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THE ASSIGNMENT OF THE PHOTOELECTRON SPECTRA OF PYRIDINE-N-OXIDES

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In a recent communication to this journal the photoelectron (p.e.) spectra of some 4-substituted pyridine-N-oxides were discussed by Weiner and Lattman.[1] However, erroneous assignments were made for the first and second ionisation processes throughout. This has prompted us to present a brief résumé of our experimental data which show unequivocally that the ground state of the ion arises by electron ejection from the π molecular orbital highest occupied MO (HOMO) where the coefficient of the oxygen πAO is dominant.

We have been engaged on an extensive study of the electronic structure of the N-oxides of aza-aromatics by high resolution p.e. spectroscopy, including the pyridine-N-oxides $\underline{\underline{1}}$ - $\underline{\underline{12}}$ (Table 1). The ionisation energies (I.E.s) are collected in Table 1 with our assignments. Detailed discussion of the spectra and the allocation to the MO character shown are presented in a full paper dealing with the pyridine-N-oxides [2].

In the p.e. spectra of all the molecules listed the bands below I.E. $\approx$13 eV are well separated and can be readily assigned by comparison with the p.e. spectra of substituted benzenes [3] and the parent molecule $\underline{\underline{1}}$. The additional bands (to that of $\underline{\underline{1}}$) in this region are due to π orbitals of the substituent, $X = N(CH_3)_2$, OCH_3 or σ lone-pairs, X = CN, or both, X = Cl, NO_2.

Table 1. Vertical Ionisation Energies (eV) of the Pyridine-N-Oxides 1 - 12

	I_1 ($\pi O{:}$)	I_2 ($\sigma O{:}$)	I_3 (πa_2)	I_4	I_5	I_6
1 ($-H_5$)	8.38	9.22	10.18	11.59 (πb_1)	13.0 (πb_1)	13.8
2 ($4-CH_3$)	8.12	9.02	10.07	11.18 (πb_1)	12.5	13.3
3 (4-CN)	8.95	9.74	10.84	11.58 (πb_1)	12.18 ($\sigma N{:}$)	13.0
4 ($4-OCH_3$)	7.74	8.78	9.97	10.50	12.08	13.7
5 (4-Cl)	8.42	9.31	10.44	11.14	11.87	13.5
6 ($4-N(CH_3)_2$)	7.21	8.65	9.03 (πb_1)	9.92 (πa_2)	11.62 (πb_1)	12.5
7 ($4-NO_2$)	9.03	9.80	10.81	11.26	11.46	12.3
8 ($3-CH_3$)	8.20	9.02	9.80	11.20	12.60	13.35
9 (3-CN)	8.93	9.68	10.56	11.90	12.50 ($\sigma N{:}$)	13.18
10 ($2-CH_3$)	8.21	8.99	9.79	11.39	12.60	13.3
11 (2-CN)	8.96	9.76	10.49	11.90	12.50 ($\sigma N{:}$)	13.2
12 ($-Cl_5$)	8.72	9.60	10.87	11.52	12.0	13.4

The I.E. values listed above differ somewhat from those which were also given by Weiner and Lattman (1,2,4). In our spectra the vibrational fine structure, always discernible on the first three bands (except 6), precludes some ambiguity in the choice of the vertical I.E. Our values for 1 were obtained on three different $\pi/\sqrt{2}$ p.e. spectrometers. The concomitant calibration with the rare gases included naphthalene and the photoelectrons generated by HeIβ (23.09 eV) ionisation of Xenon to avoid unnecessary scale extrapolation.

The band assignments are made with respect to the following considerations; here with emphasis on the first two ionisation processes:-

a) The first I.E. of $(CH_3)_3NO$ is 8.25 eV [2] and that of CF_3NO is 10.4 eV[4]. As these correspond to ionisation of the oxygen lone-pair (l.p.s) orbitals this restricts the oxygen l.p. basis to the vicinity of 9 eV from appreciation of the trends in the p.e. spectra when the $(CH_3)_3$, or CF_3, group is "converted" to the CH_3 group. This gives a reasonable estimate for the environment in 1. In addition, the mean of the I.E.s leading to the singlet and triplet states on ejection of the photoelectron from the oxygen l.p. in nitroxides is ≈9 eV[5]. Then it is straightforward to see by correlating 1 to benzene that the interaction with the nearer lying π MOs (i.e. $\pi_{e_{ig}}$ in benzene = 9.25 eV) will invariably destabilise the oxygen π l.p. with respect to the σ l.p. As consequence the HOMO is described as πO: (π 3b, in **1**) and the subsequent band relates to σO: (σb_2 in **1**).

b) This sequence is clearly confirmed by the p.e. spectra of the N-oxides of the azabenzenes[6]. In particular the p.e. spectrum of pyrazine di-N-oxide shows a single band for the lowest I.E. process (8.33 eV) while the double band (i.e. 9.7 – 9.9 eV) results from the oxygen σ l.p. combinations.

c) **6**($4\text{-}N(CH_3)_2$) and **4**($4\text{-}OCH_3$) show markedly lower first I.E.s than **1** (Table 1). The changes in the second I.E.s are smaller. Using the basis values of the nitrogen and oxygen π l.p.s in $N(CH_3)_2$ and OCH_3 established from the p.e. spectra of benzenes and naphthalenes [7] (8.6 and 10.0 eV respectively). The sequence shown is predicted. In **6** and **4** the third and fourth I.E.s respectively relate to the MOs which have the largest contribution from these l.p.s.

d) All the spectra (except for **6**) reveal vibrational fine structure on the first three bands. The vibrational frequency excited in the ground ionic state is 520 cm^{-1} while 1250 cm^{-1} dominates the first excited state of **1**. Similar frequencies are discernible in the derivatives of **1**. The former may be ascribed to the ring vibration (as often observed on π-bonds) while the latter to the N-O stretch [8].

e) In the chlorine-containing derivatives π and σ bands may be distinguished by the decrease in the Cl3p ionisation cross-section, relative to the C2p(or O2p), when the incident radiation is changed to HeII (40.82 eV). In our HeII spectra of **5**, for example, the decrease in intensity of the first band (and fourth) compared, to the second and third bands reflects the symmetry and supports the assignment.

f) The π-MO sequences for the molecules studied are in accord with MINDO/2 calculations. The least-squares linear correlation between the I.E.s and the eigenvalues yields a gradient $-1.03\pm.04$, correlation coefficient .987, 21 degrees of freedom.

g) The HOMO character has been predicted previously by calculations, e.s.r studies of the radical cations and anions, and u.v. spectroscopy to be of π-type [9] with a predominant contribution from the oxygen l.p.

Thus in the pyridine-N-oxides $\underline{\underline{1}}$ - $\underline{\underline{12}}$ the ground ionic state is invariably generated by ejection from the HOMO which is π-type (πO:), (as is the case in heterocyclic-N-oxides generally), the first excited state from the oxygen σ l.p. (σO:) and the third I.E.s (fourth in $\underline{\underline{6}}$) are linked to the πa_2 MO.

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