The Mechanism of NO Loss from the Molecular Ion of Nitrobenzene and the Fragmentation Behaviour of the Phenoxy and *p*-Aminophenoxy Cations

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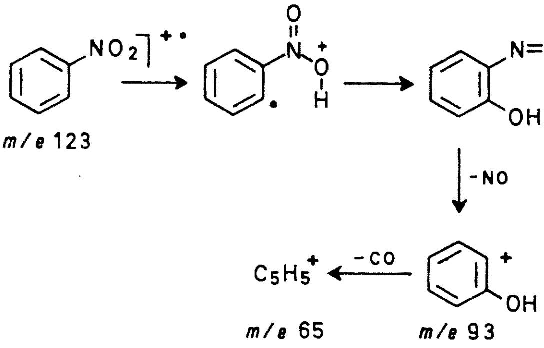
Summary The mass spectra of [1-^{13}C]nitrobenzene and [1-^{13}C]-*p*-nitroaniline reveal that in the phenoxy and the *p*-aminophenoxy cations, produced by loss of NO from their molecular ions, positional identity of the oxygen atom is retained in their subsequent fragmentations.

POSSIBLE mechanisms for the loss of NO from the molecular ions of nitro-arenes have recently been reviewed;[1] they include *in situ* nitro–nitrite isomerisation[2] and rearrangement *via* a three-membered-ring intermediate.[3] Participation of the *ortho*-hydrogen atoms in this process was considered unlikely because 2,3,5,6-tetrafluoronitrobenzene still showed loss of NO from the molecular ion.[4] Other evidence, accumulated from examination of the "flat-top" metastables accompanying NO loss from nitro-phenols,[3] supports the suggestion that the remaining oxygen atom is attached to the original ring position. However, recent experiments on *o*-nitro-arenes[5] indicate that loss of NO can be enhanced by the presence of a vacant *ortho* site. A reasonable mechanism for the nitro–nitrite isomerisation involving *ortho*-hydrogen participation can be put forward using the behaviour of the benzoic acid molecular ion as an analogy[6] (Scheme). This mechanism can be tested by examining the mass spectrum of [1-^{13}C]nitrobenzene. Complete retention of the label in the $C_5H_5^+$ ion would give support to the above suggestion while complete loss of label would rule it out. Partial loss of the label would suggest the occurrence of oxygen migration or "scrambling" and such behaviour has been reported as occurring in the ion $C_6H_6NO^+$ produced by loss of NO from the molecular ion of *p*-nitroaniline.[7] Davis and Williams[8] find this result difficult to reconcile with the metastable-ion studies which indicate retention of positional identity. In order to solve these problems we have made [1-^{13}C]nitrobenzene (I) and [1-^{13}C]-*p*-nitroaniline (II) using [1-^{13}C]benzoic acid (64·8% labelled) as starting material. Compound (I) was prepared from the latter by the procedures of Bachmann and Goldmacher[9] (conversion into aniline) and of Emmons[10] (oxidation to nitrobenzene). Compound (II) was prepared from the intermediate aniline.[11]



The 70 ev mass spectrum of (I) showed complete loss of the label in the process $(M - NO)^+ - CO \rightarrow C_5H_5^+$, proving that positional identity of the remaining oxygen atom is retained when the nitro–nitrite isomerisation takes place and that *ortho*-hydrogen atom participation is not involved. The phenyl ion, $^{13}C^{12}C_5H_5^+$, produced by loss of NO_2 from the molecular ion, was observed to lose the label in a completely random manner when it fragmented by loss of C_2H_2, a result similar to that obtained with benzene by Macdonald and Shannon.[12]

In the mass spectrum of [1-^{13}C]-*p*-nitroaniline the peaks *m/e* 80, 81; $C_5H_6N^+$, $^{13}C^{12}C_4H_6N^+$ were found to retain the ^{13}C label; at electron energies of 20 and 30 ev retention was complete and at 70 ev retention was *not less than* 95%. The lower limit given for the last figure is due to the small correction which can be made for the contribution of $^{13}C^{12}C_4H_5N^+$ to *m/e* 80. If this is assumed to be 10% (ratio *m/e* 80: *m/e* 79 in the pure unlabelled compound is 10·3) then retention is complete. The above results therefore remove the recently quoted [8] inconsistency. Both the phenoxy and *p*-aminophenoxy cations generated from the corresponding nitro-compounds retain positional identity of their oxygen atoms when they further fragment by CO elimination, and the earlier conclusion[7] concerning the *p*-nitrophenoxy cation is therefore in error.

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