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PROTONATION, ETHYLATION AND ALLYLATION OF SUBSTITUTED NITROBENZENES IN THE GAS PHASE. A STUDY BY ION KINETIC ENERGY SPECTROMETRY AND CHEMICAL IONIZATION

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INTRODUCTION. We report a study of ion structures in the gas phase using the unique combination of a chemical ionization (CI) source[1] and a reversed sector mass spectrometer.[2,3] Substituted nitrobenzenes were chemically ionized by protonation, ethylation, or allylation. The first sector of the mass-analyzed ion kinetic energy spectrometer (MIKES) was employed to select for study only ions with the appropriate m/e ratio. As the mass-selected ions traverse the second field-free region of the instrument, they fragment spontaneously or, if collision gas is introduced, by collision-induced dissociation (CID).[4] Kinetic energy analysis of the fragment ions using an electric sector then serves to fix their masses and the resulting fragmentation patterns observed for each mass-selected reacting ion are employed in the structural analysis. The tendency for CID reactions to occur by simple bond cleavages aids in structural assignment.[5]

EXPERIMENTAL. Experimental conditions were those described elsewhere.[6] The field-free region pressure was 2×10^{-7} torr in low pressure scans and 5×10^{-5} torr (air) in high pressure scans. The CI source[7] was supplied by Scientific Research Instruments and interfaced to the MIKES as described elsewhere.[2,6] Samples were introduced using the standard direct insertion probe and were used as obtained commercially. Methane, which generates 17^+, 29^+ and 41^+, was used as the reagent gas in all experiments.[1]

RESULTS AND DISCUSSION. Figure 1, column 1 shows the MIKE spectra, taken in the presence of collision gas, of the $(M+29)^+$ ions of four p-substituted nitrobenzenes. These data are representative of those obtained for other compounds. All four spectra are strikingly similar, showing the same three major fragmentations: loss of 28 (C_2H_4), 45 ($C_2H_5O\cdot$) and 75 (C_2H_5ONO). The first reaction is the lowest energy process as shown by the fact that it occurs as a metastable ion reaction in the absence of collision gas. While it is easily accommodated by a six-

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centered cyclic rearrangement of an O-ethylated ion (analogously to thermal elimination in esters), it provides at best only supporting evidence for this structure of the $(M+29)^+$ ion. The losses of EtO· and EtONO, however, strongly support the O-ethylated ion structure. It is expected that simple bond cleavages should be the predominant CID reactions[5] and these neutral losses can only be explained by simple bond cleavages from the O-ethylated structure.

Figure 1, column 2 shows the main features of the high target pressure MIKE spectra of the protonated molecular ions of four nitrobenzenes. As in the spectra of ethylated compounds, common fragmentations occur throughout the series, again pointing to one dominant ion structure. Loss of a hydrogen atom is a major reaction as is loss of 17 (OH·)[8] and loss of 47 (NO_2H).

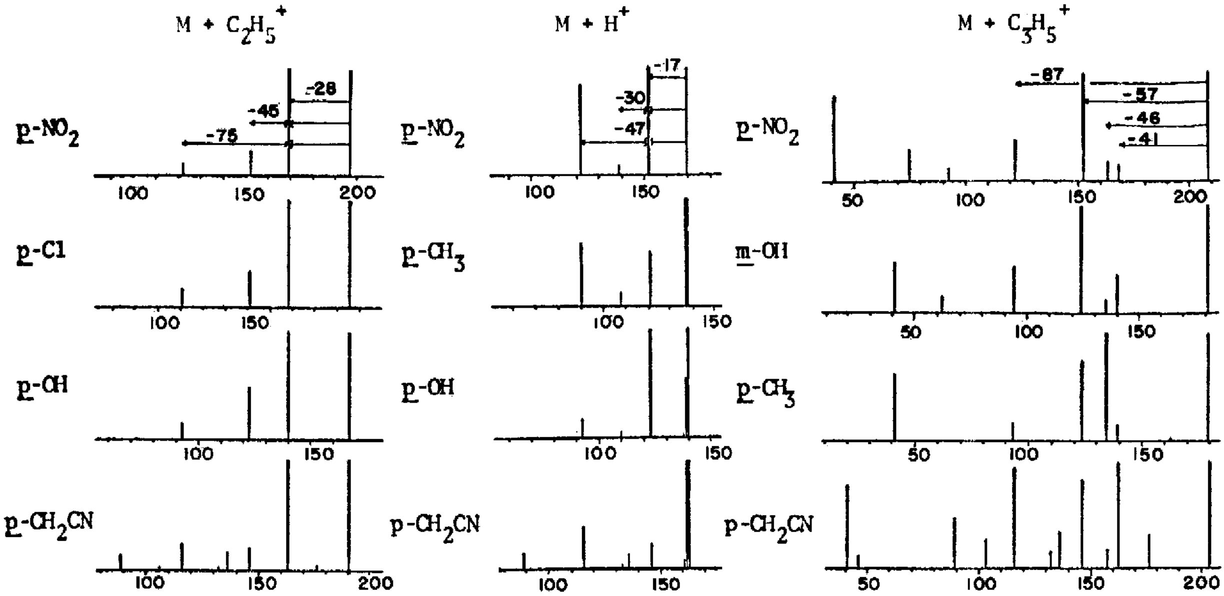
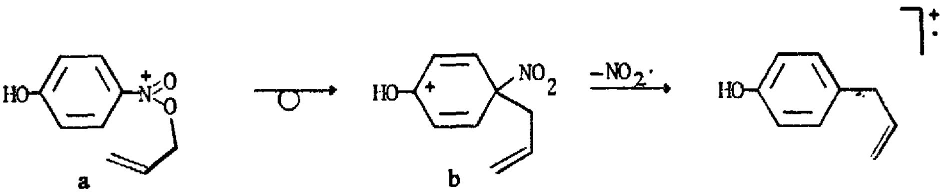


Figure 1. MIKE spectra in the presence of target gas for ethylated (column 1), protonated (column 2), and allylated (column 3) substituted nitrobenzenes. The mass scales have been shifted to align the signal for the parent ions so that daughter ions resulting from the loss of the same neutrals occur at identical positions.

The latter two reactions are the analogs of the structurally diagnostic OEt· and NO_2Et losses from the $(M+29)^+$ ions and are best explained by protonation on the nitro-group. Loss of H· (which does not have an analog in the ethylated case) was examined further to distinguish between the various possible source of this atom. The spectrum of 2,6-dideutero-4-nitrophenol showed exclusively (>90%) loss of H· consistent with loss of the atom supplied as a proton in the ionization step. Furthermore, loss of HNO_2 was not accompanied by a detectable amount of DNO_2 loss.

The protonated molecular ion of p-nitrophenylacetonitrile also fragments by loss of 27 (HCN) and 74 (HCN and HNO_2). The HCN loss could result from competitive protonation of the nitrile-nitrogen as well as the nitro-oxygen. The proton affinities of the two groups are very likely similar[9] and both possess a bond dipole of sufficient size to be attractive sites for initial reaction.

Figure 1, column 3 shows the high pressure MIKE spectra of allylated nitrobenzenes. Formation of 41^+ (allyl cation) occurs in each case in competition with simple cleavages due to loss of 41 ($C_3H_5\cdot$), 57 ($C_3H_5O\cdot$), and 87 (C_3H_5ONO). $NO_2\cdot$ loss also occurs and is best explained by Cope type rearrangement of the allylated nitrophenol (a) so that the rearranged structure (b) can fragment by homolytic cleavage. Evidence that supports this mechanism is: a) a strong substituent effect is observed for this reaction channel, b) the peak is the result of the lowest energy process for the allylated p-nitrophenol as it persists in the low pressure spectra as a strong metastable ion reaction and c) CID via this channel is much less favorable than for the competitive simple cleavage reactions.



(1)

The new methods presented in this paper employ ion/molecule reactions to independently characterize the structures of ions formed in and extracted from the CI source. They show that protonation, ethylation and allylation lead to products in which the nitro group has acted as the basic site[10,11] even in competition with loro or hydroxyl groups. These results exemplify the dominant role of intramolecular charge delocalization in stabilizing isolated gas phase ions.

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