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Mass Spectra of Nitro-substituted Aromatic Nitramines: a Novel *ortho*-Effect

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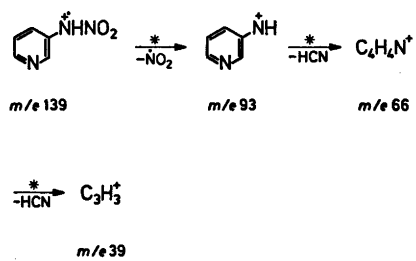
The mass spectra of nitro-substituted aromatic nitramines have been studied; compounds of this kind carrying neighbouring nitro and nitramino functions exhibit a hitherto unrecognized mass spectrometric proximity-effect. An oxygen atom is transferred from the nitro to the nitramino group, leading after elimination of NO_2 to loss of two NO fragments. The possibility of observing similar interactions in other compounds bearing nitro groups next to nitrogen substituents has been investigated.

ortho-Effects or proximity-effects are frequently observed in the mass spectral decomposition of benzenoid compounds with neighbouring substituents.[1] One of the substituents that frequently take part in *ortho*-interactions is the *nitro* group,[2,3] which has been observed to interact with neighbouring groups in two distinct ways: (i) an oxygen atom of the nitro group may abstract a hydrogen atom from the *ortho* substituent, as is seen by the formation of abundant $[M-OH]^+$ ions in the decomposition of *o*-nitrotoluene [4,5] or *o*-nitroaniline;[6] or (ii) a nitro oxygen atom may migrate to the neighbouring function, as has been observed in the fragmentation of *o*-nitrotoluene,[5] *o*-nitroanisole,[7] *o*-nitrohydrazones,[8–10] *o*-nitrostilbenes,[8,11] *o*-nitrothiobenzoic esters,[12] and *o*-nitrobenzoic amides.[13]*

In connection with studies of the photochemical reactions of aromatic nitramines [14] we have examined also the mass spectral reactions of many of these compounds to see if a correlation between the mass spectral and the photochemical behaviour should exist. The electron impact induced decomposition of a number of simple nitraminopyridines has been reported recently by Wilson and collaborators,[15] and we have been able to confirm that also more highly substituted compounds of this class decompose by the fragmentation reactions described.[15] The inclusion of substituents such as chloro or methyl on the aromatic ring does not change the fragmentation pattern appreciably, but a few additional decomposition reactions are introduced in a quite predictable way. The reactions of *N*-alkyl nitramines (see Fig. 1b) are significantly influenced by the presence of the alkyl group, but the basic decomposition reactions of aromatic nitramines remain unchanged.

The initial reaction of the nitramine molecular ion is elimination of an NO_2 radical, with formation (formally) of a protonated nitrene (see Scheme 1); similarly, the initial photochemical



Scheme 1.

* Schwarz and Bohlmann [13] report that *o*-nitrobenzpiperidide eliminates a piperidinoxyl radical upon electron impact; similar reactions have been observed by the present authors to take place in the fragmentation of the *N*-ethyl- and *N*,*N*-diethylamides of *o*-nitrobenzoic acid.

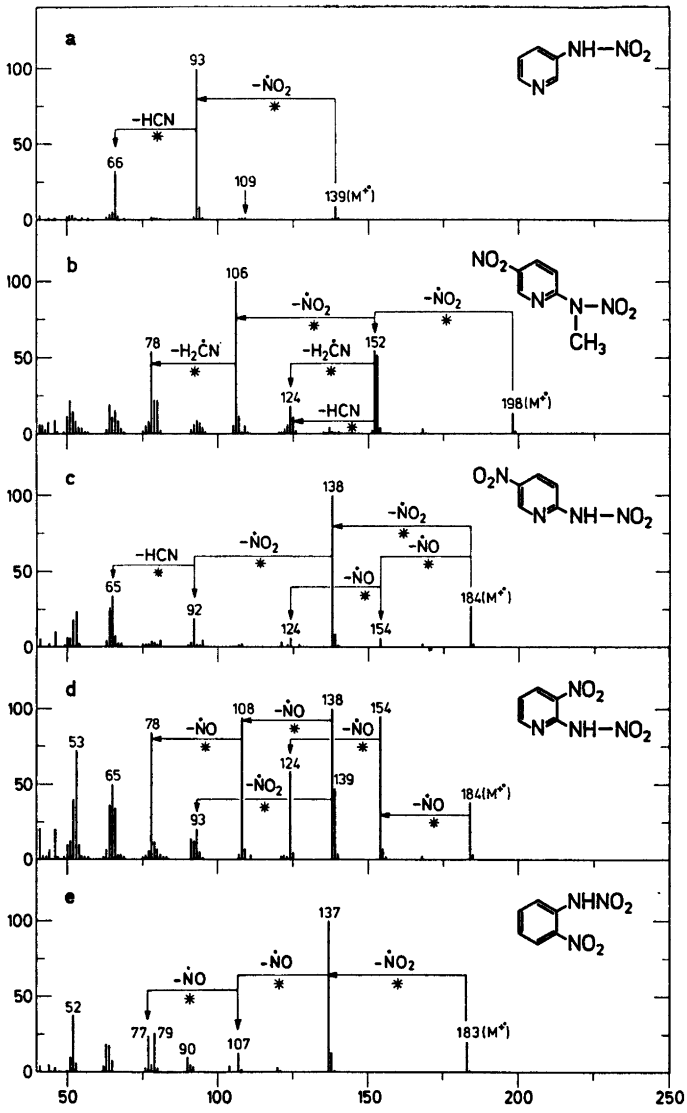
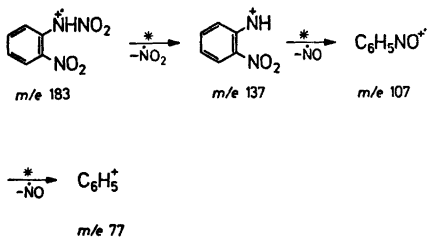


Fig. 1. Mass spectra (at 70 eV) of (a) 3-nitraminopyridine; (b) *N*-methyl-5-nitro-2-nitraminopyridine; (c) 5-nitro-2-nitraminopyridine; (d) 3-nitro-2-nitraminopyridine; (e) 2-nitro-*N*-nitroaniline.

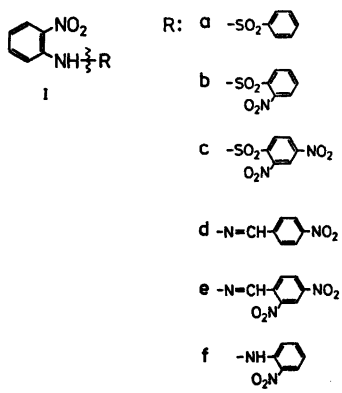
reaction is NO_2 expulsion.[14] In most cases the $[M-NO_2]^+$ ion then decomposes by elimination of another substituent, if present, or by cleavage of the aromatic nucleus (see Fig. 1a). For nitro-substituted nitramines a similar situation exists (Fig. 1c), except when the nitro and nitramino substituents are situated next to each other. In these cases the reactions subsequent to NO_2 loss take a different course (see Scheme 2 and Figs. 1d and 1e). Two NO fragments are eliminated in succession, showing that one of the oxygen atoms of the nitro group has become bonded to the remaining nitrogen atom of the nitramino function. The proximity of the nitro and nitramino substituents has consequences also for other decomposition reactions. Comparison of the spectra of the 5- and 3-nitro-2-nitraminopyridines (Figs. 1c and 1d)



Scheme 2.

shows that NO loss from the molecular ion is much more pronounced in the latter case, where it is followed by loss of another NO fragment. Whether the amide nitrogen atom is lost also in these reactions is not clear; a definitive decision would require isotopic (^{15}N) labelling. A low intensity peak in the spectrum of 2-nitro-*N*-nitroaniline (Fig. 1e) shows that an OH· radical may be lost from the $[M-NO_2]^+$ ion, probably also as a result of an *ortho*-interaction similar to that observed in *o*-nitroaniline.[6]

In an attempt to investigate whether the *ortho*-interaction uncovered in the present work is common to compounds that under electron impact generate ions with nitro groups *ortho* to aromatic -NH+ groups (protonated nitrenes) we have examined the mass spectra of the compounds shown in Scheme 3. Fission of the bond indicated in (I) with a wavy line occurs in the decomposition of the sulfonamides (Ia–c) and hydrazones (Id,e), but always with charge retention in R; 2,2′-dinitrohydrazobenzene (If), likewise does not give an *m/e* 137 peak (*cf.* Scheme 2) but decomposes instead by elimination of a water molecule and formation of nitrophenyldiazonium ions. It is thus not possible yet to assess the general nature of the *ortho*-effect described above.



Scheme 3.

Thermal effects. Wilson and coworkers [15] noted that the nitramines examined by them suffered decomposition if the heated inlet of the mass spectrometer was used for introduction of the samples into the ion source rather than the direct inlet (solid probe). We have observed that not even use of the direct inlet will completely eliminate reactions prior to ionization. In most cases peaks originating from an "impurity" with an apparent molecular ion of mass 45 a.m.u. less than that of the nitramine appeared in the spectra. This contaminant is presumably the parent amine generated by wall reactions of the nitramine. The intensity of the impurity peaks was found to increase with the temperature of the ion source and with the length of time elapsing from introduction of the compound to the spectrum was actually run. Spectra of the pure parent amines [16] support the suggested identity of the contaminant.

$[M+1]^+$ peaks were encountered in the spectra of several compounds; the additional hydrogen atom is "picked up" at the source walls rather than by bimolecular reactions of two nitramine molecules, since the [M + 1] peaks were replaced by [M + 2] peaks upon saturating the spectrometer with D_2O.

EXPERIMENTAL

The mass spectra were recorded on an AEI MS-902 mass spectrometer by Ms. E. Wolff-Jensen. The ion source temperature was kept as low as possible, typically at 100 °C.

The nitraminopyridines examined were prepared as given in the literature.[17] *o*-Nitro-*N*-nitroaniline was prepared by dehydration of *o*-nitroanilinium nitrate according to Hoff.[18] The sulfonamides (Ia–c) were prepared from *o*-nitroaniline and the appropriate sulfonyl chloride, and the hydrazones (Id,e) were prepared by condensation of *o*-nitrophenylhydrazine with the appropriate benzaldehyde. 2,2′-Dinitrohydrazobenzene was obtained from the corresponding azobenzene by reduction with ammonium hydrosulfide as described by Green and Rowe.[19]

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