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# MASS SPECTROMETRY OF ONIUM COMPOUNDS - XV[1]
# IONIZATION POTENTIALS OF AMINO PYRIDINES.

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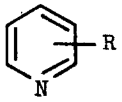
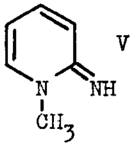
Recently we have reported on the ionization potential of the tautomeric hydroxy and mercapto pyridines.[2] From the IP values it was concluded that these in the gaseous phase exist as the hydroxy and mercapto tautomers.[2] In the solid state and solution, however, it is well established that the 2- and 4-isomers exist in the <u>on</u>-form, while the form of the 3-isomer is dependent on conditions.[3] In contrast, the tautomeric pyridonimine forms of 2- and 4-amino pyridines have been found non-important in the solid state and solution.[4] This report deals with the gaseous species from the three amino pyridines. For comparative purposes N-methyl analogues have been included. The ionization efficiency curves were recorded as previously described[5] and interpreted by the semilog plot method.[6] The figures obtained (Table 1) are the average of three determinations, the deviation being±0.05 eV except for IX as discussed below.

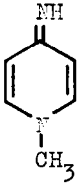
Table 1



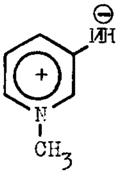
| | | | | | |
|---|---|---|---|---|---|
| I | 2-$NH_2$ | 8.85 eV | IV | 2-$NHCH_3$ | 8.26 eV |
| II | 3-$NH_2$ | 9.03 eV | V | 3-$NHCH_3$ | 8.53 eV |
| III | 4-$NH_2$ | 9.27 eV | VI | 4-$NHCH_3$ | 8.75 eV |



VII 7.91 eV



VIII 7.85 eV



IX 7.45 ± 0.1 eV

Compounds I-VII were introduced into an AEI-MS 902 mass spectrometer by indirect insertion at 50-100°C, VIII by direct insertion at 20°C, and IX by direct insertion as described below. The temperature of the ion source was kept at 230°C.

The IP values of the aminopyridines are about 0.4 eV lower than in the respective hydroxy analogues[2] while the difference between phenol (9.16 eV)[7] and aniline (8.32 eV)[7] is twice this figure. The ionization potentials in the amino series (I-III) and in the methylamino series (IV-VI) drop in steps of 0.2-0.3 eV in going from the 4- to the 2-position in analogy with the corresponding hydroxy and methoxy series.[2] The dipole moments for the aminopyridines in benzene decrease from 3.9 D through 3.1 D to 2.1 D in the same positional order.[8] The same directional decrease in IP and dipole moment is in agreement with the electrostatic polarization model which predicts IP increase with increasing distance of the substituent from the heteroatom.[2,9]

The IP values for the 2- and 4-onimines VII and VIII are significantly different from the corresponding exocyclic N-methyl derivatives IV and VI. The observed decrease in IP is attributed to higher polarity due to partial charge separation, which in the gaseous state cannot be dispersed by solvation or other intermolecular interactions.[2]

The 3-amino and the 3-methylaminopyridine have properties as the corresponding aniline and undoubtedly will be present in the gaseous phase in the amine form. As pointed out above, both the amino and methylamino series show the same gradual positional change in IP value, the substituent effect of the methyl group being 0.5 eV. On the other hand the methyl isomers VII and VIII of the onimine series have a much lower IP value. From the data, as discussed above, it must qualitatively be concluded that the amino pyridines in the gaseous state exist in the amino form.

The amino betaine IX would be expected to have IP below those of the onimines as found for the analogous oxygen series.[2] Due to low stability, however, we failed to obtain the betaine IX and the spectra recorded were of its hydrochloride and hydroiodide.[10] The strong peak in the spectra at m/e 108 corresponds to the molecular weight of the betaine. With the evaporation temperature around 200°C the ionization potential was measured to 8.4 eV, which should be compared with 8.5 eV for the 3-methylamine (V). The similar spectra also show that nearly complete transalkylation to V has taken place, as previously found in the corresponding thioxide series.[2] Decrease in the evaporation temperature led to a marked change in the spectra around 180°C. The spectra from the hydrochloride, however, were essentially the same from 110°C to 170°C. In the spectrum of V the intensities of [M] and [M-H] are 100% and 93% respectively while the relative intensity of the [M-H] species has been reduced to 35% in the spectrum of the hydrochloride.[10] The chloride has also an important signal at m/e 81 [M-HCN], nearly absent in the spectrum of V.[10] IP measured at three different temperatures in the 110-170°C interval gave 7.45 ± 0.1 eV. It is noticed that this is 1 eV below the IP for the covalent methylamine (V). Furthermore, this is about 0.4 eV below the IP of N-methylpyridinium-3-oxide,[2] which corresponds to the difference, pointed out above, between the oxygen and nitrogen series for the 2- and 4-isomers. The conclusion therefore must be that the species in the gas phase under these conditions are in fact the mesoions from IX. The findings discussed above again demonstrates the usefulness of IP measurements in structural elucidations of gaseous molecules.[1,2,5,11]

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