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PHOTOELECTRON SPECTRA OF 4-SUBSTITUTED PYRIDINE N-OXIDES

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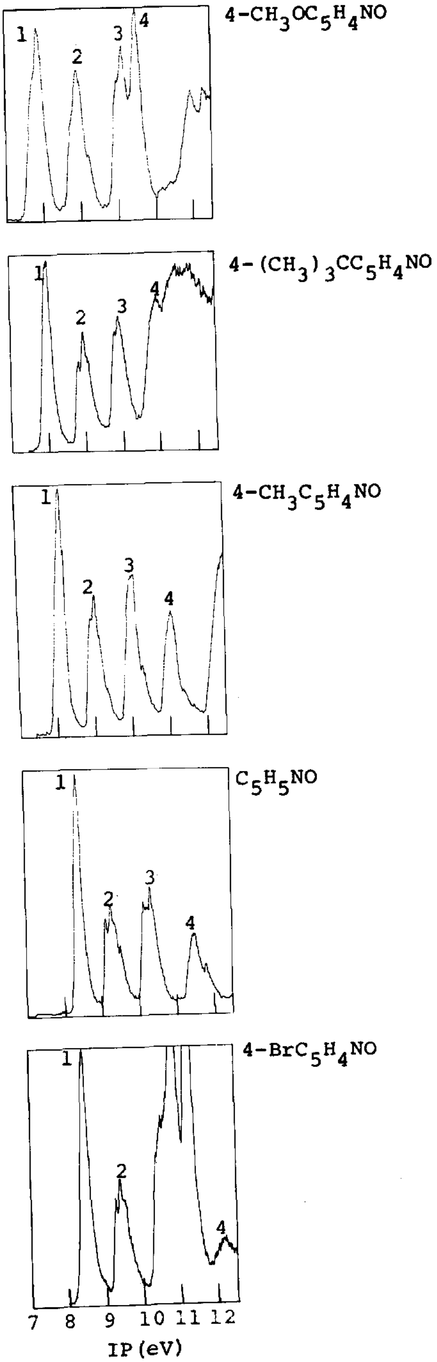
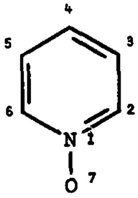
The pyridine N-oxide system is an excellent one for demonstrating the usefulness of ultraviolet photoelectron spectroscopy in the measurement and interpretation of substituent effects. Band assignments are made in a straightforward manner, in accordance with recent SCF calculations on pyridine N-oxide by Kobinata and Nagakura[1], as well as with the earlier calculations of Kubota[2], and substituent effects can be easily traced and accounted for[3]. This communication deals with the pes of a series of substituted pyridine N-oxides, including some organometallic derivatives.

The trend in the IP values shown in Table I (with the few exceptions discussed below) follow the generally accepted order of electron donating ability for the halo, alkyl and alkoxy substituents on the pyridine N-oxide molecule[3] (e.g. the halo substituent is clearly less electron donating than hydrogen). A decrease in the IP's of the ring electrons is associated with release of charge from the substituent into the ring, while removal of charge from the ring results in a lowering of ring orbital energies and an increase in the IP's. This substituent effect would also be true, to a lesser extent, for the oxygen lone pair electrons. Moreover the elongation of the peak shapes (particularly IP_4), as the substituent becomes more electron donating (Figure 1), can be attributed to a shift of electron density toward the oxygen[4].

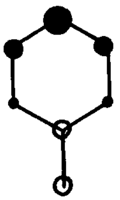
The peak due to the first IP in each spectrum can be assigned to ionization of the oxygen 2p lone pair electrons, on the basis of its fairly narrow band width, unaffected by the nature of the substituent. The second band is assigned to ionization from the highest occupied π molecular orbital ($3b_2$) which is considered to be highly localized on the oxygen.[1,2] This assignment

Figure 1. Pes of pyridine N-oxides. The numbered peaks refer to IP's listed in Table I. The other peaks appear to be due to the substituents.

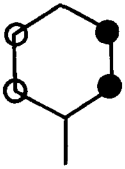




$2b_2$



$1a_2$



$3b_2$

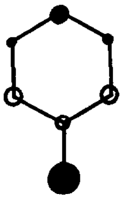


Table I. Vertical Ionization Potentials (eV) of 4-Substituted Pyridine N-Oxides[a]

Substituent	IP_1	IP_2	IP_3	IP_4
CH_3O[b]	7.89	8.96	10.17	10.54
$(CH_3)_3C$	8.00	9.03	9.95	11.00
CH_3	8.17	9.09	10.13	11.19
H	8.46	9.34	10.36	11.59
Br	8.44	9.44	---	12.24
$(CH_3)_3Si$	8.19	9.13	10.06	---
$(CH_3)_3Ge$	8.12	9.08	---	11.39
$(CH_3)_3Sn$	8.04	9.02	---	11.27

[a] Spectra obtained with a Perkin-Elmer Model PS-18 photoelectron spectrometer, and calibrated with xenon and argon. The direct inlet probe and temperatures of 55-100° were necessary for proper sample vapor pressures.

[b] No assignment in this region due to the methoxy electrons. The pes of 4-methoxypyridine showed no peak below 11.5 eV due to ionization from the methoxy group. See reference 4a for a discussion of the spectrum of anisole.

would be consistent with the calculated energy of the $3b_2$ orbital relative to the other π orbitals, and with a peak shape and position which varies in a regular manner with the nature of the substituents but is less sensitive to substituent effects than IP_4 (vide infra).

The third ionization would then be from the occupied a_2 π orbital, containing a nodal plane through positions 1, 4 and 7. This is consistent with its calculated relative energy and somewhat smaller and irregular change of band position with changing substituent. Despite the fact that this orbital has no value at the 4-position, its energy can be affected somewhat by the substituents, as was shown in the case of substituted benzenes[5], but presumably the substituent effect here is only through an inductive mechanism.

The shape and position of the fourth peak is very sensitive to substituent effects and is therefore assigned to ionization from the $2b_2$ π orbital. The $2b_2$ orbital has been shown[1,2] to have a large value at the 4-position, and therefore any substituent effect will be felt most sensitively.

Previous results from this laboratory[6] on pyridine N-oxides substituted in the 4-position with R_3Si, R_3Ge, and R_3Sn groups provided evidence that these substituents were poorer electron donors than alkyl substituents and even hydrogen itself with respect to the pyridine N-oxide moiety. This was attributed to an electron withdrawing component in the behavior of these substituents, resulting from dative π bonding between the ring and the organometallic group. Therefore it appears that the organometallic derivatives show unexpectedly low IP's (Table I), particularly the first and second IP. Moreover the bromo derivative shows an unexpectedly low first IP. It may be suggested here that this result arises not so much from diminished electron withdrawing behavior in the neutral molecule, but from a reorganization of charge in the radical cation, leading to a stabilization of the cation and a lowering of the net energy necessary for ionization. This phenomenon has been discussed previously.[7] In the present situation, the first and second IP's result from the loss of an electron from orbitals highly localized at the oxygen. The positive charge thus produced in one part of the molecule is effectively spread throughout the molecule by a drift of electrons from the polarizable substituents at the 4-position into and through the ring.

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