Mass Spectrometry: The Elimination of CO from Substituted Nitro Naphthalenes

J. H. Beynon *, B. E. Job **, and A. E. Williams *

Imperial Chemical Industries Limited

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The mass spectra of 1-nitronaphthalene, 2-nitronaphthalene and eight substituted nitro naphthalenes have been studied. The loss of neutral CO from the molecular ions of these compounds has been established by high resolution techniques and study of "meta stable" peaks. The probability of elimination has been related to the electron density at the 8-position.

Experimental

The mass spectra of 1-nitronaphthalene, 2-nitronaphthalene and eight substituted nitronaphthalenes have been obtained using an A.E.I. M.S. 9 double focusing mass spectrometer [1] under conditions of both high and low resolution.

Results

The base peak in the mass spectra of 2- nitronaphthalene and 1-nitronaphthalene (Fig. 1) is at *m/e* 127. This elimination of the nitrogroup from the parent ions can occur by simple bond cleavage and is accompanied by a "meta-stable peak" (m. s. peak) at *m/e* 93.2.

A study of m.s. peaks permits the identification of ions that are the result of a single fragmentation of the parent ion. Thus, the loss of the NO moiety (m.s. peak at *m/e* 118.4) is observed, as in aromatic nitro compounds previously studied [2]. However, a third fragment ion observed from 1-nitronaphthalene (but not from the 2-nitro isomer) is the ion of *m/e* 145 which again results from a single fragmentation of the parent ion (m.s. peak at 121.5). Accurate mass measurement has established the *m/e* 145 ion to be $C_9H_7NO^{\cdot +}$; neutral carbon monoxide has therefore been eliminated from the parent ion.

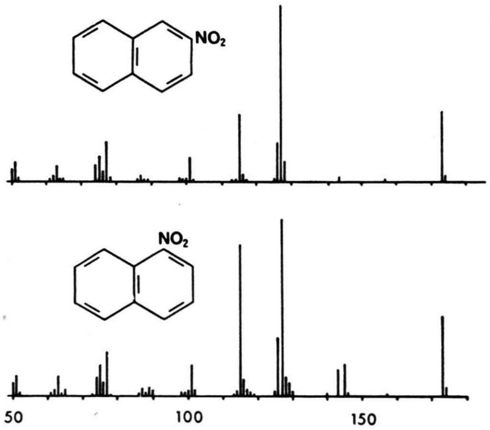
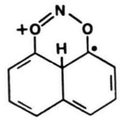


Fig. 1. The mass spectra of 2-nitronaphthalene and 1-nitronaphthalene.

As this interesting and novel fragmentation is not observed in 2-nitronaphthalene or in nitrobenzene [2] it is reasonable to propose that the intermediate through which it occurs involves the 8-position in the naphthalene nucleus. This is confirmed by the fact that neither 1-nitro, 8-amino- nor 1,8-dinitronaphthalene shows loss of CO from its parent ion (see Figs. 4 and 5).

Several decomposition routes may be postulated to explain the elimination of CO from the 1-nitronaphthalene parent ion. The first of these involves the initial isomerisation of the nitro group to the nitrite form, as must happen during the initial loss of nitric oxide from many aromatic nitro compounds [2]; this would be followed by the formation of a six membered ring to the 8-position in the naphthalene nucleus to produce an intermediate state such as:



However, it can readily be deduced that this does not occur; were such an activated complex formed, its

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* Dyestuffs Division, Research Department, Hexagon House, Manchester 9.

** Petrochemical and Polymer Laboratory, The Heath, Runcorn, Cheshire.

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[2] J. H. Beynon, R. A. Saunders, and A. E. Williams, Ind. Chim. Belge **29**, 311 [1964].

structure would be the same for borth the 1,4- and 1,5-dinitro isomers and their spectra show marked differences as is described below. In some other reactions of nitro compounds that have been studied, it has also been shown that the nitrite form is not an intermediate in the reaction [3].

Two mechanisms that do not require the initial isomerisation of the nitro group are proposed. These are illustrated in Figs. 2 and 3; the symbolism used is that proposed by DJERASSI [4] and subsequently recommended by SHANNON [5].

The ultimate indenyl or "isoindenyl" ion is the second most abundant in the spectrum of 1-nitronaphthalene, and clearly has a particularly stable structure.

These schemes involve different transition states, but both involve the formation of a keto species as an intermediate. Loss of carbon monoxide from such a structure is well known [6]. Subsequent loss of nitric oxide is easily visualised. The ion of m/e 115 thus formed does also occur as a result of initial loss of NO followed by CO elimination. Both these reaction paths are recognisable from the presence of m.s. peaks

$173^+ \rightarrow 145^+ + 28$; m.s. peak 121.5
$C_{10}H_7NO_2{\cdot}^+ \rightarrow C_9H_7NO{\cdot}^+ + CO$
$145^+ \rightarrow 115^+ + 30$; m.s. peak 91.2
$C_9H_7NO{\cdot}^+ \rightarrow C_9H_7^+ + NO^{\cdot}$

and also

$173^+ \rightarrow 143^+ + 30$; m.s. peak 118.4
$C_{16}H_7NO{\cdot}^+ \rightarrow C_{10}H_7O^+ + NO^{\cdot}$
$143^+ \rightarrow 115^+ + 28$; m.s. peak 92.4
$C_{10}H_7O^+ \rightarrow C_9H_7^+ + CO$

Loss of two successive CO molecules from the parent ion is feasible, the second being removed as the result of similar mechanisms to those proposed for the initial loss. The ease of NO removal after the initial CO elimination causes loss of a second CO molecule to occur with low probability. However, the presence of a peak at mass 117 of formula $C_8H_7N{\cdot}^+$ indicates that two CO molecules can be

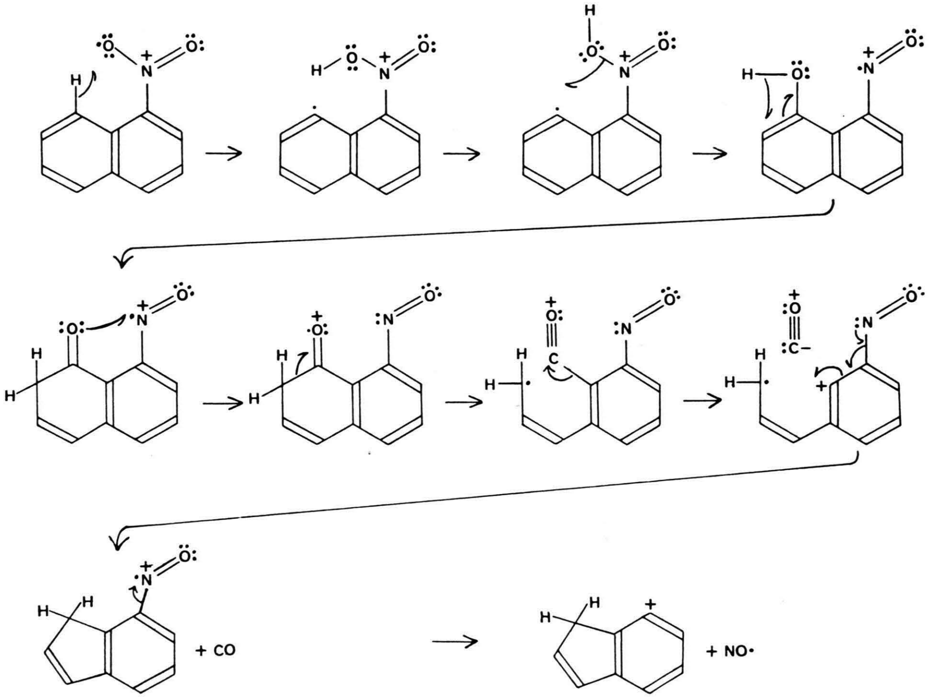

Fig. 2. A proposed mechanism to explain the loss of neutral CO from 1-nitronaphthalene.

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[3] J. H. BEYNON, R. A. SAUNDERS, and A. E. WILLIAMS, J. Chem. Soc. **1965**, 6403.

[4] H. BUDZIKIEWICZ, C. DJERASSI, and D. H. WILLIAMS, Interpretation of Mass Spectra of Organic Compounds, Holden-Day, San Francisco, 1964, pp. XI, XII.

[5] J. S. SHANNON, R. A. C. I. 323, Sept. 1964.

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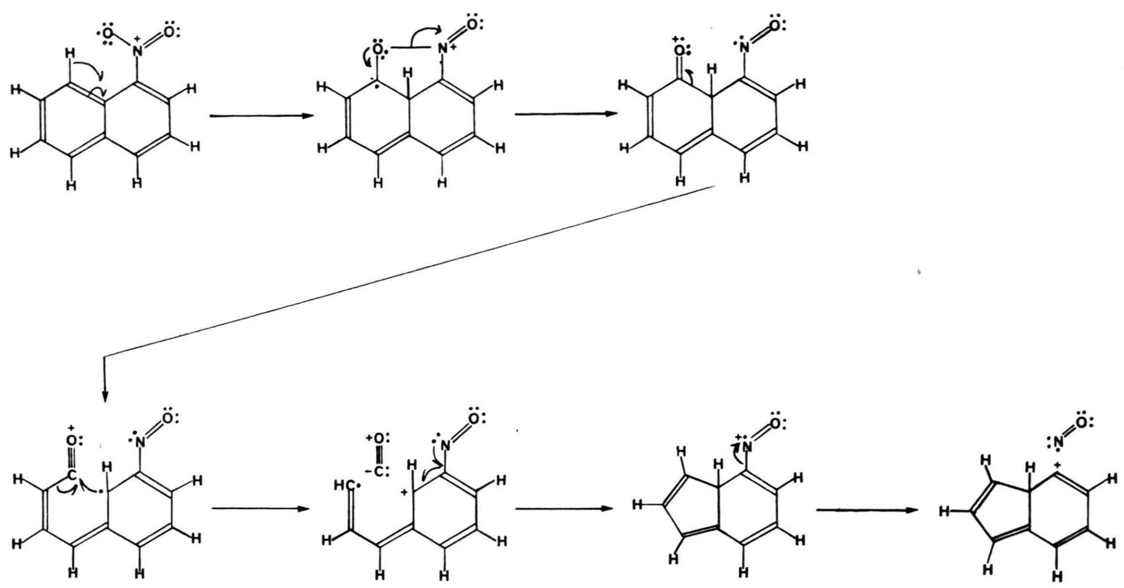

Fig. 3. An alternative proposed mechanism to explain the loss of neutral CO from 1-nitronaphthalene.

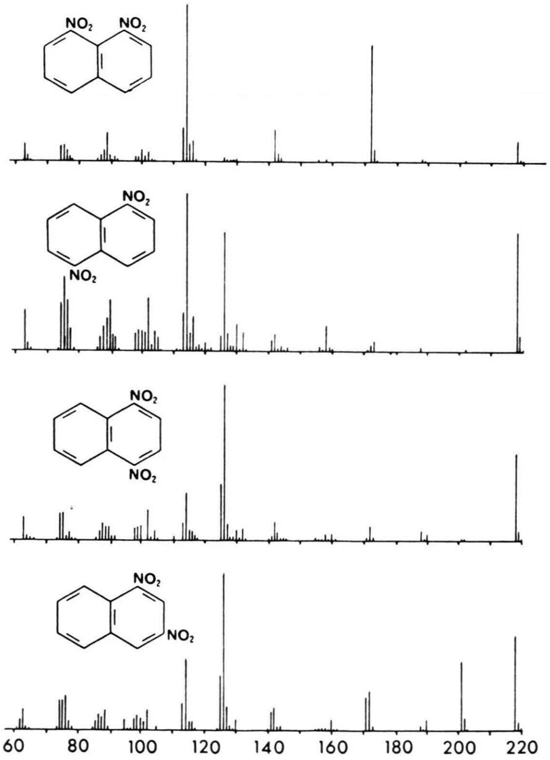

Fig. 4. The mass spectra of some di-nitronaphthalenes.

removed from the parent ion. A m.s. peak at *m/e* 69.2 ($117^{+} \rightarrow 90^{+} + HCN$) is observed and indicates a further decomposition of this $C_8H_7N^{\cdot +}$ ion.

The two mechanisms proposed for the initial loss of CO from the molecular ion of 1-nitronaphthalene require the initial removal of a hydrogen atom, along with one of the electrons through which it was bonded to the 8-carbon atom. According to this mechanism, therefore, the loss of CO will be hindered if there is an electron deficiency at this position. A study of the amount of CO lost from the parent ions of some dinitronaphthalenes (shown in Fig. 4) supports this hypothesis. Using molecular orbital theory it is possible to derive comparative values for the electron population at each carbon atom in the naphthalene system. Although these calculations were for the neutral molecules, the order in which they can be placed with respect to the electron density at the 8-position may be used as a guide to the situation in the positively charged molecular ions. In order of decreasing electron density this is:

1,3-dinitro > 1-nitro > 1,4-dinitro ≫ 1,5-dinitro .

The elimination of the CO fragment occurs with a probability that is related to the electron density at the 8-position. This is most dramatically illustrated in the case of 1,5-dinitronaphthalene; here a high electron deficiency results in zero loss of carbon monoxide from the parent ion.

1,3-dinitronaphthalene is apparently anomalous in that its electron excess suggests a higher CO loss than that observed. Here, however, there exists the possibility that the positive charge will be located at the 3 nitro group, a ring position from which CO cannot be lost (vide 2-nitronaphthalene). The schemes proposed indicate that an unpaired electron on an oxygen atom is necessary for the first intermediate structure to be formed. In this case therefore the probability of the positive charge residing on the nitro group in the 1-position also governs the fragmentation under examination.

In the case of the amino substituted 1-nitronaphthalenes (Fig. 5) it would be predicted from the electronic charge densities that the parent ion of 1-nitro-5-amino naphthalene would lose CO more readily than that of 1-nitro-4-amino naphthalene and this is, in fact, observed. However, on the basis of electronic charge densities alone, one would predict that loss of CO for both nitro amino naphthalenes studied should be much greater than for 1-nitronaphthalene.

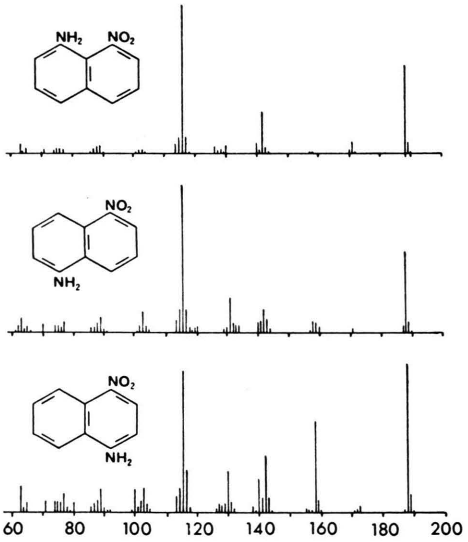

Fig. 5. The mass spectra of some amino-substituted 1-nitronaphthalenes.

Ionisation at the amino group will occur at a potential comparable with that for ionisation at the nitro group; the elimination of carbon monoxide is correspondingly reduced therefore in these di-substituted naphthalenes as in the case of 1,3-dinitronaphthalene.

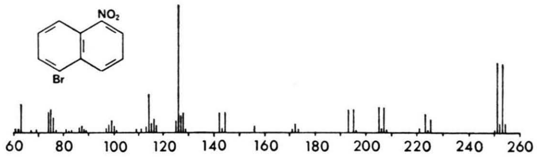

Fig. 6. The mass spectrum of 1-nitro-5-bromo-naphthalene.

One further compound has been studied; the spectrum of 1-nitro-5-bromo naphthalene (Fig. 6) shows a prominent peak corresponding to loss of CO from its parent ion. No estimate is available for the charge density at the 8-position in this compound. It may be concluded, as a result of the correlations made above, that the Br atom can donate its p-electrons to the aromatic system sufficiently to counteract the inductive removal of electrons, so leaving an electron excess at the 8-position comparable with that for 1-nitronaphthalene. Since the Br atom could presumably carry the positive charge to a small extent the electron excess would need to be correspondingly higher in order to explain the observed CO loss.

Acknowledgement

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