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Dissociative Ionisation of Nitro-derivatives of Arenes and Heterocyclic Compounds

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The mass-spectrometric behaviour of nitro-derivatives of aromatic and heterocyclic compounds is examined. Attention is concentrated on the influence of the relative positions of nitro- and other functional groups on the mode of decomposition in the mass-spectrometry of positive and negative ions.
The bibliography includes 92 references.

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I. INTRODUCTION

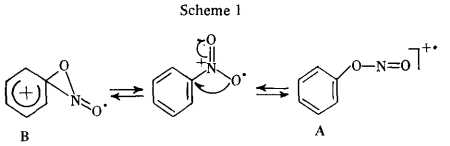
Numerous mass-spectrometric studies have been devoted to analysing the behaviour of various classes of organic compounds on electron impact. However, it has now become necessary to examine various classes of compounds containing functional groups which have a decisive influence on the mode of fragmentation. The types of decomposition associated with different positions of the functional groups in the aromatic or heterocyclic ring are particularly important. One of the most important and frequently encountered functional groups in organic compounds is the nitro-group, whose presence frequently leads to specific modes of decomposition of molecular ions. There are no reviews in the literature of studies on these problems; the aim of the present review is to fill this gap. It includes studies published up to the end of 1975.

II. NITROARENES

The first studies on the mass-spectrometric behaviour of mono- and polynitrobenzenes [1-7] established the occurrence in their dissociative ionisation processes of three main characteristic pathways: the formation of the ions $(M - O)^+$, $(M - NO)^+$, and $(M - NO_2)^+$. However, under these conditions the probability of the first process was very low and the intensity of the corresponding peak in the mass spectrum did not usually exceed 1-2% (of the maximum peak).

It has been suggested [1] that the molecular ion derived from nitro-compounds partly rearranges with formation of aryl nitrite ions A before dissociation:

Scheme 1



B A

However, according to other workers [2], the rearranged ion has the *spiro*-structure B.

The occurrence of the isomerisation of the nitro-group was subsequently confirmed and accepted all by investigators of the mass spectra of nitro-derivatives of aromatic and heterocyclic compounds.

Having compared the mass spectra of all the isomeric dinitrobenzenes (see Table), Beynon et al. [1] and Fields and Meyerson [3] concluded that the modes of decomposition of these compounds and other nitroarenes are similar. It was noted that the mass-spectra of *meta*- and *para*-isomers are very similar, but differ markedly from that of the *ortho*-isomer [1,4]. Thus the intensity of the M^+ peak is appreciably lower in the mass spectrum of the *ortho*-isomer, which reflects its lower stability. In this connection one should note that the mass spectrum of *ortho*-dinitrobenzene exhibits [8] the peak of the $(M - O_3)^+$ ion (mass 120), to which the authors attributed the structure of benzo[3,4]-1,2,5-oxadiazole and showed that this compound is indeed formed also in the pyrolysis of *o*-dinitrobenzene at 650°C.

The peak intensities of the characteristic ions in the mass spectra of isomeric dinitrobenzenes (as percentages of the total ionic current). [1,4]

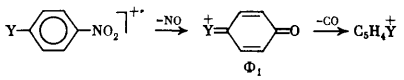
Ion	Position of nitro-group		
	ortho-	*para*-	*meta*-
M^+	6.98	11.00	10.30
$(M—O)^+$	0.24	0.63	0.57
$(M—NO)^+$	0.07	0.21	0.34
$(M—NO_2)^+$	0.41	4.76	4.12
$(M—NO—NO)^+$	0.03	0.04	0.09
$(M—NO—NO_2)^+$	1.66	5.82	3.64
$(M—NO_2—NO_2)^+$	3.84	11.20	9.18
$(M—NO_2—HNO_2)^+$	2.03	10.80	11.30
NO^+	26.70	17.20	21.30

The nature of the decomposition of the negative molecular ions of mono- and poly-nitrobenzenes [9,10] does not differ fundamentally from that of the processes described above, although the fragmentation of such ions is more selective.

Meyerson et al. [5] used the defocussing method and high-resolution mass spectrometry for a detailed study of 1,3,5-trinitrobenzene. For 23 ions, they observed 96 corresponding metastable peaks, which enabled them to devise a very complex scheme relating the precursor ions to daughter ions; the authors reduced the main "chains" of molecular ion decomposition processes to six pathways, resembling the pathways in the fragmentation

of dinitrobenzene (see Table). It is very remarkable that in the first stage the elimination of NO_2 plays the main role. In contrast to mono- and di-nitrobenzenes[1,6,7], the abstraction of O from M^+ is not observed for trinitrobenzene. It is also of interest to note that the mass spectrum of nitrosobenzene contains the peak of the $(M - N)^+$ ion with a mass of 93, but the authors did not express a view concerning the process involving its formation[11].

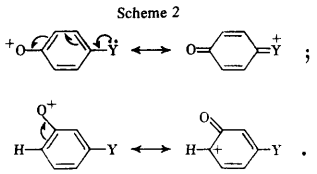
The studies of Bursey and McLafferty[2] showed that the abstraction of NO from M^+ for certain substituted aromatic nitro-compounds is associated with the appearance of peaks with a flat top due to metastable ions, which indicates the liberation of kinetic energy. The generation of a metastable peak associated with the elimination of NO is characteristic of all 27 compounds investigated, but the formation of the peaks with a flat top was noted for only five of them, the amount of energy liberated being in the range 0.38–0.84 eV. The liberation of kinetic energy is associated with the following type of decomposition of the system:



Φ_1

in which the ion Φ_1 formed undergoes resonance stabilisation by the electron donor substituent in the *ortho*- or *para*- (but not *meta*-) position[2]:

Scheme 2

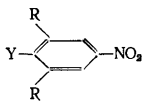


Indeed the liberation of kinetic energy was observed only for *para*-substituted nitrobenzenes and only for substituents with $\sigma_Y > 0.40$.

A study of the dissociative ionisation of mono- and di-nitro-phenyl sulphones[12,13] also showed that the probability of the nitro–nitrite isomerisation of M^+ is determined by the position of the nitro-group in the molecule. It occurs most readily when one or both nitro-groups are in the *para*-positions relative to the sulphone group. We need only note that a competing S–O migration of the aryl group, leading to the formation of aryl esters of arene sulphinic acids, is observed in the decomposition of the above sulphones.[14]

In full agreement with the above considerations, the liberation of the greatest amount of kinetic energy was noted in the mass spectra of the negative ions[9] of isomeric dinitrobenzenes on formation of the ion $(M - NO)^+$ (0.89 eV) from the *para*-isomer, the value for the *meta*-isomer being significantly smaller (0.36 eV). As was also to be expected, the intensity of the $(M - NO)^+$ ions in the mass spectra of negative ions (in full contrast to the mass-spectra of positive ions) was directly proportional to the electron-accepting properties of the substituent in the *para*-position[10].

Many other studies on the mass spectra of both negative[15,16] and positive[17-20] ions support the maintenance of the non-identity of the positions in the series of nitroarenes in both the first and subsequent decomposition stages. In particular, having analysed the mass spectra of three series of sterically hindered *para*-substituted nitroarenes having the general formula



Y=HO, CH_3O, H_2N, or $(CH_3)_2N$; R = H, Cl, or Br.

Bursey[21] showed that the displacement of the substituent Y from the plane of the benzene ring, which promotes a decrease of the p–π conjugation between them, reduces the intensity of the peak of the $(M - NO)^+$ ion. These data also support the view that substituents influence the decomposition of nitroarenes.

The results of an earlier study[22], dealing with the ionisation potentials (IP) and appearance potentials (AP) of ions arising, apparently, in the competing reactions involving the decomposition of $M^{+\cdot}$ with formation of the $(M - NO_2)^+$ ion and the rearrangement of the molecular ion with formation of the (M – NO) fragments in the series of *meta*- and *para*-substituted nitrobenzenes (with the substituents Y = NH_2, OH, OCH_3, CH_3, H, Cl, Br, CN, or NO_2), lead to the same conclusion. The differences between the IP and AP, which represent the approximate activation energies (ϵ_0) for the decomposition of the molecular ion leading to the formation of the $(M - NO_2)^+$ fragment are the same for the *meta*- and *para*-positions, whereas in the formation of the $(M - NO)^+$ ion they are different. Finally, having compared the shapes of the peaks due to metastable ions in the mass spectra of *para*-substituted anisoles and nitrobenzenes, Davies and Williams[23] concluded that the structures of the $(M - CH_3)^+$ ions of anisoles and the $(M - NO)^+$ ions (Φ_1) of nitrobenzenes are identical, which suggests that there is no randomisation in these processes.

Nevertheless there have been a number of studies in which the possibility of the randomisation of hydrogen in the fragmentation of benzene[24] and its derivatives[11,25] was demonstrated fairly convincingly. It has also been established[26] that, in the mass spectrum of 4-nitroaniline containing ^{13}C in the 1-position, the $(M - NO)^+$ ion loses one-sixth of the labelled carbon in the form of CO, which indicates a randomisation process involving at least this ion. However, later these data were disproved[27].

Thus, there is as yet no unanimous view concerning the retention or non-retention of the identity of the position of the substituent in the molecular ions of nitroarenes.

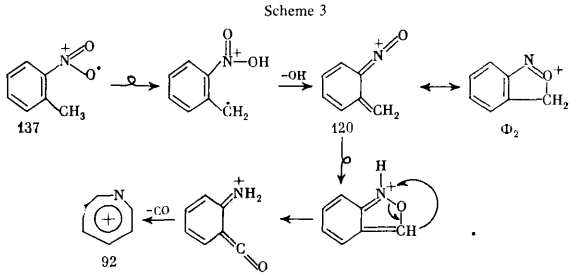
Comparison of the mass spectra of the isomeric nitrotoluenes leads to the conclusion that the decomposition reactions of their *meta*- and *para*-isomers are very similar to the decomposition of nitrobenzene[1]. Thus both isomers are characterised by intense peaks due to the molecular ion (>70% of the maximum), the intensity being comparable to the intensity of the peak of the $M^{+\cdot}$ radical-ion derived from nitrobenzene (49%). For all three compounds, the maximum peak in the mass spectrum corresponds to the $(M - NO_2)^+$ ions, the intensity of the peaks due to the $(M - NO)^+$ ions is 10%, while the peak of the $(M - O)^+$ ions amounts to 1–2% of the maximum peak.

At the same time the mass spectrum of *o*-nitrotoluene exhibits significant differences. The peak of the M^+ ion amounts to only 25%, there is no peak due to $(M - O)^+$ ions, and the maximum peak corresponds to ions with a mass of 120, which are absent from the mass spectra of the *meta*- and *para*-isomers.

The use of high-resolution mass spectrometry and of data for metastable processes, enabled Beynon et al.[1] to establish unambiguously that these ions can have the elemental composition C_7H_6NO, i.e. correspond to the $(M - OH)^+$ ions with the probable structure Φ_2. Subsequently ions having this mass lose 28 atomic mass units (a.m.u.) (CO) and are converted into ions with a mass of 92, which probably have the structure of the azatropylium ion, because the last stage in its decomposition involves the elimination of hydrocyanic acid.

Thus the characteristic pathways leading to the fragmentation of *o*-nitrotoluene reduce to three consecutive processes†:

Scheme 3



Only the $(M - NO)^+$ and $(M - NO_2)^+$ ions were observed in the mass spectra of *m*- and *p*-nitrotoluenes. The $(M - OH)^+$ ions were characteristic of both nitro-*p*-xylene and of polynitrotoluenes[1]. Similar processes are characteristic also of the mass spectra of the negative ions of nitrotoluene or analogous compounds[10,28], whereas the ions $[(M + H) - OH_2]^+$ were observed in the mass spectrum of trinitrotoluene obtained by chemical ionisation[29].

When one of the hydrogen atoms of the methyl group in *o*-nitrotoluene is replaced by an amino-group, the $(M - OH)^+$ ion subsequently loses NO and not CO, which indicates its non-cyclic structure[30].

The formation of the $(M - OH)^+$ ions is observed also in the series of isomeric nitroanilines[1,31]. Thus, whereas the mass-spectrum of *o*-nitroaniline contains the peak of the $(M - OH)^+$ ion (although it is less intense than in the mass spectrum of *o*-nitrotoluene), such a peak is not characteristic of the *meta*- and *para*-isomers. The same process, involving the loss of an OH group, is also typical for the mass spectra of negative ions derived from *o*-nitrotrifluoroacetanilides and it has also been shown that the hydrogen ion is eliminated from the NH group[32].

On the basis of the foregoing considerations, one can conclude that the early studies on the mass spectra of nitroarenes already gave rise to the necessity for a detailed investigation of the influence of the *ortho*-effect[33,34] on dissociative ionisation. This influence applies particularly when the substituent in the *ortho*-position relative to the nitro-group contains a hydrogen atom, which makes possible the abstraction of the hydroxy-group from M^+.[35] Such elimination of OH does not occur for the *meta*- and *para*-isomers.

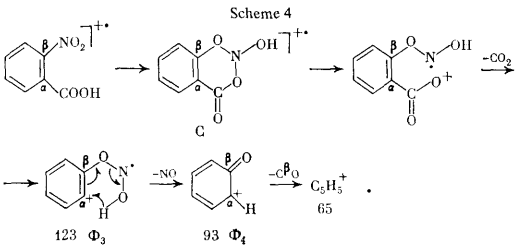
†Here and henceforth the number under the formula of the ion represents the corresponding value of *m/e*, the number in round brackets represents the intensity of the peak of the given ion as a percentage of the maximum peak in the spectrum, and the number in square brackets represents the intensity of the peak of the given ion as a percentage of the total ionic current.

It has been suggested[1] that this process proceeds via a six-membered transition state with migration of a hydrogen atom to an oxygen atom of the nitro-group and the OH group is eliminated from the non-rearranged M^+ ion and not from the ion in the nitrite form.

Williams and coworkers[36] investigated the *ortho*-effect in the mass spectra of certain nitroarenes, where the substituent in the *ortho*-position contained oxygen. All the decomposition mechanisms involved interaction between the *ortho*-groups; however, this was accompanied by unexpected effects, which may be associated with the presence of impurities or with thermolysis of the nitro-compounds.

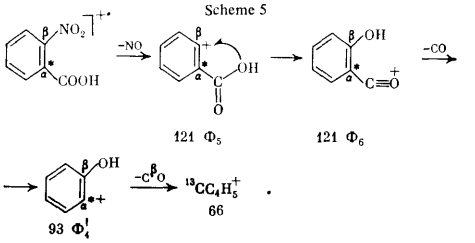
Benoit and Holmes[37] examined this problem in relation to the dissociative ionisation of *o*-nitrobenzoic acid, *o*-nitroanisole, *o*-nitrobenzamide, *o*-nitrobenzyl alcohol, and *o*-nitrobenzaldehyde. Some of the compounds investigated were labelled with deuterium, while in other cases the ^{18}O label was used. It was concluded that there are two types of *ortho*-effects. The first was already noted above in connection with the migration of a hydrogen atom from one substituent to another. In the compounds under consideration such migration to an oxygen atom of the nitro-group is usually accompanied by a complex rearrangement and leads to the elimination of a neutral species (a molecule). Such a process proceeds as a rule with the intermediate formation of a five- or six-membered cyclic structure. In the case of *o*-nitrobenzoic acid, *o*-nitroanisole, and *o*-nitrobenzaldehyde the formation of a cyclic intermediate structure is accompanied by the nitro–nitrite isomerisation (Scheme 4). The same processes characterise also the mass spectra of negative ions[10,38].

Scheme 4



The second type of *ortho*-effect is associated with the migration of an atom or group of atoms from the substituent to a vacant site in the ring (probably a positive hole) located in the *ortho*-position relative to the substituent and formed after the elimination of some species. In *o*-nitrobenzoic acid, *o*-nitroanisole, *o*-nitrobenzaldehyde, and *o*-nitrobenzamide the OH group migrates from the COOH and NO_2H groups: in *o*-nitrobenzamide the NH_2 group migrates from the $CONH_2$ substituent[37]:

Scheme 5



Here the asterisk denotes a ^{13}C atom.

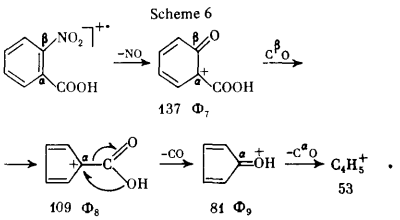
Many efforts have been made to elucidate the mechanism and the pathways leading to the formation and decomposition of the ion with a mass of 93 in the mass

spectrum of *o*-nitrobenzoic acid. Benoit and Holmes [37] proposed two alternative mechanisms, the first of which (Scheme 4) presupposes the migration of acid hydrogen to the isomerised nitro-group with formation of a cyclic structure C, which, having eliminated CO_2, gives rise to the ion Φ_3. The latter next ejects an NO molecule and forms an ion with a mass of 93 (Φ_4). The loss of CO by the latter leads to the formation of the hydrocarbon ion $C_5H_5^+$ (with a mass of 65). The second probable pathway leading to the formation of an ion with a mass of 93 presupposes the ejection of the nitro-group (the Φ_5 ion), the migration of the hydroxy-group (Φ_6), and the loss of CO (the Φ_4 ion) (see Scheme 5).

Having investigated the mass spectra of *o*-nitrobenzoic acid containing ^{13}C in the 1-position using ionising electron energies of 17 and 15 eV, Djerassi and coworkers [39] found that the label is not lost up to the ion with a mass of 65. However, analysis of the mass spectrum of the compound containing ^{18}O in the hydroxy-group showed that the label is not lost on formation of the ion Φ_5, but the ion Φ_4 contains only part of the label. Thus both mechanisms (Schemes 4 and 5) operate.

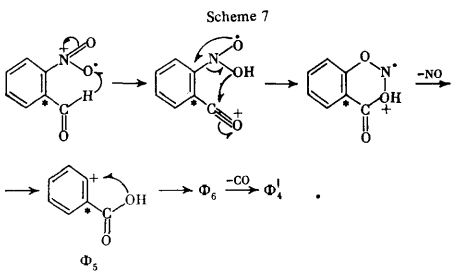
Benoit and Holmes [37] proposed also a third mechanism for the dissociative ionisation of the molecular ion of *o*-nitrobenzoic acid (Scheme 6), which is also consistent with Djerassi's data [39]. However, the ions $\Phi_7 - \Phi_{10}$ formed via this pathway give rise to much less intense peaks than the ions $\Phi_2 - \Phi_6$, so that one can assume that the above pathway does not play a significant role in the overall decomposition mechanism:

Scheme 6



The migration of hydrogen to the oxygen of the nitro-group is observed also in the mass spectrum of *o*-nitrobenzaldehyde in which the $(M - NO)^+$ ion next loses CO and the process proceeds via Scheme 7, proved by Djerassi and coworkers [39] by analysing the mass spectrum of the compound containing ^{13}C in the formal group:

Scheme 7

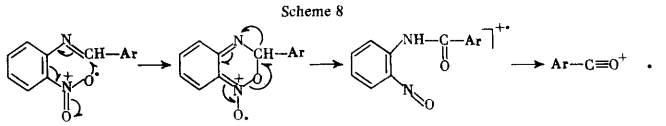


Here the asterisk denotes a ^{13}C atom. There is a possibility of the migration not only of a hydrogen atom but also of an amino-group to an oxygen atom of a neighbouring nitro-group [40], while in the mass spectra of negative ions even the phenyl group can migrate [41], as has been shown for the isomeric phenyl nitrosalicylates and *o*-nitrophenyl ether [42].

The replacement of oxygen by nitrogen in *o*-nitrobenzaldehyde does not change significantly the primary decomposition in both positive [43] and negative [44] mass spectra.

However, there is no $(M - OH)^+$ ion in the mass spectra of the benzylidene derivatives of *o*-nitroaniline, [42] but the transfer of the oxygen of the nitro-group to the methylidyne carbon atom with the simultaneous migration of hydrogen and the formation of the $(Ar - CO)^+$ ion are observed:

Scheme 8



A similar transfer of the oxygen of the nitro-group to the C=C double bond has been observed for esters of α-benzylidene-*o*-nitrobenzoylamino acids [45]. The same type of migration of an oxygen atom of the nitro-group to a neighbouring double bond [(C=C) or C=N] was noted by investigators [46] who studied the dissociative ionisation of 40 compounds comprising nitrophenylhydrazones, aromatic aldehydes and ketones, nitrostilbenes, and nitrobenzylideneacetophenones.

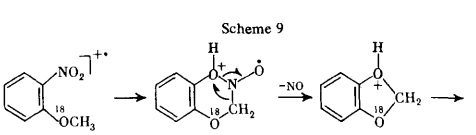
An analogous transfer of an oxygen atom from the nitro-group has been observed in the mass spectrum of *o*-nitrostyrene [there are intense peaks due to the $(M - CO)$, $(M - CHO)$, and $(M - CH_2O)$ ions]. [47] Finally, the migration of an oxygen atom of the nitro-group to a sulphur atom with subsequent elimination of the *p*-tolyl sulphoxide residue has been observed in the molecular ion derived from *p*-tolyl *o*-nitrothiobenzoate. [48]

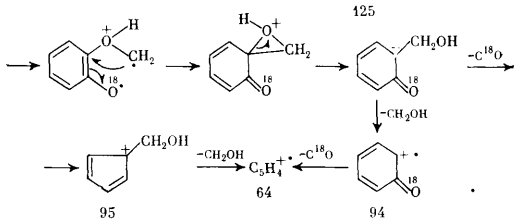
The study of the behaviour of *o*-nitroanisole under electron impact showed [37] that the main primary process in the decomposition of its molecular ion is the loss of 30 a.m.u. with formation of an ion having a mass of 123. Using high-resolution mass spectra it was established that the loss of CH_2O proceeds to an extent that 80% and that of NO only to an extent of 20%.

Analysis of the mass spectrum of *o*-nitroanisole containing ^{18}O in the methoxy-group established unexpectedly [39] that the elimination of CH_2O does not entail the loss of labelled oxygen. Schemes 9 and 10 explain all the experimental facts and include, as in the previous instance, the migration of the OH group to a vacant site at a ring carbon atom. It must be emphasised that the thermal decomposition processes involving *o*-nitroanisole proceed with loss of HNO and HNO_2. [49]

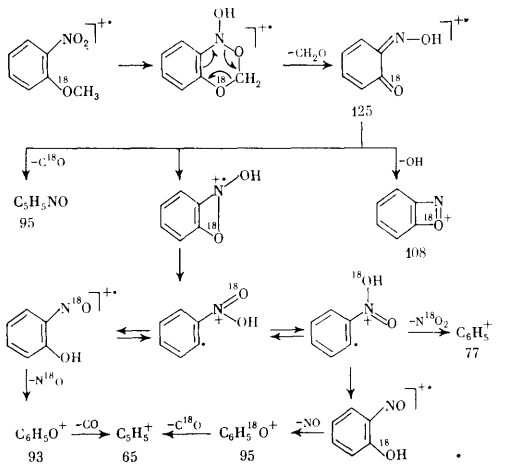
Hydrogen can also migrate to the nitro-group from the *peri*-position. Thus the mass spectra of nitro-compounds exhibiting *peri*- and *ortho*-effects have been examined [36] and the authors observed a number of analogies in the behaviour of nitro-compounds in photochemical reactions and under electron impact. The study of the decomposition of 1-nitronaphthalene showed [36] that the mass spectrum contains the ion Φ_{12} [$(M - 28)^+$] with a mass of 145, which was identified as the $(M - CO)^+$ ion on the basis of high-resolution mass spectrometric data. The appearance of such ions was not noted in the mass spectra of nitrobenzenes.

Scheme 9



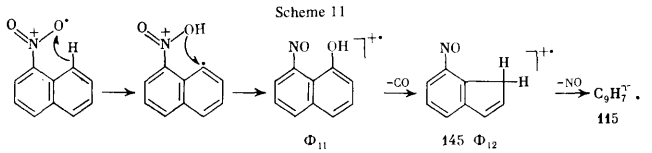


Scheme 10



Its formation is most probably caused by the formation of a new bond between the $C_{(8)}$ *peri*-carbon atom and an oxygen atom of the nitro-group, which enabled the authors to propose a mechanism for the elimination of CO:

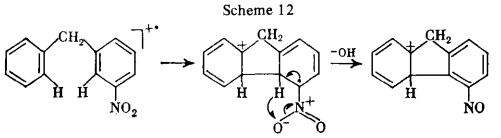
Scheme 11



According to this scheme, there is initially the migration of a hydrogen atom in the $M^{+\cdot}$ species derived from nitronaphthalene and then the migration of the hydroxy-group. The ion Φ_{11} with a nitrosophenol structure formed in this process can eliminate CO, similarly to the process observed for phenols[50]. The subsequent decomposition of the ion Φ_{12} is confirmed by the proposed mechanism. It is important to emphasise that 1,5-dinitronaphthalene does not eliminate CO under electron impact. An analogous reaction has been observed[51] in the photolysis of 6-nitrocholesteryl acetate.

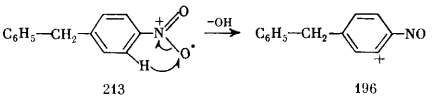
Similar processes involving the migration of an aromatic hydrogen atom in a neighbouring aryl group have also been discovered[52] in the mass spectra of the isomeric *o*-, *m*-, and *p*-benzylnitrobenzenes. It was established that the $(M - OH)^+$ ion, the formation of which can be readily accounted for in the case of the *ortho*-isomer, is observed also in the mass spectra of other isomers. The study of the dissociative ionisation of the deuterium-labelled compounds made it possible to show that the process involving *m*-benzylnitrobenzenes proceeds via the scheme

Scheme 12



In the *para*-isomer, where the $(M - OH)^+$ ion is formed with a low probability, hydrogen also migrates, but from the CH_3 group and not the *ortho*-position:

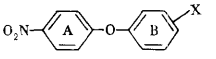
Scheme 13



It was later established that the formation of the (M – OH) and even (M – 2 OH) (in the case of *ortho*-isomers) ions is characteristic of the mass spectrometric behaviour of nitrodiphenylamines.[53] Beynon and coworkers observed the peaks of the (M – NO) ions also in the mass spectra of esters, amides, thioamides, hydrazides, and iminoesters of *p*- and *m*-nitrobenzoic acids. They explained their formation by a multistage migration of a hydrogen atom from the substituent to an oxygen atom of the nitro-group[54].

The migration of a hydrogen atom from a neighbouring ring was also observed for nitrodiphenyl ethers[53,55] and in the mass spectra of the negative ions of cyclic thioacetyls and of *o*-nitrobenzaldehyde[56].

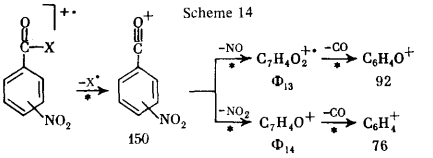
A careful study of the mass-spectrometric behaviour of nitrodiphenyl ethers made it possible[57] to examine the problem of the possible migration of the charge in the excited ion, which has been frequently the subject of a critical discussion in the literature[58,59]. It has been concluded[57] that the nature of the substituent (X) in the B ring plays an important role in the intensity of the fragment ions produced as a result of the nitro–nitrite isomerisation in the ether:



Furthermore, a linear relation has been observed between the intensity of the peaks of the $(M - NO)^+$ ions and the IP, on the one hand, and between the intensity of the peaks of the $(M - NO)^{-}$ ions and the Hammett constant, on the other. According to the authors[57], the results show that the substituent X in the B rings of the nitroether derivatives investigated has a considerable influence on the electronic state of the A ring and that the electron density in the ion with an odd number of electrons migrates from the electron-depleted A ring to the B ring.

Shapiro and Serum[60] investigated the mass spectra of derivatives of *m*- or *p*-nitrobenzoic acids $O_2NC_6H_4COX$, where X = OCH_3, NH_2, or $NHCH_3$, in order to study the behaviour of the ion with a mass of 150 and an even number of electrons (the nitrobenzoyl cation), formed on elimination of the substituent X and subsequently decomposing via two alternative pathways leading to the formation of the ions Φ_{13} and Φ_{14}, having odd numbers of electrons‡:

Scheme 14



It was shown that the removal of NO from the ion with a mass of 150 for *p*-nitro-compounds proceeds with a much greater probability than for the *m*-isomers.

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‡Here and henceforth an asterisk in the Schemes denotes a process confirmed by the presence of a metastable ion.

Analogous data were obtained in the study of the behaviour of $(M - X)^+$ ions with an even number of electrons and a mass of 136, formed in the dissociative ionisation of the nitrobenzyls *m*- or *p*-$O_2NC_6H_4CH_2X$, where X = Br or OC_6H_5, which decompose subsequently with the elimination of NO and NO_2.[60] It was concluded that, regardless of the pathway leading to the formation of the initial ion and its structure, the ion with a mass of 136 does not have the nitrotropylium structure and its structure is more likely to be of the nitrobenzyl type.

A correlation between the electronic properties of the substituents and the intensity of the peaks of fragment ions as well as their AP in the series of nitroarenes has also been observed in the mass spectra of negative ions, and has been demonstrated convincingly in a series of studies by Bowie and coworkers[15,16,41,42,44]. They established that in carbonyl-containing nitroarenes (nitrobenzophenones, nitrobenzoates, etc.) the negative charge is localised preferentially at the oxygen atom of the carbonyl group. Thus in the series of isomeric nitrobenzophenones the IP and the AP of the $(M - C_6H_5CO)^+$ ions and the heats of their formation are similar to those of the *meta*- and *para*-isomers, but differ from the corresponding values for the *ortho*-isomers.[61]

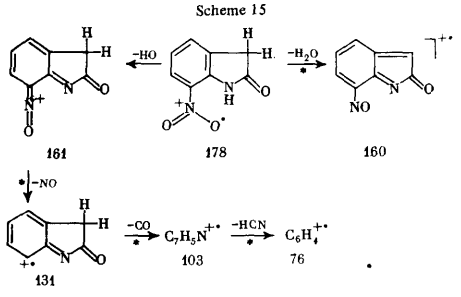
The same workers[61] showed that the mass spectra of negative ions of nitroarenes do not indicate their valence isomerisation or randomisation processes. Similar conclusions were reached also in the analysis of the mass spectra of the negative ions of nitrophthalic anhydride.[62] A considerable similarity between the main dissociative ionisation pathways of this compound in the mass spectra of negative and positive ions[63] and even the mass spectra obtained under the conditions of ion–molecule reactions[64] was noted.

III. NITRODERIVATIVES OF HETEROCYCLIC COMPOUNDS

In contrast to nitroarenes, nitro-derivatives of heterocyclic compounds have been studied to a much lesser extent. The results are difficult to survey owing to the fragmentary nature of the available information about the decomposition reactions of many types of heterocyclic compounds, in the study of which high-resolution mass spectrometry and labelled compounds have been rarely used.

Analysis of the mass spectra of 5-nitro-,[65] 7-nitro-, and 5,7-dinitrooxindoles[66] showed that 7-nitro-oxindole decomposes via the elimination of OH and H_2O from $M^{\ddagger}$ species (Scheme 15), whereas in the fragmentation of 5-nitro-oxindole such ions are not observed and only the $(M - NO)^+$, $(M - HCO)^+$, and $(M - CO)^+$ ions with masses of 148, 149, and 150 are formed:

Scheme 15



The mass spectrum of 5,7-dinitro-oxindole is characterised by decomposition pathways similar to those of 7-nitro-oxindole. Together with the molecular ion, it contains peaks due to the $(M - OH)^+$, $(M - H_2O)^+$, and $(M - OH - NO)^+$ ions with masses of 206, 205, and 176 respectively.

As was to be expected, the introduction of the nitro-group into the molecules of alkylindoles destabilises the molecular ion[67,68]. The primary dissociative ionisation processes are characterised in the first place by the formation of the $(M - NO)^+$ and $(M - NO_2)^+$ ions. Since the nitro–nitrite rearrangement always takes place in the first stage of the decomposition process, the ratio of the peak intensities of these ions reflects qualitatively the statistical weight of the isomerised structure of the molecular ion.

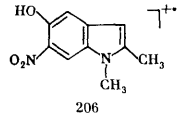
It has been shown[65] that, for an energy of 50 eV, the non-isomerised $M^{\ddagger}$ structures predominate and the fraction of nitrite ions is high only for 1-methyl-3-nitro-indole. The isomerisation proceeds more readily when the nitro-group is in the 6-position and not in the 5-position. The isomerisation of $M^{\ddagger}$ involving the 4- and 7-positions is probably hindered by the stabilisation of the nitro-group as a result of the *peri*-interaction. A decrease of the energy of ionising electrons, which increases the relative probability of rearrangements, increases the probability of the formation of "nitrite" ions approximately by an order of magnitude.

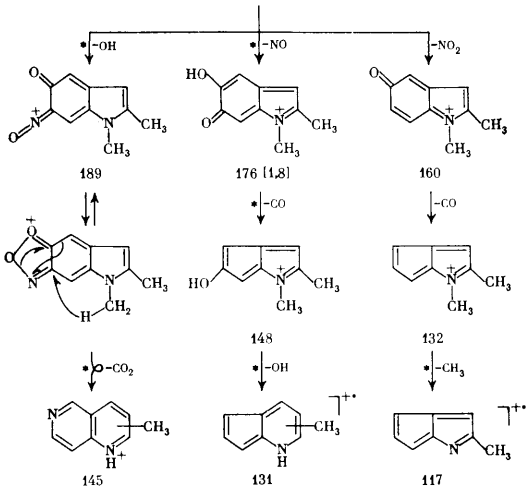
The β-decomposition processes (loss of hydrogen or of an alkyl group), which are typical of methyl indoles[69,70], proceed only in the second decomposition stage in the series of isomeric methylindoles. The presence of a methyl group in the *peri*-position relative to the nitro-group[68] or in the *ortho*-position[71] leads to the appearance of intense $(M - OH)^+$ ions, which permits a reliable identification of the isomers formed in the nitration of methylindoles. Although it is known that the presence of $(M - OH)^+$ ions is also characteristic of the mass spectra of *o*-nitroaniline and its derivatives[1,31], such ions are not observed in the mass spectrum of 7-nitroindole,[68] which is probably associated with the change in the nature of the amino-group in these compounds and the stabilising influence of the fused pyrrole ring.

The introduction of the hydroxy-group into the methyl-nitroindole molecule stabilises somewhat the molecular ion[68,72]. In contrast to oxindoles,[73] significant differences are observed between the mass spectra of the isomeric compounds. Although the stabilities of the $M^{\ddagger}$ species derived from 5-hydroxy-1,2-dimethyl-4-nitroindole and 5-hydroxy-1,2-dimethyl-6-nitroindole are similar, the intensities of certain characteristic ions [for example, $(M - OH - CO_2)^+$, $(M - NO_2 - CO)^+$, and a number of others], typical of *o*-nitrophenol,[1,29] differ by a factor of 2 and more. This indicates the absence of randomisation at the molecular ion stage, probably owing to the presence of the nitro-group. Analogous conclusions were reached in Bowie's study, already mentioned[32].

However, the characteristic pathways leading to the fragmentation of two isomeric nitro-oxindoles, illustrated in Scheme 16 in relation to the 6-nitro-isomer and confirmed by the determination of the elemental compositions of the fragment ions, are fundamentally similar.

Scheme 16

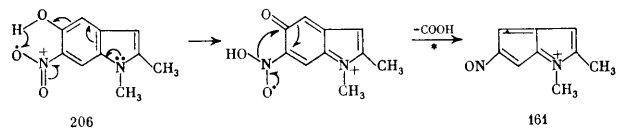




It must be emphasised that, as for methylnitroindoles, the intensity of the $(M - H)^+$ ionic peak in the mass spectra of hydroxymethylnitroindoles does not exceed 0.3–0.4% of the total ion current. This finding suggests a virtually complete suppression of processes typical for the decomposition of alkylindoles, whereas in the mass spectra of hydroxyscatoles peaks of the $(M - H)^+$ and $(M - alkyl)^+$ ions are fairly intense [68].

The presence of a pyrrole ring fused to a benzene ring promotes the stabilisation of intermediate transition states arising in complex rearrangements. Thus, although the principal pathways leading to the dissociative ionisation of nitro-oxindoles, [68,72] containing these functional groups in the 4- and 5-positions or in the 6- and 5-positions, are similar to the fragmentation of *o*-nitrophenol (the successive loss of OH and CO_2 by the moleculer ion or nitro–nitrite rearrangement with elimination of NO), the loss of NO from indole derivatives is three times more intense than in the case of *o*-nitrophenol. Furthermore, the possibility of the elimination of CO_2H from a series of nitro-oxindoles must also be explained by the stabilising influence of the pyrrole ring:

Scheme 17



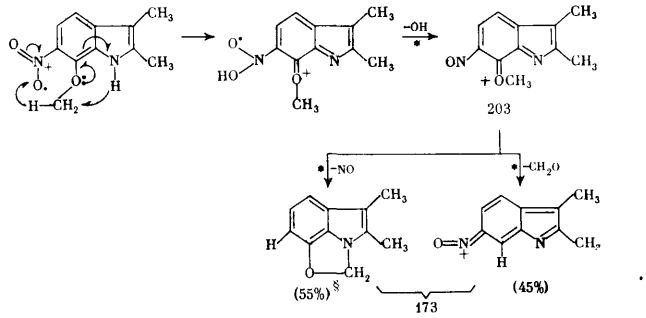
The decomposition pathways of isomeric methoxynitroindoles [68,72] are even more characteristic and differ in many respects from the dissociative ionisation of *o*-nitroanisole. Analysis of the intensities of the characteristic ions in the mass spectra of six isomeric methoxymethylnitroindoles, containing nitro- and methoxy-groups in the *ortho*-positions relative to one another, makes it possible to isolate fragments characteristic solely of the given compound. This permits the identification of each isomer from its mass spectrum. Thus the intense peaks of the $(M - CH_3)^+$ ion (whose intensity in the spectrum of *o*-anisole is low) are characteristic solely of methoxynitroindoles containing the methoxy-group in the 6-position. The rapid loss of the hydroxy-group by the molecular ion is characteristic only of compounds containing the nitro- and methoxy-group in the 6- and 7-positions respectively. However, if there is a methyl group in the 1-position of indole under these conditions, an intense peak of the $(M - NO_2)^+$ ion, which is virtually absent from the mass spectrum of the analogous unsubstituted indole, is observed.

The $(M - OH)^+$ ion mentioned above is completely uncharacteristic of the mass spectra of *o*-nitroanisole and its formation has been attributed [68,72] to the presence in the above structures of the N–H or CH_2–H group in the *peri*-position relative to the methoxy-group, which favours the push–pull transfer of hydrogen to an oxygen atom of the nitro-group (Scheme 18).

When the indole molecule contains simultaneously nitro- and carboxy-groups [71,74], the primary decomposition processes are characterised in the first place by the elimination of an ethoxy-group or an ethanol molecule, which is typical for ethoxycarbonylindoles. [75,76] The elimination or isomerisation and decomposition of the nitro-group take place only in the second stage, i.e. the formation of the primary ions is controlled only by one of the functional groups.

Thus, in contrast to *ortho*-substituted nitroarenes, the *ortho*-substituted nitroindoles decompose via specific channels, which depend on the position of the nitro-group and another functional group relative to the pyrrole nitrogen atom.

Scheme 18



In the series of nitrocarbazoles [77] there are no characteristic pathways which would permit the identification of the isomeric compounds and the most intense fragment ions are $(M - NO)^+$ and $(M - NO_2)^+$. The probability of the nitro–nitrite rearrangement increases by an order of magnitude when the ionisation energy is reduced from 50 to 15 eV. Nevertheless one should note that the ratio of the intensities of the ions $Z = I_{M-MO}/I_{M-NO_2}$ for 3,6-dinitrocarbazole is 1.1, whereas in the case of 3,8-dinitrocarbazole the probability of the elimination of the nitro-group is greater ($Z = 0.72$).

Analogous differences between the values of Z were observed in the series of nitrodibenzofurans, [78] where the 3-nitro-isomer, in which the nitro-group is conjugated with the oxygen atom of the heterocycle, shows the greatest capacity for rearrangement. The same conclusions also follow from the analysis of the mass spectra of a series of isomeric nitroxy-4-oxo-2-chromenes [79] and nitro-substituted N-aryliminopyridyl- and isoquinolinyl-betaines [80] and from the analysis of the mass spectra of negative ions of nitrophenyltriazoles. [81]

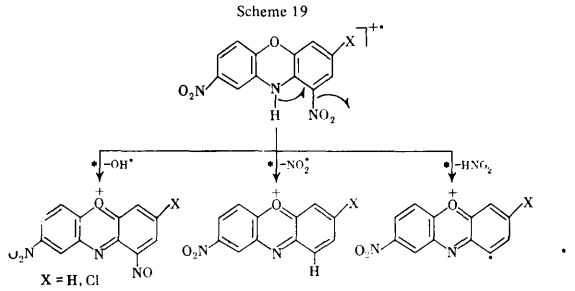
In the dissociative ionisation of nitrophenoxazines and azaphenoxazines [82] the fraction of rearranged ions is very low and the main primary decomposition processes are associated with the elimination of the nitro-group from the molecular ion and, in the case of the 4,6-dinitro-derivative, of a nitrous acid molecule, In the latter case

§The fraction of the ion having the given composition in the ion with $m/e = 173$.

the $(M - OH)^+$ ion, formed with participation of the hydrogen atom of the NH group, is also observed (Scheme 19).

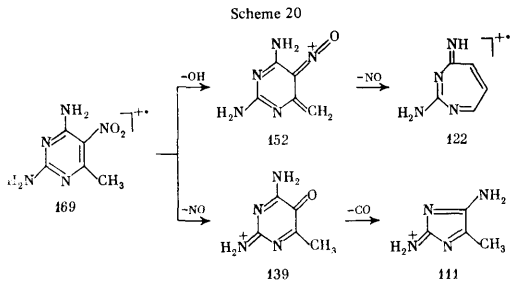
In many instances the occurrence or non-occurrence of the nitro–nitrite rearrangement is associated with the conditions under which the mass spectrum is recorded. Thus the mass spectra of *N*-nitroaminopyridines [83] can be obtained only when they are cautiously introduced into the mass spectrometer by direct injection into the ion source. In this case dissociative ionisation leads to intense peaks of the $(M - NO_2)^+$ ions. On the other hand, the introduction of *N*-nitroaminopyridines via the filling cylinder or using a glass system entails intense pyrolysis, as a result of which the mass spectrum consists of NO_2^+ and NO^+ ions and the products of the dissociative ionisation of aminopyridine, probably formed as a result of an ion–molecule reaction. The mass spectrum of 2-(*N*-methyl-*N*-nitro)aminopyridine, obtained on apparatus with direct injection [into the ion source] shows that the only important decomposition pathway of the molecular ion involves the abstraction of NO_2.

Scheme 19



At the same time the $(M - NO_2)^+$ ions are completely absent from the mass spectra of 4-substituted 2-amino-6-methyl-5-nitropyrimidines [84] and the primary decomposition pathways of these compounds involve the elimination of NO (the main process) or the ejection of OH (as a result of the *ortho*-effect):

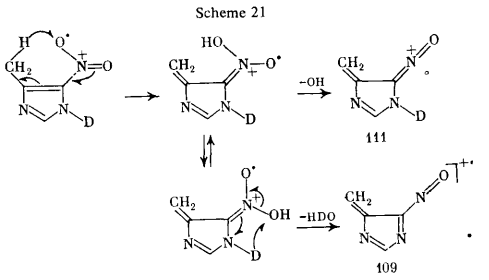
Scheme 20



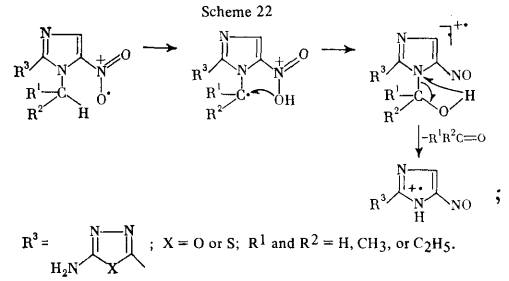
It is of interest that the mass spectrum of this compound also contains the $(M - OH - H_2O)^+$ ion, whose formation is apparently to be accounted for by a double rearrangement of the type found by Lord and Millard [85]. In a study of the mass spectrum of 4(5)-methyl-5(4)-nitroimidazole they observed the so-called "double *ortho*-effect", as a result of which water is eliminated from the molecular ion (Scheme 21), which has been demonstrated by the analysis of the mass spectra of deutero-derivatives.

Van Lear [86] reported an unusual rearrangement associated with the migration of the oxygen of the nitro-group from the nitrogen atom to a carbon atom, which he observed in the dissociative ionisation of a series of 1-alkyl-2-substituted 5-nitroimidazoles. In contrast to the instances described above, the $(M - 30)^+$ ion in the mass spectra of compounds of this type corresponded to the abstraction of CH_2O and not the elimination of NO. In order to account for the findings, a complex mechanism of the rearrangement was proposed, involving double hydrogen transfer and migration of the hydroxy-group (Scheme 22).

Scheme 21

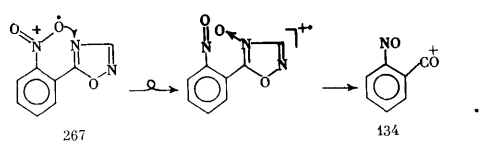


Scheme 22



It must be emphasised that, when the substituents R^3 are alkyl groups, the $(M - 30)^+$ ion is the usual $(M - NO)^+$ ion.

The unusual migration of an oxygen atom of the nitro-group to the nitrogen atom of the heterocyclic ring has also been noted for 5-(*o*-nitrophenyl)-1,2,4-oxadiazole [87]:



Kato and Hirao [88] showed in relation to the mass-spectrometric decomposition of a series of nitrofuryltriazoles that in the case of bisheterocycles the ring containing the nitro-group is mainly cleaved. The kinetic energy liberated as a result of the elimination of the nitroso-group (~0.77–0.81 eV) actually exceeds the value for the analogous processes in the mass spectra of 5-nitro-2-furonitrile and *o*-nitrophenol. [19,20]

Unfortunately, the partial mass spectra of triazoles presented in the literature [88–91] do not permit a sufficiently accurate assessment of the probability of the nitro–nitrite rearrangement when the nitro-group is located in this type of heterocyclic ring. In the case of 10-alkyl-3-nitrophenothiazines and their oxides [92] the $(M - NO)^+$ and $(M - NO_2)^+$ ions were observed solely in the mass spectrum of the 10-methyl derivative without the oxide group.

In the dissociative ionisation of isomeric nitrophenylisoxazoles [93–95] the intensity of the $(M - NO)^+$ ionic peaks is as a rule higher than that of the peaks due to the $(M - NO_2)^+$ ions and a definite correlation has been established between their intensity and the stability of the conjugate cyclic structures where the charge is localised at the oxygen atom.

In the spectra of saturated heterocycles such as isoxazolidines, containing a nitro-group in the 8-position,[96,97] $M^{+\cdot}$ species are not observed at all and the ions with the maximum mass are $(M - NO_2)^+$.

Thus examination of processes involving the dissociative ionisation of nitro-derivatives of arenes and heterocyclic compounds shows that the occurrence of rearrangements in the molecular ion itself and in the first stages of its decomposition is characteristic of these compounds. The nitro–nitrite rearrangement takes place with a high probability in compounds without any substituents in the *ortho*-position. In this case the probability of the nitro–nitrite rearrangement is related to the electronic influence of the substituents in other positions in the aromatic ring. When an *ortho*-substituent is present, the principal rearrangements are determined by the interaction of the nitro-group with the substituent, which leads to the suppression of the nitro–nitrite rearrangement and the appearance of new decomposition channels characteristic of the given substituent.

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