Photoelectron Spectra of C-Nitro & N-Nitro Compounds

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Photoelectron spectra of aliphatic nitro compounds have been studied and assignments made on the basis of molecular orbital calculations and electronic absorption spectra. Substituent effects on PES bands due to the nitro group are discussed. PES of dimethylnitramine and dimethylnitrosamine are compared.

PHOTOELECTRON spectra (PES) is the best available technique for the direct determination of molecular energy levels[1]. Ionization energies obtained from PES are related to the orbital energies by Koopmans' theorem. Orbital energies can in turn be calculated by molecular orbital methods and such calculations provide the basis for the interpretation of the PES of molecules.

Photoelectron spectra characteristic of various types of chromophoric groups have been reported in recent years[1-3]. In particular, the variation of ionization energies of the lone pair orbitals in organic halides and carbonyl compounds have been examined in some detail[1,4,5]. In the present paper, we have investigated the PES of aliphatic nitro compounds with specific reference to the orbitals of the nitro group. The PES of nitro and nitroso groups in similar compounds have also been compared. The PES characteristic of these functional groups are discussed in the light of molecular orbital calculations and electronic absorption spectra.

Materials and Methods

All the compounds were purified by fractionation. PES were recorded on a Perkin-Elmer PS 18 photoelectron spectrophotometer and also with a instrument built at the University of Oxford.

Results and Discussion

PES of nitroalkanes and halonitroaklanes — Molecular orbital calculations of McEwen[6] and Kato et al.[7] have shown that the ordering of the occupied energy levels of the nitro group in nitromethane is $a_1(n^*)$, $b_2(n)$, $a_2(\pi_2)$ and $b_1(\pi_1)$. The two non-bonding orbitals essentially consist of oxygen $2p_x$ and $2p_y$ functions and the coefficients for the atomic orbitals of nitrogen are negligibly small. Furthermore, the two non-bonding orbitals appear to be nearly degenerate. A schematic representation of the first three occupied orbitals are shown in Fig. 1. CNDO/2 calculations, however, show the $a_2(\pi)$ orbital to be the highest occupied orbital followed by the $a_1(n)$ orbital. The $a_2(\pi)$ orbital has non-bonding character while the n orbital is due to the bonding combination of oxygen orbitals.

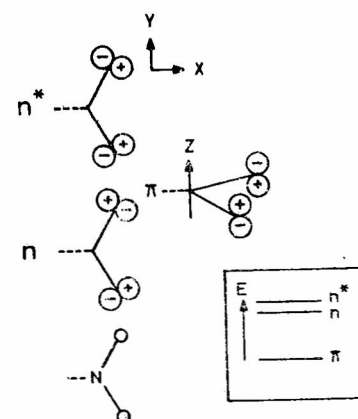The electronic absorption spectrum of CH_3NO_2 shows a characteristic n-π^* transition around 270

Fig. 1 — Schematic representation of the NO_2 group orbitals in nitroalkanes [Ordering of energy levels is shown in the inset]

nm and a π-π^* transition around 200 nm[8]. A band due to an n^*-π^* transition is not distinctly seen, but is expected to be close to the n-π^* band[6] (calc. 280 nm). Based on the electronic spectrum, therefore, we would expect the n orbital to be the highest occupied orbital followed by the π orbital.

PES of nitromethane shows two bands at 11·35 and 11·85 eV (Fig. 2) and the remaining bands are at much higher energy (>14 eV). The 11·35 and 11·85 eV bands are assigned to the ionization of n and π orbitals respectively. The second band at 11·85 eV is very sharp indicating the non-bonding character of the orbital. The bands at higher energies (>14 eV) obviously involve σ-ionization and are difficult to assign to specific orbitals.
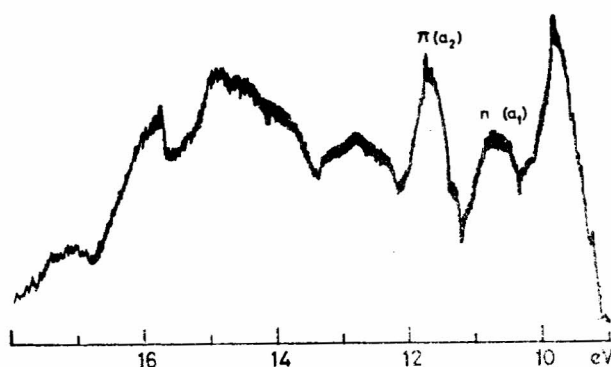
The 11·35 and 11·85 eV bands of CH_3NO_2 are shifted when the alkyl substituent is varied. Thus, in $C_2H_5NO_2$, these bands appear at 11·15 and 11·60 eV. Both the n and π ionization energies of the NO_2 group in simple nitroalkanes give linear relations when plotted against the ionization energies of the corresponding alkyl iodides (Fig. 3). Alkyl iodides, it may be recalled, give sharp peaks due to the ionization of the lone pair orbital of the iodine atom and the IE values are therefore very reliable[4]. To rationalise the substituent effects of alkyl groups on the n and π ionization energies of nitroalkanes, the aliphatic substituent constants, σ^*, of Taft[9]

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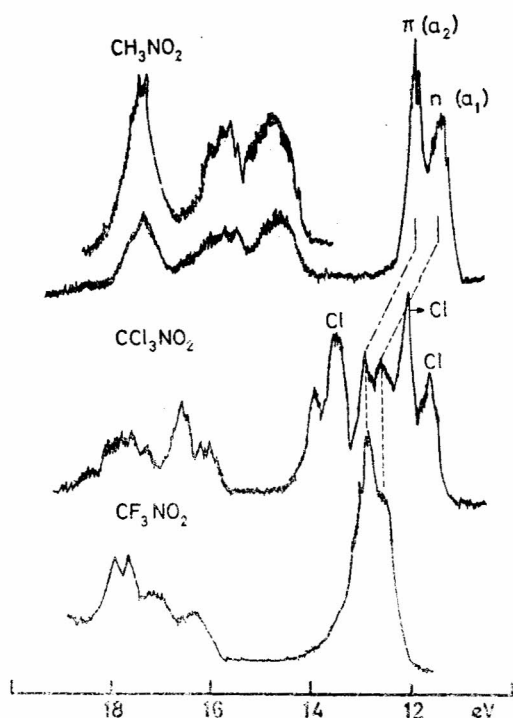
Fig. 2 — Photoelectron spectra of nitro compounds, RNO_2
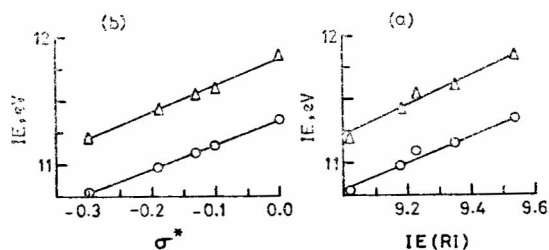
Fig. 3 — Correlation of n and π ionization energies of the NO_2 group of nitroalkanes (circles and triangles respectively) with (a) ionization energies of alkyl iodides, RI, (b) aliphatic substituent constants, σ^* [In the order of decreasing σ^* values, the points refer to R = CH_3, C_2H_5, n-C_4H_9, i-C_3H_7 and t-C_4H_9]

Fig. 4 — Photoelectron spectrum N,N-dimethylnitramine, $(CH_3)_2NNO_2$

were plotted against n and π ionization energies. The plots are indeed linear, the slopes being nearly the same. Both the n and π ionization energies of the NO_2 group decrease with the increasing electron donating power of the alkyl substituent. These trends are in the expected direction and similar variation of the n ionization energy with alkyl substituents has been observed earlier in the case of aliphatic ketones[4].

In order to further substantiate the assignment of the PES bands of the NO_2 group in nitroalkanes, the spectra of CCl_3NO_2 and CF_3NO_2 have been recorded (Fig. 2). Since CCl_3 and CF_3 groups are both highly electron-withdrawing in nature ($\sigma^* \approx$ 2·6), we would expect the PES bands of the NO_2 group to appear at considerably higher energies. PES of CCl_3NO_2 shows bands due to the ionization of the Cl lone pair orbitals just as in $CHCl_3$, but the bands due to the NO_2 group can still be seen around 12·4 and 12·75 eV (Fig. 2). The spectrum of CF_3NO_2, on the other hand, clearly shows the

bands due to n and π orbitals around 12·6 and 12·8 eV respectively, the former appearing as a shoulder on the latter. It appears that the "perfluoro effect" is slightly greater on the n orbital than on the π orbital. In conjugated molecules like butadiene, substitution by fluorine mainly affects σ bands leaving the π bands unchanged[10]. The n and π ionization energies of CCl_3 and CF_3 derivatives do not fall on the linear σ^* plot of simple nitroalkanes (Fig. 3) just as in the case of the n bands of aliphatic ketones[4]. This is because, the interaction of the halogen atoms with the NO_2 group is not properly represented by the σ^* constants which account only for the inductive or field effects.

PES of nitrosamines and nitramines — When an electron donating substituent like NH_2 is directly attached to the NO_2 group, the n-π^* transition is shifted only slightly, since the non-bonding electrons of NO_2 are almost entirely located at the oxygen atoms. Close to the n-π^* transition, we would expect to see an intramolecular charge transfer band involving charge transfer from NH_2 to NO_2. PES of N,N-dimethylnitramine, $(CH_3)_2NNO_2$, shows evidence for such effects (Fig. 4). The PES bands at 10·8 and 11·8 eV are similar to the n and π bands of CH_3NO_2. The additional sharp band at 9·75 eV is most likely due to the n orbital of the $N(CH_3)_2$ group just as in methyl amines [n band of CH_3NH_2, 9·8 eV; $(CH_3)_2NH$, 9·0 eV]. It is instructive to compare the PES of $(CH_3)_2NNO_2$ with that of N,N-dimethylnitrosamine, $(CH_3)_2NNO$, where the non-bonding orbital of the nitroso group, unlike that of the NO_2 group, contains contributions from both the oxygen and nitrogen atomic orbitals. Before proceeding to discuss the PES of $(CH_3)_2NNO$, we shall briefly examine the energy levels of the NO group.

Molecular orbital calculations show that in the C-nitroso group, the highest filled orbital is the n^* orbital arising from the antibonding combination of the lone pair orbitals of N and O atoms. This is followed by the n orbital due to the corresponding bonding combination of the atomic orbitals. The π orbital of the NO group lies below the n orbital. Electronic absorption spectra[11-13] of nitrosoalkanes are consistent with this energy level scheme and the n^*-π^*, n-π^* and π-π^* bands appear in the order of increasing energy (absorption maxima around 700, 290 and 220 nm respectively). PES of nitroso-
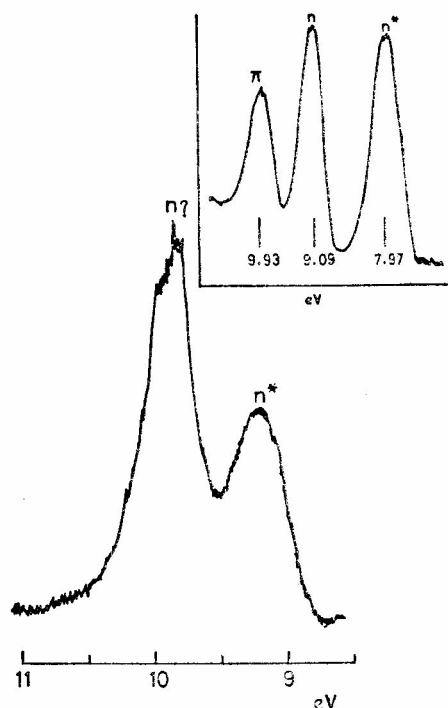
Fig. 5 — Photoelectron spectrum of N,N-dimethylnitrosa-
mine, $(CH_3)_2NNO$. [In the inset, the three characteristic
bands of the nitroso group in t-nitrosobutane are shown]

alkanes[14] show that ionization energy increases in
the order n^*, n and π.

If an electron donating group (D) is directly
linked to the NO group and D has low ionization
energy and can conjugate with the NO group, then
intramolecular charge transfer can occur[13]. The
n^*-π^* transition is shifted to the blue and D-π^*
transition can occur at lower energies than the
n-π^* transition. Accordingly, in $(CH_3)_2NNO$, the
n^*-π^* transition is at 380 nm while the D-π^* transi-
tion is at 230 nm. The n-π^* transition is not seen
above 200 nm. Generally, greater the tendency
of electron transfer from D to π^*, larger is the
blue shift of the n^*-π^* transition. A similar situ-
ation is also found in n-π^* transitions of aliphatic
carbonyl compounds[15,16]. PES of $(CH_3)_2NNO$ shows
a band at 9·1 eV probably due to the n^* orbital
ionization (Fig. 5). The strong sharp band centred
around 9·7 eV has a shoulder around 10 eV. These
two ionization energies are likely to correspond
to the donor, $N(CH_3)_2$, lone pair orbital and $n(NO)$
orbital.

The appearance of donor levels in between the
n^* and n levels of the NO group is also seen in
nitrosobenzene. The PES spectrum of nitroso-
benzene[17] shows a band due to the ionization of
the n^* (NO) orbital at 8·9 eV followed by two bands
due to the a_2 and b_1 levels of aromatic π system.
The electronic absorption spectrum of nitroso-
benzene[12] shows the n^*-π^* transition in the visible
region followed by two π-π^* transitions at lower
wavelengths. Clear evidence for the n level of NO
is not seen in either the PES or the electronic
absorption spectrum. In nitrobenzene, on the
other hand, PES bands due to ionization of the
n and π levels of the NO_2 group appear at higher
energies than those due to the π levels of the
aromatic[17]. The n-π^* transition of nitrobenzene
is indeed masked by the intense π-π^* transition
of the aromatic system[16].

Acknowledgement

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