Transmission of Electronic Effects in Substituted Pyridine-N-Oxides Studied by ESCA

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Since the first electron spectroscopic (ESCA) studies dealing with substituents effects upon core ionization energies (I.E.) of organic compounds [1], little has been published on the subject. This was probably because the reported data did not always seem very meaningful. The absolute I.E. values obtainable in the solid phase are not very certain and also, the "shake-up" phenomena and the consequent broadening of the bands, which affect the I.E. values [2], were not always taken into account. None the less we think that ESCA is a valuable tool for the study of substituent effects, and in particular of the transmission of electronic effects in aromatic systems.

Previous work in this area has been published [2, 3], and more specifically an example of steric inhibition of resonance observed by means of ESCA I.E.'s and shake up data was recently reported [4]. Here we would like to report a further case in which the transmission of electronic effects through an aromatic ring is observed using ESCA.

Experimental

The binding energy measurements were carried out with an AEI ES 100 Electron Spectrometer, using MgK_α and/or ALK_α radiation.

The samples were sublimed in vacuo and condensed as thin films on a cooled gold surface. The $Au_{4f_{7/2}}$ line (83.8 eV) from this surface was obtained, together with the signals from the samples, and used for calibration purposes. The samples used in these measurements were very thin such that the signal from the gold was in all cases much more intense than that from the sample. Two nearly parallel sets of values for the core I.E.'s have been obtained with Al and Mg radiations, the Al values being, with a few exceptions, about 0.4 eV higher.

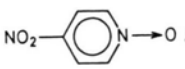
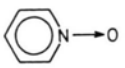
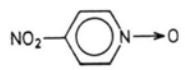
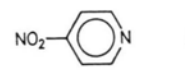
Due to the uncertainties involved in the calibration procedure, the absolute values of the reported values may be in error by as much as 1 eV. However, the relative error between couples of values obtained with the same radiation should not exceed ± 0.2 eV, the reproducibility being of this order of magnitude. The O_{1s} band from p-NO_2 pyridine N-oxide and all the C_{1s} bands are rather broad since they are composed of different unresolved contributions. For this reason the corresponding I.E. values are less reliable.

The samples have been prepared following standard methods in the literature.

Results and Discussion

Table 1 gives the I.E. values (O_{1s}, N_{1s} and C_{1s}) obtained for pyridine N-oxide and some related compounds studied for comparison.

Table 1. Core ionization energies in some N-oxide derivatives (eV).

	O_{1s}		N_{1s}			C_{1s}
	NO_2	NO	NO_2	NO	NH_2·N	
	533.4	531.8	406.0	403.3		285.7
		531.6		403.0		285.3
		531.8		402.2	399.1	285.1
$(CH_3)_3N\rightarrow O$		531.5		403.6		286.2
$C_6H_5-N=O$		532.6		401.6		
	533.4		406.0		399.7	

The reported values are averages between the values obtained by using MgK_α and AlK_α radiations.

The assignments reported in the table when two signals are present in the O_{1s} and N_{1s} energy regions are based on the assumption that the negative charge density is higher on the oxygen of the NO group than on the O atoms of the NO_2 group and that the positive charge on the N atom increases in the series $NH_2 < NO < NO_2$.

Often shake up transitions have been observed in various energy regions. Their main features have been previously discussed [3]. It is to be noted that the absolute values for O_{1s} and N_{1s} I.E.'s from the NO_2 group are very close to those reported for nitroaromatic compounds [5] and that the C_{1s} values are, as expected, slightly higher than that of unsubstituted benzene [6].

The electronic effects of the para substituent are reflected in the core I.E.'s of the N-O group of the pyridine N-oxides. In particular, the strong electron-withdrawing NO_2 group causes the I.E.'s of both O_{1s} and N_{1s} of the NO group to increase with respect to the values in the unsubstituted compound, whereas the strong electron-releasing NH_2 group lowers these values. On going from the NH_2 to the NO_2 substituted derivative the N_{1s} and O_{1s} I.E. values of the NO group increase by 1.1 and 0.5 eV respectively.

These variations are of the same order of magnitude as those obtained [7] in the gaseous phase (0.8 – 1.5 eV) for the four highest occupied MO's (assigned [8] to oxygen lone pair and delocalised π MO's), using UV photoelectron spectroscopy.

It is also interesting to note that the variation of I.E.'s obtained for R_3NO and C_6H_5NO with respect to the Pyridine N-oxides are in agreement with what is expected on the basis of the known modifications of the electronic structures of these molecules with respect to the title compounds.

The reported data therefore further support the fact that ESCA may be used to study substituent effects * and in particular the transmission of electronic effects through an aromatic ring. However, to improve the quality of data and correlation with electronic structure, gaseous phase measurements are needed.

We are therefore confident that X ray photoelectron spectroscopy of samples in the gaseous phase can be used with great effect for the study of mesomeric interactions alongside U.V. photoelectron spectroscopy and other spectroscopic techniques **.

We hope that this paper may serve to stimulate further studies in the gaseous phase.

* This is confirmed by a recent paper [9] showing that remote inductive effects may be conveniently evaluated by ESCA measurements.

** Note added in prof: In a recent paper (UUIP-909) Kai Siegbahn shows this to be the case. Gaseous Phase C_{13} ESCA chemical shifts in some para monosubstituted and disubstituted benzene derivatives have been shown to be linearly correlated with Hammett σ constants. On going from NH_2 to NO_2 derivatives a range of $\sim$1.5 eV was found.

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[2] S. Pignataro and G. Distefano, J. Electr. Spectr. **2**, 171 [1973].

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[4] S. Pignataro, R. Di Marino, and G. Distefano, J. Electr. Spectr. **4**, 90 [1974].

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[6] S. Pignataro, A. Foffani, and G. Distefano, Chem. Phys. Letters **20**, 350 [1973] and references therein.

[7] G. Distefano and S. Pignataro unpublished results. Our values for p-NO_2 pyridine N-oxide are in very good agreement with those reported by Maier and Muller [8].

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