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Application of the Mass Spectrometry of Negative Ions to Organic Chemistry

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Experimental work on the dissociative capture of electrons by organic molecules is surveyed, and the main processes involved in the interaction between such molecules and electrons are discussed. Special attention is paid to the specificity of mass spectra. The mass spectrometry of negative ions not only supplements traditional mass spectrometry but also enables several novel problems to be solved. A list of 100 references is included.

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I. INTRODUCTION

The formation of negative ions by interaction between electrons and molecules has been less investigated than has the formation of positive ions, although experimental study of the capture of electrons by molecules with mass-spectrometric recording of the negative ions was begun as early as the 1930s, at the same time as study of the formation of positive ions. This was due to the absence of reliable methods for the mass-spectrometric investigation of negative ions and the experimental difficulties of working with such ions. However, discovery of the ability of negative ions to excite vibrational and rotational levels of molecules in radiation-induced reactions, by the elastic and inelastic resonant scattering of electrons, has caused the recent increase in the number of publications on the formation of negative ions.

The study of negative ions has shown a general tendency for increasingly complicated species to be investigated. Whereas in the 1950s simple diatomic and triatomic molecules were examined almost exclusively, at the present time increasing attention is being paid to complex molecules, including those of organic compounds. It is also planned to use mass spectra of negative ions to solve structural and analytical problems of organic chemistry.

Progress in the theory of resonances accompanying interaction between electrons and molecules[1-6], as well as development of electron-impact spectrometry[7], increased the interest taken in the capture of electrons by molecules with the formation of negative ions. At the same time advances in experimental technique promoted the development of improved methods of examining negative ions. The monochromatisation of electrons[8,9], enhancement of the sensitivity of the recording apparatus, and the development of objective methods for calibrating the scale of electron energies[10,11] have enabled reliable and reproducible values to be obtained for the appearance potentials of negative ions and the effective yield of ions from electron–molecule interaction.

Several monographs[12-15] and reviews[16,17], dealing broadly with the problems of studying negative ions, have appeared recently. However, they do not devote much space to organic compounds, although the negative-ion mass spectrometry of organic compounds is acknowledged to be a promising and important trend.

The present Review examines published work on the dissociative capture of electrons by organic molecules with the formation of negative ions. It does not cover the large group of publications on the mass spectrometry of negative ions[18-25] in which the experimental technique of the traditional mass spectrometry of positive ions is imitated. While recognising the importance of this work, we must note that the ambiguity in interpreting processes leading to the formation of negative ions in these cases diminishes the theoretical value of the results and prevents their practical exploitation.

II. FORMATION OF NEGATIVE IONS. RESONANCES IN SCATTERING CROSS-SECTIONS OF ELECTRONS WITH MOLECULES

The main processes involved in the formation of negative ions by single collisions can be expressed

$$1)\quad AB + e \rightarrow (AB)^* + e \rightarrow A^- + B^+ + e$$

$$2)\quad AB + e \rightarrow (AB)^- \rightarrow \begin{cases} A^- + B \\ B^- + A \end{cases} \text{(dissociative electron capture)}$$
$$\begin{cases} (AB)^* + e \text{ inelastic} \\ (AB) + e \text{ elastic} \end{cases} \Big\} \text{ electron scattering}$$

The first process consists in dissociation of a molecule, excited by electron impact, into two fragments with opposite charges. The dependence of the effective yield of ions on the energy of the electrons is the same as for the formation of positive ions, i.e. a smooth increase in yield with increase in energy from the threshold at which ions appear to a maximum (when the energy of the electrons exceeds the threshold by a factor of 3–4), which is followed by a slow decrease in yield.

The second process–capture of an electron by the molecule with formation of a short-lived negative molecular ion $(AB)^-$—is a resonance process occurring within a narrow range of electron energies (0.01–2 eV). If the law of the conservation of energy permits, the molecular ion may dissociate into negative splinter ions: i.e. dissociative capture of electrons takes place. If dissociation is impossible, the existence of the negative molecular ion ceases with the ejection of the electron (autoionisation),

and elastic or inelastic resonance scattering of electrons is observed†. Autoionisation (autodetachment of an electron) always takes place, whether or not accompanied by dissociation of the negative molecular ion (dissociative electron capture), and in the former case competes with the latter process. The mean lifetime of the negative molecular ion with respect to autoionisation τ is a characteristic of the process of electron capture by a molecule.

The mechanism of establishment of the temporary bond between molecule and electron may be that on impact the electron loses its energy in the electronic excitation of the target molecule and finds itself in a bound state which has an energy below that of the excited state of the target. The electron cannot be detached while the molecule remains in an excited state; the lifetime of the resonant state is relatively long, 10^{-13}–10^{-14} s. Such resonances have been termed "electronically excited Feshbach resonances"[4].

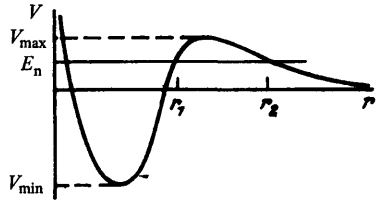


Figure 1. Typical interaction potential of electron and molecule (atom) for shape resonance: E_n is the energy of the trapped electron, and r_2–r_1 the range of effective action of the barrier.

Another mechanism for formation of temporary negative ions, without necessarily entailing excitation of the target molecule, involves the so called shape resonances (single-particle resonance, if electron capture takes place without excitation of the molecule, and electronically excited shape resonance). With shape resonance the bond between electron and molecule is established by the combined action of polarisation and exchange forces attracting the electron to the molecule and of the centrifugal force of repulsion when the incident electron possesses angular momentum relative to the target. The electron may be trapped in a quasi-discrete level of the potential well (Fig. 1) separated from the continuous spectrum by a centrifugal barrier. The reverse ejection of the electron takes place by tunnelling through the barrier. In contrast to Feshbach resonances, the parent state of the target has a lower energy, and ejection of the electron with transition of the molecule to the parent state (for the given resonance) is not energetically forbidden. The lifetime before autodetachment of the electron is determined for shape resonances by the width of the centrifugal barrier and the depth of the quasi-discrete level, and lasts 10^{-14}–10^{-15} s.

The so called vibrationally excited Feshbach resonance is due to electron capture at vibrationally excited levels of the molecular ion. If the electron affinity of the molecule is positive, the ground state of the negative molecular ion lies below that of the molecule. However, the vibrational energy of the negative ion can exceed the electron affinity of the molecule, and the vibrational levels of the ion will lie above the ground state of the molecule. An electron having positive energy may then be trapped at vibrationally excited levels of the ion. The kinetic energy of the electron is converted directly (without electronic excitation) into nuclear motion of the ion. Vibrationally excited Feshbach resonance is due to breakdown of the Born–Oppenheimer principle[4]. The lifetime before autoionisation of negative molecular ions formed with such resonance is extremely long in polyatomic molecules, reaching several tens of microseconds[15,16].

With vibrationally excited Feshbach resonance autoionisation of the negative ion may be prevented by a change in molecular configuration on conversion into the ion. A fairly long time would elapse before the configuration of the molecule–electron system would return to or approach the configuration before electron capture, from which autoionisation is possible.

Dissociative electron capture can thus be regarded as occurring in two stages: capture of an electron by a molecule with formation of a negative molecular ion (having a lifetime τ_a characteristic of a given process) is followed by dissociation along possible paths. According to O'Malley[3] the effective formation cross-section of negative ions in dissociative electron capture by diatomic molecules is given by the formula

$$\sigma = e^{-\rho} C \frac{\Gamma_a}{\Gamma_d} \exp\left[\frac{{}^1/_2\Gamma_a^2 (E-E_0)^2}{{}^1/_4\Gamma_d^2}\right]; \quad \rho \approx \frac{\tau_d}{\tau_a},$$

where $\Gamma_a = \hbar/\tau_a$ is the so called autoionisation resonance width, τ_a the mean lifetime before autoionisation, Γ_d the observed width at mid-height on the peak effective yield of negative ions, τ_d the mean time of dissociation of the molecular ion into a negative ionic fragment and a neutral atom (radical), E the energy of the electron, E_0 the energy characteristic of the given process (closely similar to the energy corresponding to the maximum yield of ions), and $\hbar$ is Planck's constant.

This formula can be written $\sigma = \sigma_{cp} e^{-\rho}$, where σ_{cp} is the cross-section for capture of the electron by the molecule and $e^{-\rho}$ the probability of dissociation into a negative ion and a neutral fragment. The term $e^{-\rho}$ is called the "survival factor", since it determines the proportion of molecular ions that have avoided autoionisation and have dissociated with the formation of stable (for the given experiment) negative ions. The dependence of τ_d on the reduced mass of the fragments that scatter on dissociation may be responsible for the so called isotope effect in

† Reverting to the mass spectrometry of negative ions by the technique used for positive ions (fixed electron energy 50–70 eV, no control of the energy distribution of electrons in the ion source), we note that two processes—dissociative capture of electrons by molecules and the dissociation of molecules into ion-pairs—yield negative ions under these conditions. Dissociative capture takes place with electrons that have lost part of their energy in collisions with the walls of the ionisation chamber and with electrons produced by secondary emission. The relative contributions by these two processes to the ion current depend on the material and the design of the ionisation chamber, i.e. on the experimental conditions, which are difficult to standardise. This explains the poor reproducibility of the mass spectra of negative ions obtained in this way[18,19,26].

the measurement of the formation cross-section of negative ions[3,27]. However, Γ_d also depends on the reduced mass, and the change in ion-formation cross-section on isotopic substitution is determined not only by the survival factor[3,28,29].

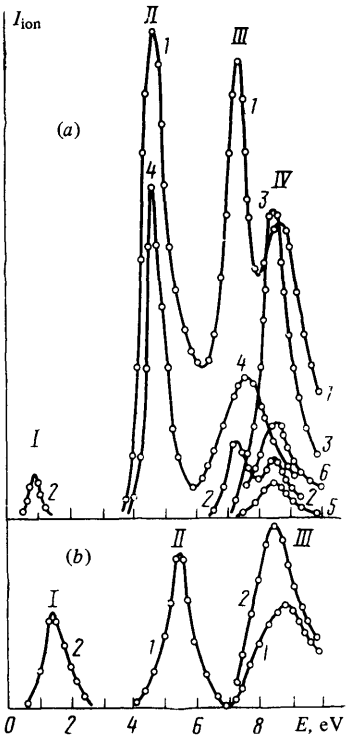


Figure 2. Curves of effective yields of negative ions for: (*a*) dimethyl sulphide: 1) S^-; 2) SCH_3^-; 3) SCH_2^-; 4) CH_3^-; 5) CH_2^-; 6) SH^-; and (*b*) di-isopropyl sulphide: 1) S^-; 2) $SC_3H_7^-$.

According to O'Malley[3] the above formula for σ is applicable also to polyatomic molecules, if all the quantities in it are assigned to separate normal vibrations of the molecule. A consequence of the multichannel breakdown of negatively charged polyatomic molecules is the formation of ions having different m/e ratios in the same resonance range of electron energies. While remaining within the same resonance region, the positions of the maximum yields of individual ions on the scale of electron energies E_{max} coincide neither with each other nor with the energy corresponding to maximum formation of the parent molecular ion. It follows from O'Malley's formula

$$E_{max} = E_0 - {}^1/_8\Gamma_d^2\left(\frac{d\rho}{dE} + \frac{1}{E}\right); \quad \frac{d\rho}{dE} > 0$$

that E_{max} for each channel of formation of an ionic fragment depends on $d\rho/dE$, which in turn is determined by the direction of dissociation of the molecular ion ($\rho = \tau_d/\tau_a$).

Another reason for the difference in values of E_{max} for ionic fragments may be the formation of ions having different m/e ratios by consecutive decomposition of the type

$$(ABCD)^{\cdot-} \xrightarrow{CD\cdot} (AB)^{\cdot-} \rightarrow A^- + B\ .$$

The AB^- ions are formed in a vibrationally excited state, and some of them, for which the energy of excitation exceeds the energy of the A–B bond, dissociate into A^- and B. With increase in the energy of the trapped electron (within the resonance range) the number of AB^- ions capable of dissociating increases: i.e. the maximum yield of A^- ions will shift to higher electron energies relative to the maximum yield of AB^- ions. This can be illustrated by the curves for the effective yield of $SC_3H_7^-$ and S^- ions from di-isopropyl sulphide[30] (Fig. 2); the latter ions are probably formed by the breakdown of excited $SC_3H_7^-$ ions. (Raising the temperature in the ionisation chamber, as would be expected, increases the yield of S^- ions.)

It is appropriate here to examine the energy balance of dissociative electron capture

$$AB + e \rightarrow (AB)^{\cdot-} \rightarrow A^- + B\ .$$

Denoting the appearance potential of A^- ions by Aptl(A^-), the energy of dissociation of A–B by D(AB), and the electron affinity of an A atom (radical) by EA(A), we have

$$\text{Aptl}\ (A^-) = D\,(AB) + EA\,(A) + \epsilon_{tr} + \epsilon_{ie}$$

where ϵ_{tr} is the translational energy of the reaction products and ϵ_{ie} the energy of internal excitation of the fragments. The corresponding expression for B^- is

$$\text{Aptl}\ (B^-) = D\,(AB) + EA\,(B) + (\epsilon'_{tr} + \epsilon'_{ie}).$$

In a series of papers Franklin et al.[31-33] obtained a formula linking the mean translational energy $\bar{\epsilon}_{tr} = \epsilon^*/\alpha N$ with the excess energy ϵ^* (the energy exceeding the threshold for dissociative electron capture: $\epsilon^* = \epsilon_{tr} + \epsilon_{ie}$) and the number of vibrational degrees of freedom of the molecule N, in which α is a semi-empirical parameter having the value 0.42 for such processes.

The chief experimental methods for studying resonances in the scattering of electrons by molecules are currently electron-impact spectroscopy and the mass-spectrometric investigation of resonant processes in the formation of negative ions. The former is characterised by relatively high energy-resolving power, which ensures accurate determination of the position of resonant levels and the possibility of recording short-lived negative molecular ions. The variety of experimental methods in electron-impact spectroscopy (each of which has its advantages) can be regarded as a virtue, permitting a flexible approach to solving a problem. Information on the energy levels of atoms or molecules is obtained by analysing the changes in momentum and energy of electrons in single collisions between electrons in the primary beam and atoms or molecules. A review has been published on electron-impact spectroscopy[7].

Negative-ion mass spectrometry involves a more reproducible technique: the rigid requirements of mass spectrometry do not permit wide variation in the design of the ion source or the experimental conditions. However, the mass analysis of the ionic fragments and the absence of a background of potential scattering (only resonance processes are recorded) make it possible to examine resonance phenomena in the interaction of electrons with complex molecules, as yet inaccessible to electron-impact spectroscopy.

Experimental procedure in mass-spectrometric investigations has been described repeatedly in reviews and monographs[12-17,34]. Study of dissociative electron capture by recording negative ions is undertaken with the usual mass spectrometers (static or time-of-flight). Changing to the registration of oppositely charged ions for the investigation of dissociative electron capture requires, of course, not only simple reversal of fields (electric and magnetic), but also several design modifications of the ion source (connected mainly with the need to monochromatise the electron beam and calibrate the electron-energy scale), and the sensitivity of the instrument must be improved. However, the conversion of commercial mass spectrometers into instruments suitable for investigating dissociative electron capture by molecules with the formation of negative ions is technically not a complicated task[11,35,36].

III. DISSOCIATIVE CAPTURE OF ELECTRONS BY ORGANIC MOLECULES

The studies considered in the present Section are not all equivalent with respect to the experimental technique used. Different workers employed apparatus of different sensitivities; different reference points were used for calibrating the electron-energy scale; and the energy distribution of the electrons was not strictly the same. In several studies attention was paid mainly to measuring the appearance potentials of the negative ions, without determining the positions of the maximum yields of ions on the electron-energy scale; in other cases the efficiency of the emission of ions was not determined[37,38]. Despite the differences in experimental technique, however, the values cited in the present Section from various publications are mutually comparable. The deviations (±0.2–0.3 eV for the positions of the resonance peaks on the energy scale, and ±20% for the relative intensities of the ions) are not so significant as to support the currently held view that data on dissociative electron capture by molecules show poor reproducibility[39-42].

1. Alkanes

Several papers have been published on dissociative electron capture by alkane molecules[37,39,43-45]. Methane exhibits two peaks representing the formation of ions having appearance potentials of 8.3 eV (H^-, CH_2^-) and 9.3–9.6 eV (H^-, CH^-, CH_2^-). Two peaks have been observed with ethane (8.3 and 9.2 eV), whereas the spectra of propane, n-butane, and isobutane contain one resonance peak corresponding to the formation of ions having appearance potentials of 7.6–7.8, 7.8, and 7.4–7.5 eV respectively[39]. The greatest probability of formation is found with H^- ions ($\sigma \simeq 10^{-19}$ cm^2). A comparatively large formation cross-section was noted for the ions CH_2^- and CH^- ($\sim 10^{-19}$ and $\sim 10^{-20}$ cm^2) from methane, CH_2^- from ethane, and CH_3^- from propane and isobutane ($\sim 10^{-20}$ cm^2). The formation cross-sections of C_2H^-, $C_2H_3^-$, and CH_4^- ions are of the order 10^{-21}–10^{-22} cm^2.[39]

In the spectrum of tetradeuteromethane the probability of formation of D^- ions is greater, while that of CD_2^- ions is smaller than those of the corresponding processes in methane[45,46]. The ratios of the formation cross-sections are $\sigma(H^-)/\sigma(D^-) = 0.8$ and $\sigma(CH_2^-)/\sigma(CD_2^-) = 25$.

2. Alkenes, Polyenes, and Alkynes

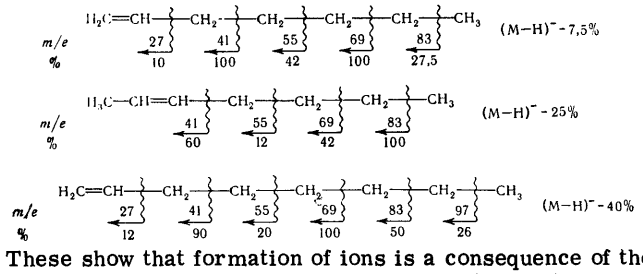
The effective-yield curves for negative ions resulting from the interaction of electrons with ethylene, propene, and isobutene molecules[39] indicate the existence of two resonance peaks of electron capture in the range of electron energies 7–13 eV. The ion-formation cross-section does not exceed 10^{-19} cm^2 in ethylene and isobutene, and 10^{-20} cm^2 in propene and but-1-ene (Table 1). The energy of excitation of the first Rydberg state ($^1B_{3u}$) of the ethylene molecules is 7.25 eV,[47] and peaks of negative ions from dissociative electron capture in ethylene can be assigned to the decomposition of $C_2H_4^-$ ions, which are formed by a mechanism of Feshbach resonances of Rydberg states of the molecules. The lowest state of the $C_2H_4^-$ ion recorded by transmitted-electron spectroscopy is responsible for the peak of resonant scattering of electrons with its maximum at 1.76 eV.[48] A molecular ion in this state breaks down without dissociation into ionic fragments. In propene a small peak due to C_2H^- ions (cross-section 10^{-21} cm^2) has been recorded with its maximum at 3.8 eV.[39]

Table 1. Appearance potentials (Aptl) of ions and their intensities*.

Ethylene			Propene			Isobutene		
ion	intensity	Aptl ± 0.3, eV	ion	intensity	Aptl ± 0.3, eV	ion	intensity	Aptl ± 0.3, eV
H^-	430	7.6;9.7	H^-	325	7.7	H^-	585	7.8
CH^-	174	7.3;8.7	CH_2^-	48	6.1;7.3; 7.8	CH^-	43.5	7.9
CH_2^-	131	8.8	CH_3^-	20	—	CH_2^-	130	7.8
C_2^-	60	10.4	C_2H^-	77	2.6;6.3; 7.6	CH_3^-	57.5	7.4
C_2H^-	520	7.1;10,0	$C_3H_3^-$	18	—	$C_3H_6^-$	58	5.8;7.6
$C_2H_3^-$	19.8	—	$C_3H_5^-$	250	5.9;7.6	—	—	—

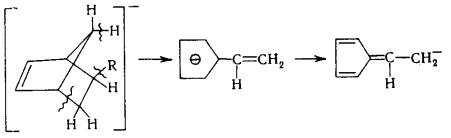
* Unit intensity corresponds to $\sigma = 10^{-22}$ cm^2.

The dissociative electron-capture mass spectra of hept-1-ene, hept-2-ene, and oct-1-ene are given below as schemes representing the rupture of the negative molecular ions together with the relative intensities at maximum effective yields of the ions, which correspond to electron-energies of ~8 eV:



These show that formation of ions is a consequence of the rupture of carbon–carbon bonds with addition of the electron to the fragment containing the double bond. However, the absolute formation cross-sections of the ions are small ($\sim 10^{-21}$ cm^2).[49]

Among 5-substituted bicyclo[2,2,1]heptene derivatives norbornene itself and 5-methylnorbornene have the simplest spectra[50,51], with three resonance peaks due to formation of the cyclopentadienyl anion $C_5H_5^-$ and one peak due to each of the ions $C_7H_7^-$, $C_4H_3^-$, and $(M - H)^-$. Formation of the $C_5H_5^-$ ion can be attributed to retrodiene decomposition, whereas the $C_7H_7^-$ ion is formed by the simultaneous rupture of carbon–hydrogen and carbon–carbon bonds:



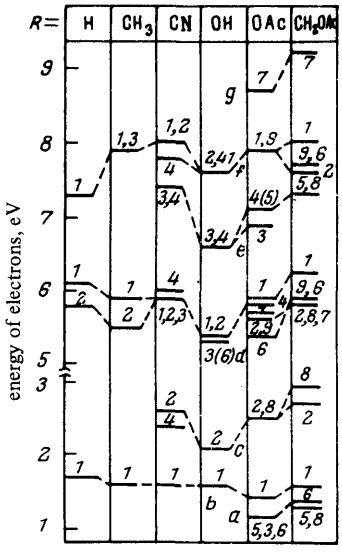


Figure 3. Positions of maximum effective yields of negative ions on scale of electron energies for interaction of electrons with norbornene and its 6-substituted derivatives: 1) $C_5H_5^-$; 2) $(M-H)^-$; 3) $RC_2H_2^-$; 4) R^-; 5) $COOCH_3^-$; 6) $COCH_3^-$; 7) C_2HO^-; 8) (M – Ac); 9) (M – OAc).

The process of lowest energy—emission of $C_5H_5^-$ ions at 1.6–1.7 eV—corresponds to the trapping of an electron in the first vacant π^* orbital. A second maximum, at 5.6–5.8 eV, can be assigned to Feshbach resonance involving the first triplet state of the molecules. The third peak, at 7.2–7.3 eV, is due to Feshbach resonance with excitation of Rydberg states of the molecule. Fig. 3 shows that the positions of maximum emission of ions vary with the substituent. For example, the low-energy peaks due to ions having m/e = 59.43 (levels *a*) are present in the spectra of molecules containing a CH_3COO group. The *a* level implies a single-particle resonance involving the lowest unoccupied orbital localised on the acetoxyl group. Levels *c* and *e* can be attributed to electron capture with $n \rightarrow \pi^*$ and $n \rightarrow \sigma^*$ excitation: they are observed when the substituent contains a heteroatom with a lone pair of electrons. Thus data on the fragmentation of the negative molecular ions supplements the spectral characterisation of the molecule over a wide energy range.

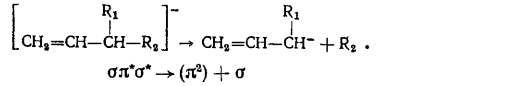
Molecules of polyenes—5-methylhepta-1,3,6-triene, octa-1,3,7-triene, 6-methylnona-2,4,7-triene, 9-methylundeca-1,3,7,10-tetraene, and 3,8-dimethyldeca-1,4,6,9-tetraene—form negative ions on interaction with slow electrons, with three ranges of electron energies in which the trapping of electrons is followed by dissociation of the negative molecular ion[52,53]. The first two ranges, corresponding to maximum effective yields of ions at 2.5 and 6 eV, consist of three mass lines due to C_2H^- (m/e = 25), or $(M - H)^-$, and $(M - C_2H_3)^-$ ions, whereas in the third range, in which the maximum effective yields are grouped around 8 eV, the mass spectrum comprises six lines. The effective formation cross-section of ions corresponding to the maximum intensity is $\sim 10^{-20}$ cm^2.

It is significant that negative ions are formed predominantly by the simple rupture of bonds, without the rearrangements inherent in the breakdown of positive ions. As a consequence, the spectra of structural isomers are sharply differentiated, as is evident in the mass spectra of 5-methylhepta-1,3,6-triene and octa-1,3,7-triene (Table 2).

Table 2. Values of m/e and relative intensities (% of I_{max}) in mass spectra of negative ions of trienes.

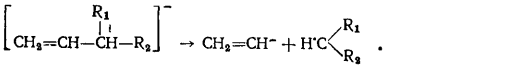
m/e	107	81	67	55	53	51	41	27	25
5-Methylhepta-1,3,6-triene	28	76	—	42	100	80	14	57	80
Octa-1,3,7-triene	15	—	100	—	40	13	20	—	20

The formation of negative ions was interpreted as $\sigma-\pi^*$ excitation with capture of the extra electron in an antibonding σ^*-orbital. This accompanied by β-cleavage relative to the double bond with retention of the negative charge on the fragment. Two electrons in σ^*- and π^*-orbitals form a new π^2-orbital of the negative ion, while the electron of the σ-orbital becomes a σ-electron of the neutral fragment:



$$\sigma\pi^*\sigma^* \rightarrow (\pi^2) + \sigma$$

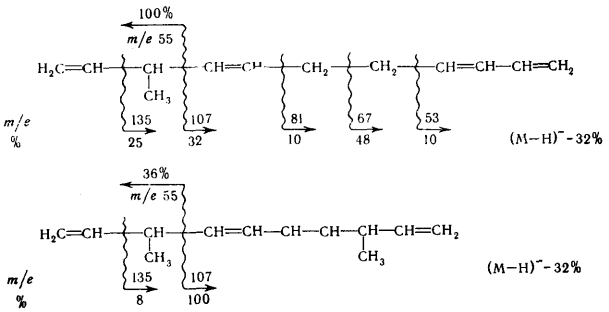
Such a process corresponds to ions of m/e 81 and 55 in the spectrum of 5-methylhepta-1,3,6-triene, and to ions 41 and 67 in that of octa-1,3,7-triene. The $\sigma\pi^*\sigma^*$-state of a negative molecular ion may lead to α-cleavage, when the negative charge will be concentrated on the fragment containing the double bond:



$$\sigma\pi^*\sigma^* \rightarrow (\sigma^2) + \pi$$

In the spectra of these trienes such cleavage corresponds to intense ions having m/e 53. In addition to the ions formed by α- and β-rupture, dissociation of a carbon–carbon bond with detachment of two hydrogen atoms results in ions with m/e 107, 51, and 25—$(M - H)^-$, $C_4H_3^-$, and C_2H^-. The intensity of the rearranged 41 peak in the spectrum of the methylheptatriene is low. The 67 peak is absent, although quite intense in the spectrum of the octatriene, whereas the latter contains no peak at 55. The corresponding ions cannot be formed by simple rupture of carbon–carbon bonds. The absence of an 81 peak from the spectrum of the octatriene is due to the fact that this fragment cannot be formed by either α- or β-cleavage: it would require either γ-rupture or α-rupture with transfer of the extra electron to the $\cdot CHR^1-R^2$ fragment, which obviously does not occur.

Three resonance ion-emission peaks are observed in dissociative electron capture by 9-methylundeca-1,3,7,10-tetraene and 3,8-dimethyldeca-1,4,6,9-tetraene. Their mass spectra can be represented by a scheme of α- and β-cleavage with the mass number and relative intensities (as percentages of the maximum intensity):



A characteristic feature of the spectra of negative ions of polyenes is the necessary presence of fragments containing an intact system of conjugated double bonds.

Fig. 4 shows the mass spectra of positive and negative ions of isomeric tetraenes. It is very significant that the slight differences in the mass spectra of positive ions of isomers bear no clear relation to the structure of the molecules. As a consequence, mass spectra cannot be used to assign a test material to a particular isomeric form. On the other hand, the mass spectra of negative ions resulting from dissociative electron capture by polyenes enable the structural formula to be determined without the use of other information.

Among compounds containing a triple bond only acetylene and propyne have been investigated. Their spectra reveal a large formation cross-section for $(M - H)^-$ ions ($\sim 10^{-18}$ cm^2).[37,39,44,53,54]

3. Benzene and its Derivatives

Electron-impact spectroscopy indicates[48,55,56] the capture of electrons by benzene molecules in the lowest unoccupied π^*-orbital (single-particle resonance, $^2E_{1u}$ state of $C_6H_6^-$) with electrons of energy 1.2–1.7 eV (various authors give differing values). The average lifetime of $^2\Sigma_{1u}$ $C_6H_6^-$ ions is short ($<10^{-6}$ s), and the ions do not appear in the mass-spectrometric investigation of benzene. Sanché and Schulz[48] observed an additional peak, in the range 4–6 eV in the spectrum of electrons scattered by benzene molecules, and ascribed it to the capture of electrons in a b_{2g}-orbital of the molecule. Negative ions are not observed in this range of electron energies, although dissociation of $C_6H_6^-$ with the formation e.g. of $C_6H_5^-$ ions is energetically possible. Resonance peaks of negative ions are recorded at electron energies of 7–12 eV.[39,40]

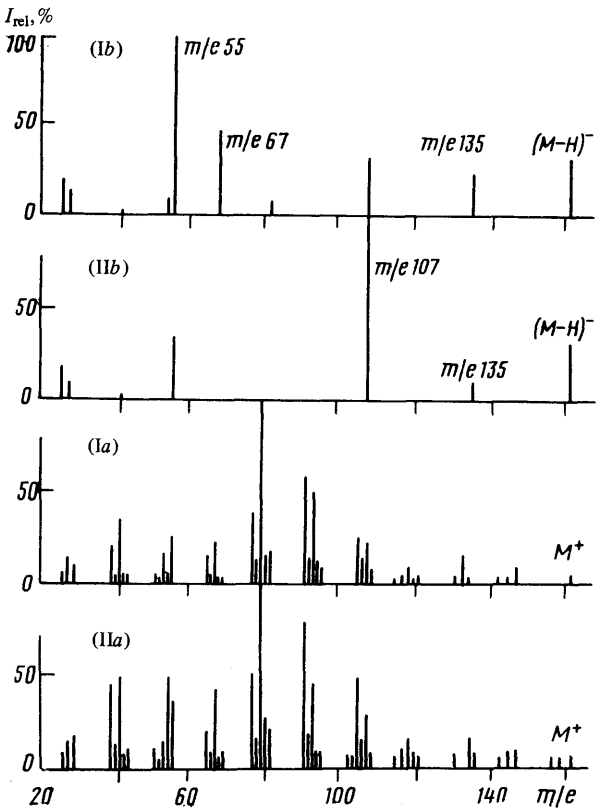


Figure 4. Mass spectra of: *a*) positive ions; *b*) negative ions of: I) 9-methylundeca-1,3,7,10-tetraene; II) 3,8-dimethyldeca-1,4,6,9-tetraene.

Table 3. Effective yields of negative ions (at maximum emissions of ions)*.[40]

Ion	Benzene	Toluene	Ethylbenzene	Isopropylbenzene	Butylbenzenes n-	s-	t-
$(M-H)^-$	100	46	24	23	41	22.2	15.7
$(M-2H)^-$	0.25	11	—	—	—	—	—
$(M-3H)^-$	1.1	0.3	2.0	—	2.0	—	—
$C_6H_5^-$	—	—	—	0.3	—	20	5.7
$C_6H_7^-$	—	—	—	4.6	2.2	—	0.3
$C_7H_7^-$	—	$(M-H)^-$	0.37	—	34	210	0.35
$C_6H_5^-$	$(M-H)^-$	0.9	6.7	21.6	6.1	15	70
$C_6H_3^-$	1.3	0.55	—	—	—	—	—
$C_4H_3^-$	7.8	0.74	—	—	—	—	—
C_2H^-	80	9.0	0.6	20.5	10.5	12	21
C_2^-	1.4	2.2	—	—	—	—	—
CH_2^-	—	—	—	—	—	—	52

* Unit intensity corresponds to $\sigma = 10^{-21}$ cm^2.

Table 3 shows that the main process in dissociative electron capture by benzene molecules is detachment of a hydrogen atom with localisation of the electron on the phenyl radical ($\sigma \simeq 10^{-19}$ cm^2 [39]). Formation of C_2H^- ions has a similar cross-section, whereas the effective yield of $C_2H_5^-$, $C_4H_3^-$, and C_2^- ions is one-tenth of this.

The minimum energy for the reaction $C_6H_6 + e \rightarrow C_6H_5^- + H$ to occur is 2.2 eV on the assumption that the electron affinity of the $C_6H_5^{\cdot}$ radical is 2.2 eV [57] and the energy of rupture of a carbon–hydrogen bond in benzene is $D(C_6H_5\text{–}H) = 4.4$ eV.[58] At the maximum yield of $C_6H_5^-$ ions (8 eV) the excess energy $E^* = 5.8$ eV is distributed between internal excitation of the $C_6H_5^-$ ion and translational energy of the reaction products. According to Franklin's formula $\bar{\epsilon}_{tr} = 5.8/0.42 \times 30 = 0.45$ eV, so that the total store of vibrational energy of the $C_6H_5^-$ ion is ~5.4 eV, which is 3.2 eV greater than the electron affinity of $C_6H_5^{\cdot}$. Even regarding this formula as a very crude approximation and bearing in mind the large excess energy of formation of the ion, we may conclude that $C_6H_5^-$ ions are formed in an autoionised state, i.e. with a sufficient store of vibrational energy for detachment of an electron.

Direct proof of the instability of $C_6H_5^-$ ions with respect to ejection of an electron has been obtained[59,60] by measuring the mean lifetimes τ with respect to autoionisation of $C_6H_5^-$ ions from C_6H_6 and of $C_6D_5^-$ ions from C_6D_6 as respectively 47 ± 5 and 37 ± 5 μs. The effect of isotopic substitution on τ is probably due to a change in the overlap of the atomic vibrational wave-functions of the ion and of the corresponding neutral radical when hydrogen atoms are replaced by deuterium atoms. The C_2H^- ions were stable, which was not surprising, since their formation involved a lower excess energy, and part of the vibrational energy was associated with the neutral fragment. Two values were obtained for the isotope effect in the formation cross-section of the ions: $\sigma(C_6H_5^-)/\sigma(C_6D_5^-) = 1.18$ [61] and 5.4.[59] It is difficult to explain such a marked discrepancy, far exceeding possible experimental errors, but later work may reveal its cause.

Alkylbenzenes form negative ions[40] in the same range of electron energies as with benzene, though the maximum effective yields are slightly displaced (up to 0.3 eV) to higher energies. The maximum peaks in the dissociative electron-capture mass spectra of s- and t-butylbenzenes correspond to the ions $C_7H_7^-$ and $C_6H_5^-$ respectively. With the other alkylbenzenes investigated, the formation of $(M - H)^-$ ions is the most probable. The presence of an alkyl substituent changes the ways in which the molecular ion breaks down: thus $C_5H_5^-$, $C_5H_4^-$, $C_4H_3^-$, and $C_4H_2^-$ ions are present only in the mass spectra of benzene and toluene, but in alkylated benzenes both the formation cross-section of $(M - H)^-$ and C_2H^- ions and the total ion current at the maximum effective yield of ions have diminished. The latter does not apply to s-butylbenzene, with which the total ion current is increased by the large cross-section for formation of $C_7H_7^-$ ions, which exceeds that of $(M - H)^-$ ions from benzene by a factor of 2.1.

Study of dissociative electron capture by certain monosubstituted benzene derivatives has shown[51] ion-formation cross-sections of ~10^{-19} cm^2, with the main processes of dissociation of the molecular ion coinciding with those in alkylbenzenes. The molecules C_6H_5X and C_6H_4XY, where X and Y respresent substituents possessing high electron affinities, exhibit effective cross-sections of dissociative electron capture larger by factors of 10^2–10^3, with several electron-capture resonance peaks. In chlorobenzene and bromobenzene the first peak with formation of halide ions is located at 0.6 eV; the capture of thermal electrons by iodobenzene molecules results in the appearance of iodide ions[62–64].

A long-lived negative molecular ion ($\tau = 40$ μs; energy of electrons ~0 eV) has been recorded in nitrobenzene[5]. The first peak in the electron-energy range 1–2 eV represents NO_2^- and $C_6H_5^-$ ions ($\sigma \simeq 2 \times 10^{-16}$ and 10^{-19} cm^2 respectively).[64,65] Maximum yields of the ions— NO_2^- ($\sigma = 2 \times 10^{-16}$ cm^2), $C_6H_5NO^-$ (3×10^{-19}), $C_6H_4NO_2^-$ (2.5×10^{-18}), $C_6H_5^-$ (1.2×10^{-18}), CN^- (1.3×10^{-18}), NO^- (6×10^{-20}), $C_6H_5N^-$ (1.2×10^{-18}), and m/e = 43, 42, 41 (10^{-18} cm^2)— are obtained with electrons of energy 4 eV. Furthermore, peaks due to O^-, C_2H^-, and m/e 92 are situated with their maximum at 5 eV, and to OH^-, C_2H^-, and $(M - H)^-$ ions at 7 eV (cross-section ~10^{-19} cm^2).

Two resonance peaks due to NO_2^- ions were observed in *o*- and *m*-nitrotoluenes[64]. It is interesting that the two peaks are of equal intensity in the *ortho*-isomer, but in *m*-nitrotoluene the intensity of the first peak with its maximum at 1.1 eV is only 15% of that of the second peak (maximum at ~3.3 eV). The energy of the resonant states has diminished by 0.3 eV in *o*-nitrotoluene. Molecular ions of *m*-chloronitrobenzene and *m*-iodonitrobenzene decompose along two channels with the emission of NO_2^-, Cl^-, and I^- ions[66]. In benzonitrile not only the molecular ion ($\tau \simeq 5$ μs) but also CN^- ions (two peaks) are observed with peaks due to $C_6H_4^-$ and $C_6H_4CN^-$ ions.

4. Fused-ring Aromatic Hydrocarbons

The only ionic fragment formed in naphthalene, fluorene, anthracene, and phenanthrene results from detachment of a single hydrogen atom from the negative molecular ion. Maxima on the effective-yield curves of $(M - H)^-$ ions from naphthalene and fluorene coincide with the corresponding maximum for benzene, but dissociative electron capture takes place over a wider range of electron energies than does the formation of $C_6H_5^-$ ions from benzene. Interaction of electrons with fluorene molecules gives rise to a further process of formation of $(M - H)^-$ ions with a maximum at 1.6 eV, which has been regarded[67] as corresponding to formation of a fluorenyl anion.

It is interesting that the dissociative electron-capture spectra of anthracene and phenanthrene are different. The effective-yield curve for $(M - H)^-$ ions from anthracene exhibits an inflexion, which is less strongly marked with phenanthrene. Furthermore, non-dissociative capture of electrons (having energies close to zero) is observed in anthracene. As a result, a negative molecular ion of anthracene is formed with a finite lifetime with respect to autoionisation ($\tau = 21$ μs). The formation cross-section of $(M - H)^-$ ions from anthracene and phenanthrene is ~10^{-17} cm^2, and the cross-section of non-dissociative electron capture by anthracene molecules is 10^{-16} cm^2. Hence negative-ion mass spectrometry may be used to detect anthracene present as impurity (up to 0.5%) in other compounds, including phenanthrene.

5. Cyclopentadiene and Metallocenes

On interaction with electrons cyclopentadiene loses a hydrogen atom and is converted into a stable $C_5H_5^-$ anion, with a maximum probability for electrons of energy 2.05 eV.[41] A further resonance process is observed at 8 eV, leading to the formation of $C_5H_5^-$, $C_5H_4^-$, $C_5H_3^-$, $C_3H_3^-$, and

C_2H^- ions with respective intensities of 3.6%, 1.6%, 1.2%, 11%, and 20.5%. At 2.05 eV the intensity of the $C_5H_5^-$ peak reaches 100%.[41]

In dissociative electron capture by ferrocene, cobaltocene, manganocene, and nickelocene molecules[68] $C_5H_5^-$ ions are formed in the range of electron energies 0.5–1.0 eV, with widely varying formation cross-sections. Ferrocene and cobaltocene have the smallest cross-section (3×10^{-21} cm^2), that of nickelocene is larger by a factor of 25, and manganocene occupies an intermediate position. The effective formation cross-section for $C_5H_5^-$ ions is relatively small, that of $C_5H_5Co^-$ ions (at 0.7 eV) is 1.8×10^{-20} cm^2, and the non-dissociative capture cross-section of thermal electrons with formation of $CoC_{10}H_{10}^-$ ions is 6×10^{-18} cm^2.

Study of dissociative electron capture by dicyclopentadienyl dichlorides $M(C_5H_5)_2Cl_2$, where M = Ti, Zr, Hf, revealed in all cases the formation of molecular ions by the capture of thermal electrons, the probability of ion formation being greater the heavier the metal M.[69]

6. Five-membered Heterocycles

Five-membered heterocycles form negative ions in two ranges of electron energies, in both of which the mass spectrum contains a relatively large number of lines[41,70]. An exception is pyrrole, with which only $(M - H)^-$ ions are observed in the first, low-energy range. Table 4 reveals greater fragmentation of molecular ions in the second than in the first range, with an increase in the relative probabilities of formation of ions having low m/e values and a decrease in the yield of $(M - H)^-$ ions. The isotope effect in the cross-section for formation of the latter ions from thiophen is 1.4 and 12.1 in the first and second resonance peaks. In both resonance regions these $(M - H)^-$ ions are in autoionisation states, with $\tau(SC_4H_3^-) = 240$ and 220 μs respectively.

Table 4. Effective yields of negative ions in two resonance peaks of selenophen, thiophen, furan, and pyrrole*.[26,70,41]

X Electrons, eV	Se 4.9–5.3	S 5.3–5.7	O 5.5	Se^{II} 7.8–8.1	S^{II} 8.3–8.5	O^{II} 9.8–10	NH^{II} 8.9–10.2
$XC_4H_3^-$	220	144	53	2.1	79	8.7	160
XC_2H^-	100	100	80	336	650	19.3	81.5
XH^-	195	157	0.1	63	136	0.2	—
X^-	320	130	—	2400	87	—	—
C_4H^-	0.4	14.4	10	61	150	3	—
$C_3H_3^-$	—	—	22.2	—	11.5	3.7	153
C_2H^-	5.5	8.5	18.7	83	100	2.5	—

* Unit intensity corresponds to $\sigma = 10^{-21}$ cm^2.

Differences between the dissociation of negative molecular ions in the first and second ranges of electron capture have been examined[26] on α-deuterated thiophen and selenophen. It was found that $(M - H)^-$ ions of the first peak were formed by the detachment of either an α- or a β-hydrogen atom, with relative probabilities of 1 : 3. The same relative probabilities applied to the formation of C_2H^- ions.

In thiophen the decomposition channels of the molecular ion with formation of $(M - H)^-$ and SC_2H^- are independent in the sense that the degradation $(M - H)^- \rightarrow SC_2H^-$ does not take place. An isotope effect is observed in the formation cross-section of $(M - H)^-$ ions, but the yield of SC_2H^- ions is almost unaffected by deuteriation of the molecule[59]. Formation of SH^- ions takes place almost exclusively by migration of hydrogen atoms from the β-position. In the second peak the formation of $(M - H)^-$ and SC_2H^- ions also corresponds to two processes, involving detachment of hydrogen atoms from α- and β-positions, but the relative probabilities of the two processes are about the same as with the first peak.

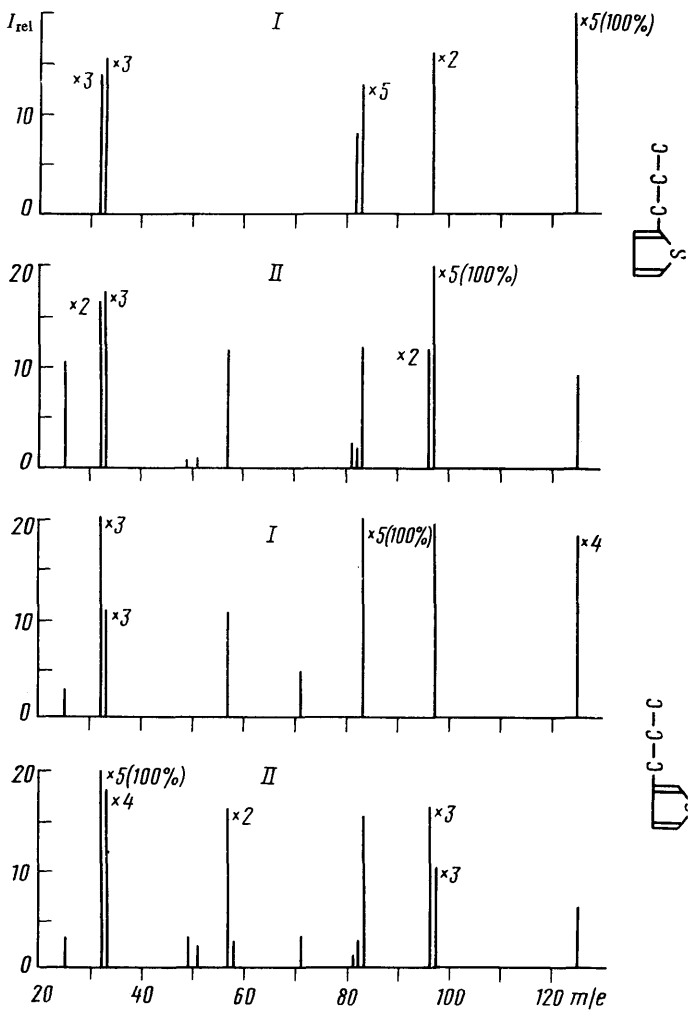
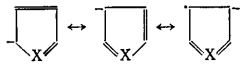


Figure 5. Mass spectra of negative ions of 2- and 3-propylthiophens: I) first range of electron capture (electrons of energy ~5 eV); II) second range (~8 eV).

Breakdown of alkylthiophen molecular ions of the first peak (maximum yields of ions at ~5 eV) is closely similar to that of the corresponding molecular ion of thiophen. Substitution has little effect on the modes of decomposition

of the molecular ion. For example, detachment of alkyl radicals from a β-position is more probable than the detachment of α-substituents, and the relative probabilities of formation of $(M - H)^-$, H^-, and C_2H^- ions in α- and β-alkylated thiophens can easily be interpreted qualitatively in terms of the relative probabilities of different modes of dissociation of the molecular ion of thiophen. In the second peak substitution has a more significant effect on the breakdown of molecular ions, which is apparent in the absence of consistency in the relative probabilities of individual modes of dissociation of molecular ions of thiophen and of alkylthiophens (Fig. 5).

While dissociative electron capture by five-membered heterocycles shows a general similarity, the most closely similar processes evidently occur with selenophen and thiophen. Formation of ions of the heteroatom does not occur in furan, although O^- ions are readily formed with other oxygen-containing compounds, and the line due to hydroxide ions is weak. Pyrrole does not exhibit NH^- ions at all. The vacant *d*-orbitals of sulphur and selenium enable the structures



to be included among those of the negative molecular ion. Such structures are impossible with furan and pyrrole. They are probably responsible for formation of the X^-, XH^-, XCH^-, and XC^- ions characteristic of thiophen and selenophen but absent from the dissociative electron-capture spectra of other five-membered heterocycles.

With indole and several alkylindoles the only negative ions that could be observed were $(M - H)^-$. Breakdown of the benzene ring, as found in fused aromatic hydrocarbons, does not occur on electron capture. The maximum effective yields of these ions from indole and 2,3,7-trimethylindole occur with electron energies of 1.55 and 1.65 eV respectively. Substitution at the nitrogen atom, as e.g. in 1,2,3,7-tetramethylindole and 1,7-propanoindole, eliminates this low-energy resonance formation of ions. From this it was deduced[41] that $(M - H)^-$ ions are formed from indole and from 2,3,7-trimethylindole as a result of rupture of the nitrogen–hydrogen bond.

7. Pyridines and their *N*-Oxides

The scattering of electrons by pyridine molecules reveals two states of short-lived molecular ions at electron energies of 1.2 and 1.6 eV,[71] or 0.84 and 1.3 eV according to other workers[56]. Single-particle shape resonances are probably involved, corresponding to electron capture at vacant π-orbitals of the molecule. Study of dissociative electron capture by pyridine and alkylpyridines[40] showed that, in contrast to benzene and alkylbenzenes, the two states of negative molecular ions break down with the formation of negative ionic fragments. The first resonance peak of ionic emission with maxima at ~4.5–4.6 eV corresponds to NC_3^-, C_2H^-, C_2^-, and in pyridine also $NC_5H_4^-$ ions. The mass spectrum of the second peak (at ~8 eV) contains more lines, and the modes of dissociation of the molecular ion are largely similar to those for benzene, only a large relative probability of formation of ions with destruction of the ring is observed (such ions as $^-N{:}CH.C{:}CH$ and $^-N{:}C{:}CH_2$).

The isotope effect in the formation cross-section of $(M - H)^-$ ions from pyridine in the second peak is also closely similar to that in benzene: $\sigma(NC_5H_4^-)/\sigma(NC_5D_4^-) = 6 \pm 0.5$. The isotope effect is smaller in the first peak (3.1 ± 0.5). The probable reason is the shorter mean lifetime with respect to autoionisation of the molecular ion of pyridine produced by trapped electrons of energy 8 eV than by those of energy 4.5 eV. The $(M - H)^-$ ions are formed in an autoionised state, with $\tau(NC_5H_4^-) = 60$ μs (8 eV) but $\tau(NC_5D_4^-) = 68$ μs (8 eV): i.e. deuteriation increases the lifetime, in contrast to the case of benzene[60].

The Reviewers have investigated the mass spectra of the *N*-oxides of pyridine and of the three isomeric alkylpyridines. The oxygen atom has a substantial effect on processes involved in the dissociative capture of electrons, resulting both in the appearance of new excited states of the negative molecular ions and in a change in the possible channels of decomposition of the molecular ions. Five main states of excited molecular ions, denoted *a*–*e*, were distinguished by the positions of the maximum effective yields of ions on the electron-energy scale and by the modes of decomposition. The low-energy state *a* was represented in the spectrum of pyridine *N*-oxide by lines due to the ionic fragments $(M - H)^-$, $NC_3H_3^-$, $NC_3H_2^-$, and NC_3^-, with peaks of relatively low intensities, while the maximum efficiency of formation is observed with electrons of energy 0.2–0.5 eV.

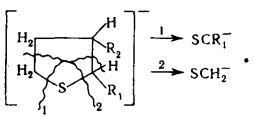
Molecular ions in state *b* break down with ejection of a C_2H_3 fragment (ions with m/e 68). The maximum of the resonance peak on the emission curve of $(M - C_2H_3)^-$ ions is located at 0.8 eV. The most intense peaks in the spectrum of pyridine *N*-oxide are due to ions formed by the dissociation of ions in state *c*, the maximum yield being observed at 3–3.2 eV. The breakdown of molecular ions in this state is represented by peaks due to $(M - H)^-$, $(M - OH)^-$, $(M - OCH)^-$, O^-, OH^-, and ions with $m/e = 64$. State *d* of molecular ions is apparent from the effective-yield curves for O^- ions, which show two poorly resolved peaks: the first (at 3.2 eV) corresponds to state *c*; the second peak (at 4 eV) indicates the existence of yet another state of molecular ions decomposing with the emission of O^-. Decomposition of molecular ions in the high-energy state *e* gives a mass spectrum rich in peaks, although their relative intensities are comparatively low. Besides the purely "pyridine" ions $NC_3H_2^-$, NC_3H^-, $NC_2H_2^-$, NC_2H^-, and C_2H^-, the fragments $(M - OH)^-$, $(M - CO)^-$, $(M - CHO)^-$, O^-, and OH^- are observed, as well as ions having m/e ratios of 41, 42, 49, and 68, whose maxima occur in the range of electron energies 8–9 eV. Replacement of hydrogen by methyl does not give rise to new states of the negative molecular ions, only some redistribution of the probabilities of different decomposition channels.

8. Sulphides

Sanché and Schulz[48] studied hydrogen sulphide molecules by transmitted-electron spectroscopy, and with electrons of energy 2 eV observed shape resonance (single-particle resonance) corresponding to capture of electrons in the lowest unoccupied $4a_1$ orbital of the molecules. Electronically excited Feshbach resonance with excitation of the lone pair of electrons on the sulphur atom takes place when the electron energy reaches ~4 eV. In the range of electron energies $\geqslant 8$ eV resonant states of H_2S^- are observed with two Rydberg electrons. The positive molecular ion H_2S^+ is the grandparent state for such states of negative ions.

Studies have been made[73-75] on dissociative electron capture by a large group of aliphatic sulphides, disulphides, and thiols. Fig. 2 illustrates effective-yield curves for negative ions of dimethyl sulphide. The resonance peaks of ion emission are denoted by Roman numerals in order of increasing energy. Peak (I) represents only SCH_3^- ions, the peak (II) CH_3^- and S^- ions. If peak (I) is assigned to single-particle resonance, and peak (II) to electronically excited Feshbach resonance with formation of a molecular ion in the $(b_1)(b_1^*)^2\ ^2B_1$ state (point group C_{2v}, with b_1 the orbital occupied by electrons of the lone pair on the sulphur atom, and a_1 the first vacant orbital), it becomes clear why CH_3^- ions ($^1A_1$) are absent from peak (II), since SCH_3^- ions (ground state ^1A, point group C_{3v}) and the $CH_3^{\cdot}$ radical in the ground state $^2A_{1g}$ do not correlate with the B_1 state of the molecular ion. Peaks (III) and (IV) of dimethyl sulphide represent S^-, SCH_3^-, CH_3^-, CH_2^-, and $(M-H)^-$ ions, and probably result from the dissociation of resonant states, of the corresponding (by Feshbach resonance) Rydberg states of the molecule. Dissociative electron capture in the other dialkyl sulphides investigated is similar to that in dimthyl sulphide, but peaks (III) and (IV) are replaced by one broad resonance peak (Fig. 2).

In contrast to aliphatic sulphides, the negative molecular ions of cyclic sulphides (thiophans) have corresponding mass spectra containing intense lines due to $(M-H)^-$ ions, the relative yield of which increases with the length of the alkyl group. With electrons of energy 8 eV decomposition occurs according to the scheme[75]



Ions corresponding to single-particle resonance were not detected, which is fully explained by the fact that the energy available is insufficient to rupture two bonds on addition of an electron to the antibonding orbital of the sulphur–carbon bond.

Alkyl benzyl and phenyl sulphides are interesting in containing both a benzene ring and sulphur–carbon bonds, so that dissociative electron capture by their molecules can be compared with corresponding processes in benzenes and in dialkyl sulphides. Benzyl ethyl, methyl, and propyl sulphides, as well as butyl, ethyl, methyl, and propyl phenyl sulphides, have been studied[51]. With electrons of energy 0–10 eV three peaks can be distinguished, as in dialkyl sulphides. With alkyl benzyl sulphides the first peak (single-particle resonance) is characterised by a very large ion-formation cross-section ($\sigma \simeq 10^{-15}$ cm^2), and the ions SR^-, CH_3^- (in benzyl methyl sulphide), and $C_6H_5CH_2^-$ are observed in the second peak. The absence of $C_6H_5CH_2S^-$ ions indicates that the second peak is due to excitation of the lone pair of electrons on the sulphur atom. The large formation cross-section of SR^- ions in the second peak ($\sim 10^{-17}$ cm^2) is explained by formation of the benzyl radical in the $^2B_1$ state: $(C_6H_5CH_2SR)^{-*} \rightarrow C_6H_5CH_2^{\cdot}\ (^2B_1) + SR^-\ (^1A_1)$. The ions $(M-H)^-$, SH^-, S^-, SR^-, and $C_6H_5CH_2S^-$ are observed in the third resonance peak.

Thus the benzene ring in alkyl benzyl sulphides does not trap electrons, the overall pattern of dissociative electron capture being determined by the molecular orbitals of the sulphur–carbon bonds. The ion-formation cross-sections are larger than with dialkyl sulphides. The benzene ring has a more significant effect in alkyl phenyl sulphides, since processes characteristic of alkylbenzenes are observed (the ions C_2H^-, $C_4H_3^-$, $C_5H_5S^-$, and C_2H^- in the third peak—Fig. 6). Increase in size of the alkyl radical makes the mass spectrum more "sulphidic": thus the formation only of C_2H^- ions in the spectrum of butyl phenyl sulphide indicates the presence of the benzene ring; the other ions are formed by processes analogous to the fragmentation of dialkyl and alkyl benzyl sulphides.

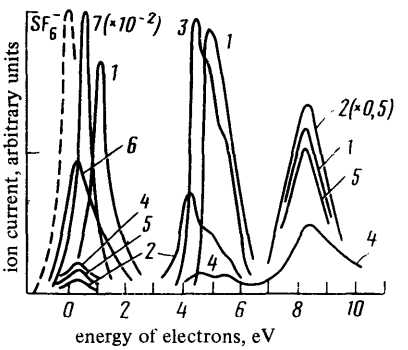


Figure 6. Effective-yield curves for negative ions from methyl phenyl sulphide: 1) S^-; 2) SCH_3^-; 3) CH_3^-; 4) $C_6H_5^-$; 5) SH^-; 6) SC_2H^-.

The existence in alkyl phenyl sulphides of a combined system comprising the ring π-electrons and the lone pair of electrons of the sulphur atom leads in the second peak to the appearance of complicated effective-yield curves, as would be expected. Fig. 6 shows that several closely spaced states of the molecular ion undergo decomposition, with the appearance of "bulges" and inflexions on the effective-yield curves of the ions.

9. Carbonyl Compounds

Study of the scattering of monoenergetic electrons on carbon monoxide have shown the existence of several Feshbach resonances in the range of electron energies 10–12.2 eV [76] and single-particle resonance at 1.7 eV. [77] The latter type of resonance has been observed also in acetaldehyde, acetone, acetophenone, benzophenone, and benzaldehyde (at 1.2, 1.2, 0.95, 0.75, and 0.72 eV). [78] In acetone it is not accompanied by formation of negative ions. When acetone molecules interact with electrons, negative ions appear as a broad peak resulting from the superposition of several resonance peaks over the range of electron energies 7–11 eV. [79,80]

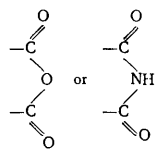
Formation of chloride ions in chloroacetone is energetically possible by dissociation of a single-particle resonant state. The maximum yield of Cl^- ions is situated at 0.6 eV. Capture of thermal electrons by hexafluoroacetone yields negative molecular ions that are long-lived with respect to autoionisation ($\tau > 10^{-6}$ s). The introduction of fluorine atoms evidently lowers the energy of the π-orbital of the carbonyl group to such an extent that the electron affinity of the molecule becomes positive.

The main processes producing negative ions in aldehydes and ketones are rupture of a β-carbon–carbon bond relative to the carbonyl group and the formation of homologous ions $CH{:}C.O^-$ (*m/e* 41), $CH_3.C{:}C.O^-$ (55), etc:

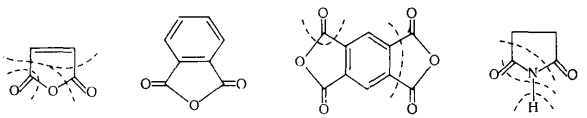
$$\left[R^1{-}C(=O){-}CH_2{-}R\right]^- \leftrightarrow R^1{-}C(=O){-}CH_2^- \leftrightarrow R^1{-}C(O^-){=}CH_2 .$$

Formation of the ions O^- and OH^- (with rearrangement of bonds), hydrocarbon ions $CH_2{:}CH^-$ (*m/e* 27), and $R_1{-}CO^-$ ions has also been observed[80].

Two resonance peaks of ion emission have been found by Cooper and Compton[81] both in acetic anhydride and in acetyl peroxide. The first resonance peak represents CH_3COO^- ions (maximum yields at ~1 and at ~0 eV respectively), and the second peak CH_3^- and O^- ions (maxima at ~7 and at ~6.6 eV). These workers also investigated the capture of electrons by molecules containing the configuration

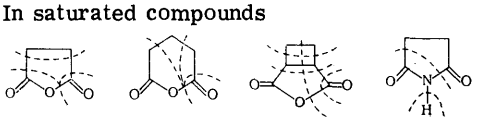


as part of a five- or six-membered ring. Unsaturated compounds



τ = 250 μs τ = 330 μs τ = 8000 μs τ = 43 μs

trap thermal electrons with the formation of long-lived molecular ions (the mean lifetimes before ejection of the electron are indicated under the above structural formulae). In saturated compounds



only the formation of short-lived molecular ions is observed. The most probable process entailing dissociation negative molecular ions of the above compounds is ejection of carbon monoxide with formation of $RCOO^-$* ions, which are metastable with respect to detachment of an electron. Similarly metastable CO_2^-* ions are also observed, as well as O^-, CH_2CO^-, CO^-, and other ions corresponding to breakdown of the molecular ions in the ways indicated by the broken lines on the above structural formulae.

Dissociative electron capture by keten[82] and formaldehyde[83] has also been investigated.

10. Peroxides

The mass spectra of t-butyl and of its hydroperoxide are almost identical[84]. Over the range of electron energies 0–3 eV the ions $(CH_3)_3CO^-$, $CH_2{:}C(CH_3).O^-$, and CH_3^- are observed (100%, 13%, and 0.1% respectively), with a metastable-ion peak corresponding to the transition

$$(CH_3)_3CO^- \xrightarrow{-CH_4} CH_2{=}C(CH_3)O^- .$$
$$m/e\ 73 \qquad m/e\ 57$$

It was supposed that *m/e* 73 ions were formed by the direct capture of electrons by t-butoxy-radicals produced by thermolysis of the compounds in the ionisation chamber.

Investigation of dissociative electron capture by $R.C(CH_3)_2OOH$ molecules (where R = CH_3, C_2H_5, C_6H_5, $C_{10}H_7$) and by perbenzoic acid indicates[85,86] that the main process with all the compounds, when low-energy electrons are trapped, is the formation of $(M - OH)^-$ ions, in an autoionisation state, i.e. in an excited state with an average lifetime of $\sim 10^{-3}$ s before spontaneous ejection of an electron. The mass spectra contain a metastable-ion peak corresponding to the transition

$$R(CH_3)_2O^- \xrightarrow{-CH_4} RC(CH_2)O^- .$$

In the mass spectrum of perbenzoic acid the transitions

$$(C_6H_5CO{-}OOH)^- \xrightarrow{-OH} C_6H_5CO_2^- \xrightarrow{-CO_2} C_6H_5^-$$

are observed.

11. Nitro-compounds, Nitrites, [Nitrates,] and Nitriles

A relatively large number of papers have been published on the capture of electrons by nitromethane[65,87–90], whose negative molecular ion has six resonant states, which dissociate with the formation of negative ionic fragments[90]. Table 5 gives only ions from primary processes of electron capture, but $CH_2NO_2^-$ and $CHNO_2^-$ have also been observed, resulting from secondary reaction of O^- ions with nitromethane molecules, as well as OH^- and CH_2NO^- ions produced by an ion–molecule reaction involving NO_2^-.

Table 5. Negative ions from nitromethane (relative intensity of NO_2^- ions at 0.6 eV taken as 10 000).

Electrons, eV	Ion	Relative intensity	Electrons, eV	Ion	Relative intensity
0.6	NO_2^-	10 000	7.8–7.9	$CH_2NO_2^-$	37.5
	CH_2NO^-	5		CH_2NO^-	25
3.7	CNO^-	10		NO^-	2.5
	CN^-	10	8.3	CNO^-	10
	OH^-	50		OH^-	37.5
	CH^-	2.5		CN^-	10
5.6	O^-	250			
	OH^-	—			

A rather lower yield of negative ions is obtained in nitroethane[65] than in nitromethane, and the maxima on the effective-yield curves are displaced to higher energies (by a few tenths of an electron-volt).

Nitrites are characterised[65,91] by a large cross-section for ion-formation ($\sim 10^{-15}$ cm^2) on the capture of thermal electrons, by the reaction $Alk.O.N{:}O^- \rightarrow AlkO^- + NO$. The effective cross-section diminishes as the alkyl chain becomes longer. Formation of NO^- and NOH^- ions also occurs.

The $\cdot O{-}NO_2$ bond in ethyl nitrate also readily undergoes cleavage when the molecule traps an electron of energy close to zero:

$$(C_2H_5O{-}NO_2)^{-*} \begin{cases} \rightarrow C_2H_5O + NO_2^-, & \sigma \sim 2 \cdot 10^{-15}\ \text{cm}^2; \\ \rightarrow C_2H_5O^- + H_2NO_2, & \sigma \sim 5 \cdot 10^{-16}\ \text{cm}^2 . \end{cases}$$

Rupture of the $O-NO_2$ bond is also involved in the reactions

$$(C_2H_5O-NO_2)^- \begin{cases} \longrightarrow C_2H_5O^- + NO_2, & \sigma \sim 6 \cdot 10^{-17}\ cm^2; \\ \longrightarrow C_2H_4O^- + HNO_2, & \sigma \sim 2 \cdot 10^{-17}\ cm^2. \end{cases}$$

Effective-yield curves have been obtained for the ions CN^-, $CHCN^-$, CHN^-, and CH_3CH^- from CH_3CN^- and $C_2H_5CN^-$.[38] Resonance peaks of negative-ion emission and their relative intensities have been recorded for the interaction of electrons with azoisobutyronitrile[92] and cyanonorbornene[50].

12. Peculiarities of the Formation of Negative Ions

In conclusion we make a general comparison of the dissociative electron-capture mass spectra with the mass spectra of positive ions, noting the most significant features of resonance processes.

Dissociative electron capture by molecules is characterised by a marked dependence of the effective ion-formation cross-sections on the functional groups present in the molecule. In alkyl benzyl and phenyl sulphides, nitrates, and hydroperoxides, for example, the effective cross-sections reach 10^{-14}–10^{-15} cm^2 (vibrationally excited Feshbach resonances and shape resonances); in alkenes and alkylbenzenes the cross-sections of formation of negative ions do not exceed 10^{-19} cm^2 (electronically excited Feshbach resonances)‡. Such marked differences in total ionisation cross-sections are not observed in the mass spectrometry of positive ions.

In contrast to the formation of positive ions, when most of the fragments may be positively charged, the extra electron can be retained only by fragments whose electron affinity is positive. For example, processes involving formation of N^- ions are excluded in nitrogen-containing compounds, since the electron affinity of the nitrogen atom is negative; this is probably why $C_2H_5^-$ ions are not formed, although detachment of $C_2H_5^-$ radicals is observed in dissociative electron capture by molecules containing alkyl chains. The small number of lines in such mass spectra in comparison with those of positive ions undoubtedly is largely due to the fact that not all possible channels of decomposition of a negative molecular ion yield fragments having positive electron affinities. However, the existence of several resonant states of molecular ions to some extent compensates for the paucity of lines in the dissociative electron-capture mass spectra. In many cases we can speak of several such mass spectra of a given substance according to the number of resonances observed.

Dissociative electron capture via electronically excited Feshbach resonances usually involves a large excess energy, so that ionic fragments are likely to be formed in vibrationally excited states. Dissociation of the molecular ions thus occurs in ways leading to ionic fragments whose energy of vibrational excitation is less than some critical value, since a high energy of vibrational excitation may cause either further dissociation of the ionic fragment or ejection of the extra electron within times $\tau < 1$ μs (ions with such short lifetimes are not recorded by the mass spectrometer). Negative ions of energetically less advantageous structures are often formed preferentially precisely because of their lower energy of vibrational excitation[94]. It is noteworthy that, in the mass spectrometry of positive ions, the stability of the fragments formed plays an important role in determining the predominant direction of dissociation, where stability of the decomposition products implies mainly energetically favourable structures of the ion and of neutral fragments.

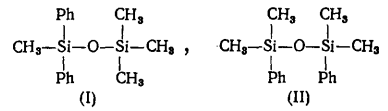
The finite lifetime of negative molecular ions before spontaneous detachment of an electron restricts the possible processes of dissociation. As a consequence, a smaller contribution is made by processes involving rearrangements, which require times comparable with that for detachment of the electron. For this reason negative ionic fragments are formed almost solely by simple cleavage of bonds in the molecular ion[86,94,95].

‡ Differences in the effective ion-emission cross-sections can be used to solve several problems in determining minor quantities of one substance in another[93].

Table 6. Dissociative electron-capture mass spectra of isomers (I) and (II).

m/e	Relative intensity		m/e	Relative intensity		m/e	Relative intensity	
	I	II		I	II		I	II
285	100	8.0	211	13.0	—	135	—	2.0
269	25.0	6.0	207	60.0	100	89	32.0	5.0
213	13.0	—	151	—	7.5	73	16.0	2.4

For the above reasons the dissociative electron-capture mass spectra of structural isomers show marked differences. In contrast, the intensity of rearrangements makes the positive-ion mass spectra of structural isomers either completely identical or only slightly different (cf. e.g. the two types of mass spectra for polyenes and mass spectra of the former type for two isomeric propylthiophens—Figs. 4 and 5). Another illustration is provided[86] by the preparation of two isomers of molecular weight 286 and composition $Si_2O(CH_3)_4(C_6H_5)_2$ as shown by elementary analysis, infrared spectra, and positive-ion mass spectra. However, these mass spectra gave no indication of the isomeric structures, since they were almost identical for the two specimens. The dissociative electron-capture mass spectra (Table 6) make it easy to assign the structures



(I) (II)

The great sensitivity of dissociative electron-capture mass spectra to variation in molecular structure follows from the conditions of dissociation of the parent molecular ion. The identification of isomeric structures may therefore be a possible field for the practical application of this type of mass spectrometry.

IV. SOLUTION OF SPECIAL PROBLEMS BY NEGATIVE-ION MASS SPECTROMETRY

1. Recording of Free Radicals in the Gas Phase

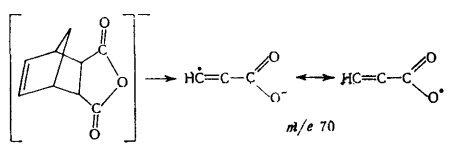
Iminoxyl radicals (di-t-butyliminoxyl and 2,2,6,6,-tetramethylpiperidinoxyl), on trapping thermal electrons, form negative molecular ions with $\tau = 16$ and 21 μs respectively,

the effective cross-section of the process being $\sim 10^{-17}$ cm^2.

Positive-ion mass spectrometry cannot record iminoxyl radicals, since their spectra contain no characteristic fragments, and in the presence of impurities it is impossible to isolate the spectrum corresponding to the radical[96] (the use of electron spin resonance spectra is applicable only to the liquid phase). The recording of iminoxyl radicals from the peaks of negative molecular ions is free from the problems of "background" and the superposition of peaks due to impurities, since the probability that the resonance peaks of ion emission for the radical and for the impurity molecules will coincide, with simultaneous coincidence of the mass numbers of the ions, is very slight[92,97].

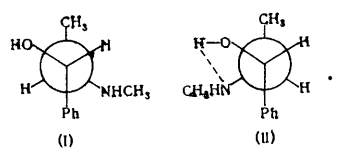
2. Stereoisomerism of Organic Compounds

Examination of the spectra of *endo*- and *exo*-5-cyanonorbornenes and of *endo*- and *exo*-norbornenedicarboxylic acids has shown that their differences can be used to identify stereoisomeric derivatives of norbornene and related bicyclic compounds. Thus the effective yield of m/e 70 ions from *endo*-norbornenedicarboxylic acid reaches a maximum with electrons of energy 6 eV, whereas with the *exo*-isomer the maximum is located at 4.7 eV. This means that $(H_2C_2CO_2)^-$ ions having m/e 70 can be formed, with maximum yields at 6 and 4.7 eV, by two resonance processes from both molecules



but the probability ratios of these processes are different. This applies also to the formation of ions with m/e 52, 91, 103.[95]

Ephedrine and pseudoephedrine exist predominantly as the respective conformers[98]



Considerable differences in the relative intensities of peaks due to ions of the two isomers are observed only with certain mass lines[99]. Fig. 7 shows the dependence of the total currents of negative ions of (I) and (II) on the energy of the electrons. Thus the stereochemical differences do not result in the appearance of new resonant states of the molecule–electron system. However, the absolute effective capture cross-sections of electrons change in all the resonance peaks other than the second, which is due to $(M - H)^-$ ions. The cross-sections for formation of negative ions of ephedrine in the resonance peaks *1* and *3* are somewhat lower than for pseudoephedrine, but at peak *4* they are almost double. Ephedrine is characterised by an increased relative probability of formation of ions having m/e 146, 133, and 117, whereas in pseudoephedrine the proportion of ions having m/e 17 and 30 increases. The effective-yield curves for ions from the two isomers differ markedly in the region of electron energies of ~6.5 eV. Many other quite significant differences between the spectra of ephedrin and pseudoephedrine have been discussed[97]. The positive-ion mass spectra of the isomers, obtained under standard conditions, are almost identical.

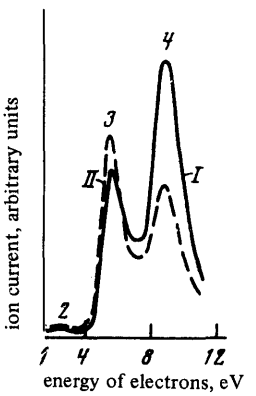
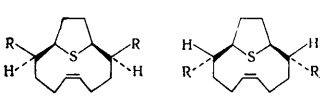


Figure 7. Dependence of total ion current on energy of electrons for: I) ephedrine; II) pseudoephedrine.

Study of the stereochemistry of 13-thiabicyclo-[8,2,1]tridec-*cis*-5-ene derivatives



has shown that, when R = H, no new states of the negative molecular ion appear in comparison with dialkylthiophans. The situation is greatly changed by the introduction of two acetoxy-groups (R = $OCOCH_3$). In particular, ions having m/e 119 are detected, with the empirical formula $(OCOCH_3)_2H^-$. Since peaks due to metastable and rearranged ions are absent from dissociative electron-capture mass spectra, it was concluded[100] that the negative molecular ions exist in an excited state for only a short time. From this point of view the formation of m/e 119 ions indicates the steric proximity of the acetoxy-groups in the thiabicycloalkane diacetate. Ions of type $(R_2H)^-$ are also detected in the spectra of thiabicycloalkanes with R = OCH_3, NO_2. These results have provided part of the evidence for the *cis*-arrangement of the substituents in 2,9-disubstituted derivatives of 13-thiabicyclo[8,2,1]tridec-*cis*-5-ene.

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The results given in this Review of the mass spectra of negative ions in the dissociative capture of electrons by organic molecules cover little more than a hundred individual compounds belonging to 10–15 classes, incomparably fewer than the data on the mass spectra of positive ions. It is not surprising, therefore, that there remain many unsettled questions on the mechanism of dissociation accompanying the capture of electrons by molecules. It is indisputable that further work is needed on such problems as e.g. the structure of ions and neutral fragments, the internal energy of excitation of the resulting ions, and the classification of resonant states of the molecule–electron system.

Nevertheless, the material presented here is in our opinion evidence that even now we can regard such mass spectrometry of negative ions as a method which may be useful in solving several specific problems in organic chemistry.

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