta-1,3-diene, bicyclo[2,2,1]-hepta-2,5-diene[103], and 7d-cycloheptatriene[104] has shown that always the intermediate excited particle produced by dissociative ionisation is the tropylium ion, $C_7H_7^+$, from which other fragmentation ions are formed:

$$C_7H_8^+ \rightarrow C_7H_7^+ \rightarrow C_3H_5^+ \rightarrow C_3H_3^+ \text{ and } C_7H_8^+ \rightarrow C_5H_6^+.$$

The cyclic structure of ions in the gas phase, in particular the structure of the tropylium ion and its homologues, explains the absence of substantial differences between the mass spectra of isomers of dienyne hydrocarbons and also the analogies of these spectra to the spectra of alkylbenzenes, cycloheptatriene, and some compounds other than hydrocarbons.

Examination of the mass spectra of hydrocarbons containing different numbers of multiple bonds in the molecule shows that the quantity of ions produced by rearrangement increases with the number of multiple bonds in the molecule[98,105]. In other words, rearrangement ions in the mass spectra of hydrocarbons are characteristic of the degree of unsaturation and may be used for the qualitative and quantitative analysis of hydrocarbons.

A characteristic such as complete ionisation is directly related to the structure of hydrocarbons and their degree of unsaturation, and it can be used in the quantitative evaluation of interactions of ionising electrons with molecules. The available experimental results clearly prove that any attempt to express the relative ionisation cross-section of molecules as the sum of the cross-sections of the atoms would not reflect the true situation.

It has been shown that different isomers of many types of highly branched hydrocarbons containing multiple bonds differ in their complete ionisation potentials, which is probably due to wide differences in the electron-density distribution of the molecules. Thus, Table 1 gives the values for complete ionisation (relative to benzene) of isomeric diene hydrocarbons.

TABLE 1.

| $C_8H_{14}$ | Complete ionisation | $C_{10}H_{18}$ | Complete ionisation |
|---|---|---|---|
| $(CH_3)_3C'-CH=CH-CH=CH_2$ | 1.18 | $H_3C-H_2C-HC=C=CH-CH_2-CH_2-CH_2-CH_3$ | 1.81 |
| $CH_3-CH=CH-CH_2-CH_2-CH_3$ | 1.40 | $H_3C-CH_2-HC=C=CH-CH_3-C(CH_3)_2$ | 1.81 |
| $CH_2-CH_3$ | | | |
| $H_3C-HC=C=CH-CH_2-CH_2-CH_2-CH_3$ | 1.87 | $CH_3(C_2H_5)_2C-CH=CH-CH=CH_2$ | 2.19 |

Complete ionisation is certainly not always directly related to molecular weight. In the alkylbenzene homologous series, complete ionisation is a linear function of the number of carbon atoms in the molecule, but the converse is true of 1,5-diynes, as is shown by the figures in Table 2.

At present there is no explanation of this effect, and the problem remains to be solved.

The establishment of empirical relationships between the structure of the molecule and its mass spectrum leads to the elucidation of the general principles that govern dissociative ionisation. Although the apparatus necessary for the quantitative calculation of mass spectra of individual compounds is not available, quantitative characteristics common to types of compounds can be calculated. In this connection, the use of curves showing the distribution of intensities against the number of carbon atoms in ions has proved very fruitful. Since the position of the maxima on the curves is determined by the value of $z$ in the formula $C_nH_{2n+z}$, it is possible to establish the composition of a homologous series of ions specific to the hydrocarbon groups whose spectra are unknown[106]. On the other hand, the curves reflect special features in the molecular structure of isomers; this has been used as a basis for the determination of cyclopentane and cyclohexane hydrocarbons in complex mixtures, and for the identification of types of monoalkenes[61,63].

Mathematical treatment of the relationship between the characteristic intensity and the degree of unsaturation of different types of hydrocarbons has permitted the calculation of the corresponding mass-spectrometric coefficients for naphthene hydrocarbons with different numbers of condensed rings in the molecule. As a result, the lack of experimental calibration coefficients has been no hindrance to the development of methods of determining paraffins and naphthenes present in high-boiling petroleum fractions[107,108].

TABLE 2.

| Number of carbon atoms in molecule | Complete ionisation | |
|---|---|---|
| | alkylbenzenes | 1,5-diyne hydrocarbons |
| 6 | 1 | 1 |
| 7 | 1.4 | 0.92 |
| 8 | 1.8 | 0.78 |

Correlations in the mass spectra of hydrocarbons have also been used in a new method of analysis, chromato--mass-spectrometry, developed by Tal'roze and co-workers[109-115].

These workers studied the problem of the minimum amount of mass-spectrometric information necessary for the unambiguous identification of individual compounds. It was shown that any individual compound reaching the mass spectrometer from the chromatograph can be identified with a high degree of probability, provided that two types of ratios of mass-spectrometric peaks are known in the 39–45 range of mass numbers. This enabled a mass spectrometer of low dispersion and resolving power to be used. The above authors have developed methods for the analysis of hydrocarbons and their derivatives by chromato-mass--spectrometry.


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