Free Energy Relationships of Ionization Energies measured by Ultraviolet Photoelectron Spectroscopy in Substituted Pyrroles

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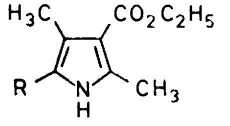
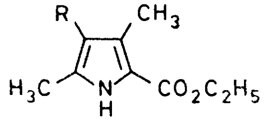
The ionization energies of some substituted pyrroles have been determined by u.v. photoelectron spectroscopy. Relationships between the lowest ionization potentials and the Hammett σ constants have been determined. The different influence of substituents in the α- and β-positions is discussed.

IN connection with studies by some of us on the reactivity of polysubstituted pyrroles,[1,2] we attempted a correlation between the ionization energies in the gas phase measured by u.v. photoelectron spectroscopy (u.p.s.) and chemicophysical parameters for the following series of compounds: 5-R-3-ethoxycarbonyl-2,4-dimethylpyrrole (α) and 4-R-2-ethoxycarbonyl-3,5-dimethylpyrrole (β).



(1α) R = H
(2α) R = CH_3
(3α) R = $COCH_3$
(4α) R = $CO_2C_2H_5$
(5α) R = Cl
(7α) R = NO_2

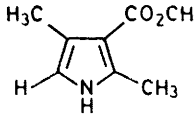


(1β) R = H
(2β) R = CH_3
(3β) R = $COCH_3$
(4β) R = $CO_2C_2H_5$
(5β) R = Cl
(6β) R = Br
(7β) R = NO_2

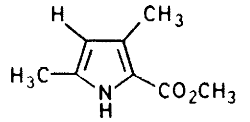
Free energy relationships between ionization energies determined by u.p.s. and σ constants have already been set up for many benzene derivatives;[3-5] for pyrroles, correlations of this kind have been only made by using electron impact data.[6]

RESULTS AND DISCUSSION

Representative He^{I} u.p. spectra of the two series are shown in Figure 1 and the measured ionization energies (IEs) are reported in Tables 1 and 2. The assignment of the spectra of the various compounds is quite straightforward, when the sequence of the MOs of unsubstituted pyrrole[7] and the ionization characteristics of the substituents are taken into account. We also performed CNDO/2 and INDO calculations on the model molecules (8a and b).



(8a)



(8b)

The two lowest IEs refer, in all the molecules investigated, to the two highest MOs (π_3 and π_2), the composition of which is similar to that of pyrrole ($\pi_3 = z_2 - z_5$; $\pi_2 = z_3 + z_4 - z_1$).[7] More precisely, our computations indicate that in (8a) there is a significant contribution of the π-type oxygen orbital of the C=O group to the second MO, whilst in (8b) the analogous

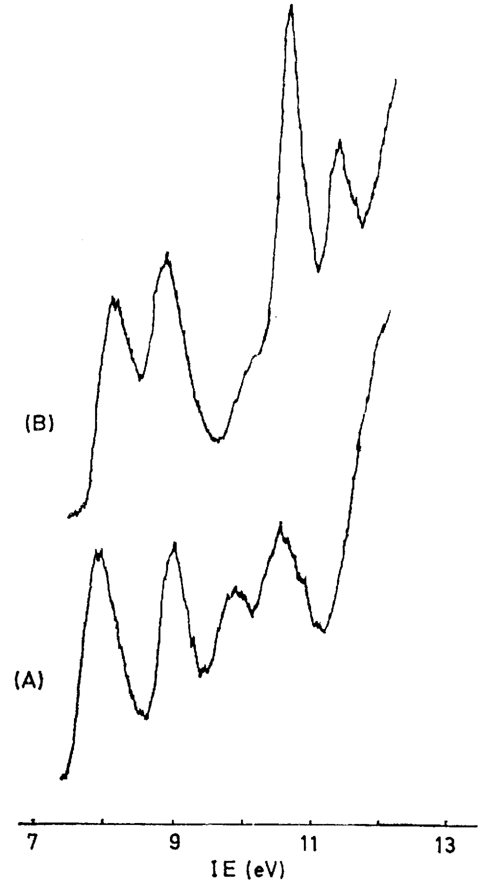


FIGURE 1 (A) U.v. photoelectron spectrum of 5-methyl-3-ethoxycarbonyl-2,4-dimethylpyrrole (2α); (B) u.v. photoelectron spectrum of 4-bromo-2-ethoxycarbonyl-3,5-dimethylpyrrole (6β)

TABLE 1

IEs (eV) for 5-R-3-ethoxycarbonyl-2,4-dimethylpyrroles

R	π_3	π_2	$n_{(C=O)}$	$\pi\left(\mathrm{C}{<}^{\mathrm{O}}_{\mathrm{O}}\right)$		Σ_σ and π_1
H	7.95	8.83	9.76	10.36		>11.5
CH_3	7.82	8.90	9.88	10.52		>11.5
$COCH_3$	8.23	9.19 [a]	9.80	10.52		>11.5
$CO_2C_2H_5$	8.15	9.03	9.96 [b]	10.56 [b]		>11.5
Cl	7.94	9.08	9.74	10.48	11.64 [d]	>12
NO_2	8.78	9.62	10.28 [c]	10.80 [c]		>12

[a] Together with ionization of the lone pair of the acetyl oxygen.[3] [b] Double. [c] Together with $n\left(\mathrm{N}{<}^{\mathrm{O}}_{\mathrm{O}}\right)$ and $\pi\left(\mathrm{N}{<}^{\mathrm{O}}_{\mathrm{O}}\right)$ ionizations.[8] [d] Chlorine lone pair ionizations.

TABLE 2

IEs (eV) for 4-R-2-ethoxycarbonyl-3,5-dimethylpyrroles

R	π_3	π_2	$n_{(C=O)}$	$\pi\left(\mathrm{C}{<}^{\mathrm{O}}_{\mathrm{O}}\right)$				Σ_σ and π_1
H	7.91	8.95	9.95	10.44				>11.5
CH_3	7.71	8.55	9.88	10.36				>11.5
$COCH_3$	8.26	9.13 [a]	10.16	10.83				>11.5
$CO_2C_2H_5$	8.15	9.03	9.96 [b]	10.56 [b]				>11.5
Cl	8.03	8.87	10.16	10.64	11.12		11.96 [e]	>12
Br	8.03	8.79	10.08	10.56 [c]		11.28 [f]		>12
NO_2	8.76	9.67	10.36 [d]	10.88 [d]				>12

[a] Together with ionization of the lone pair of the acetyl oxygen.[3] [b] Double bond. [c] Together with the first bromine lone pair ionization. [d] Together with $n\left(\mathrm{N}{<}^{\mathrm{O}}_{\mathrm{O}}\right)$ and $\pi\left(\mathrm{N}{<}^{\mathrm{O}}_{\mathrm{O}}\right)$ ionizations.[8] [e] Chlorine lone pair ionizations. [f] Second bromine lone pair ionization.

contribution to the first MO is much less important. This is consistent with the experimental results: the IE of the second band in the u.p. spectrum of (1α) is 0.12 eV lower than the IE of the corresponding band in (1β), due to the conjugation of the ethoxycarbonyl group with the π_2 orbital in the former compound.

We now point out some interesting aspects emerging from the analysis of the data. The nitro-group induces a shift of the same order of magnitude to the highest IEs of the first two bands of the u.p. spectra in both (7α and β). This suggests that it exerts its influence predominantly *via* an inductive effect.

The influence of the acetyl group on the MOs of (3α and β) is uncertain because it is impossible to determine accurately the value of the π_2^{-1} energies; the second band of the u.p. spectra, to which both the π_2^{-1} and the oxygen lone pair ionization contribute, is quite broad and not well resolved.

The other substituents (methyl, ethoxycarbonyl, chloro, bromo) exert their influence not only by the inductive effect but also by interaction of some of their orbitals with the π orbitals of the ring.

In (2α and β) the methyl group seems not to have a large electron-donating ability while interacting with a π_3 orbital in the α-series and with a π_2 orbital in the β-series (hyperconjugation). The alternative interactions with either the π_3 or the π_2 orbitals [which are destabilised with respect to the corresponding orbitals in (1α and β)] are easily explained by taking into account the composition of the π_3 and π_2 orbitals: the p_z orbital of the α-carbon atom bearing the substituent contributes to the former, the p_z orbital of the β-carbon atom to which the methyl substituent is bound contributes to the latter.

The strong electron-withdrawing ethoxycarbonyl group pushes π_3 and π_2 to lower energy with respect to both (1α and β); however, the effect is considerably attenuated for π_2 in series β due to the already mentioned interaction of this orbital with the π-type orbital of the C=O group.

In (5α and β) there is again a balance of the inductive and resonance effects of the chlorine atom. An interesting phenomenon is the splitting of the band related to the β-chlorine lone pairs into two components, at 11.12 and 11.16 eV, whilst the corresponding band of the α-chlorine atom, at 11.64 eV, is broadened but not split. This indicates that the interaction of the π-type chlorine lone pair with π_2 in series β is greater than the analogous interaction with the higher π_3 orbital in series α, as confirmed by the destabilisation of π_2 in series β with respect to (1β).

The same effects can be observed for (6β) in which the conjugative interactions are more pronounced than in (5β), due to the fact that the π-type bromine orbital lies closer in energy to π_2 than the corresponding chlorine orbital.

Correlation of Substituent Effects.—The IE values (π_3^{-1} and π_2^{-1}) were plotted against the constants σ_m, σ_p, and σ_p^+.[9] The correlations are linear and the best fit was observed with the σ_p constants which account for both inductive and resonance effects (Figures 2 and 3).

The correlations improve slightly (*i.e.* r 0.97—0.98) when the σ_m and σ_p constants were employed according to inductive alone or both inductive and resonance effects of the substituents, as suggested by the analysis of the u.p. data.

The slopes of the plots of the two IEs (π_3^{-1} and π_2^{-1}) have the same value (m 0.99 and 0.98) for series β and

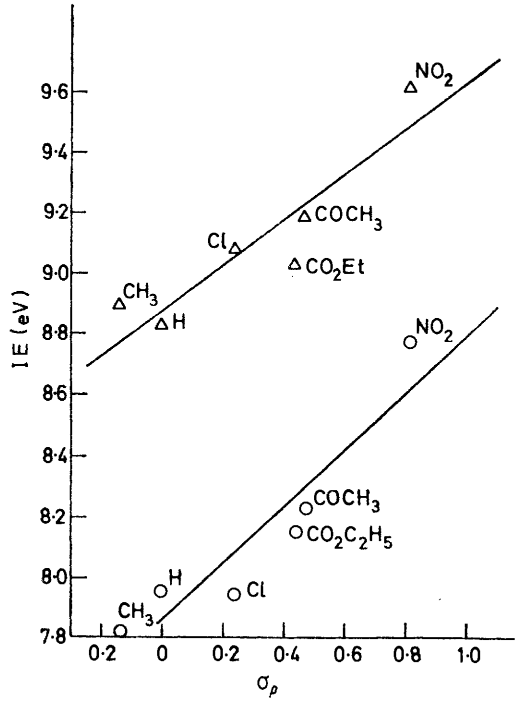


FIGURE 2 Plot of π_3^{-1} (○) and π_2^{-1} (△) *versus* σ_p (*r* 0.93 and 0.91) for series α

have different values (*m* 0.93 and 0.74, respectively) for series α.*

This is consistent with the results above: the contribution of ethoxycarbonyl-based orbitals to the π_2 MO, when the ethoxycarbonyl group is in position 3, reduces the sensitivity of this energy level to the influence of a substituent in position α of the aromatic ring, and therefore the lowest value is observed. By way of contrast, the sensitivity to β-substitution is the same for the two orbitals π_3 and π_2 for which the contribution of the carbonyl oxygen π orbital is negligible, so that almost coincident *m* values are found.

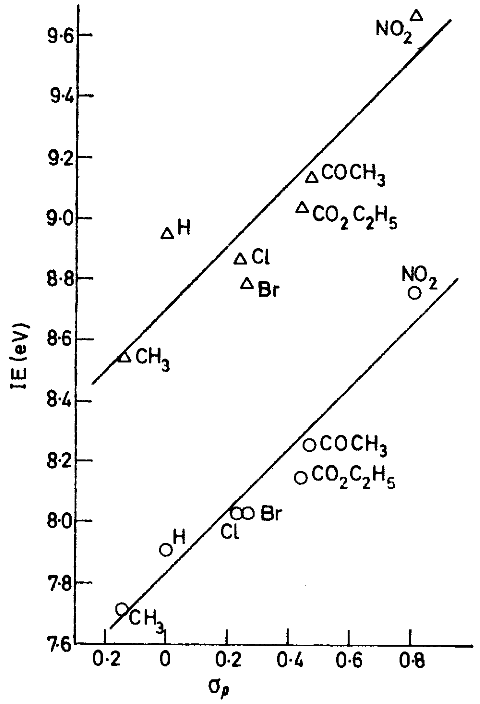


FIGURE 3 Plot of π_3^{-1} (○) and π_2^{-1} (△) *versus* σ_p (*r* 0.97 and 0.90) for series β

We have also examined the correlation of the lowest two IEs with the pK_a values of 4-R-3,5-dimethylpyrrole-2-carboxylic acids (R = H, CH_3, NO_2, $COCH_3$, $CO_2C_2H_5$).[10] The best fit is found (*r* 0.99) for π_3^{-1} *versus* pK_a; the slopes of π_3^{-1} and π_2^{-1} *versus* pK_a have the same value in this case also. No reasonable correlation could be obtained for 5-R-2,4-dimethylpyrrole-3-carboxylic acids with the same substituents owing to the scatter of the pK_a data. This is in agreement with the observation that $n_{(C=O)}^{-1}$ and $\pi_{\left(\mathrm{C}{<}^{\mathrm{O}}_{\mathrm{O}}\right)}^{-1}$ of the $CO_2C_2H_5$ group in the α-position in our series β correlate with σ_p, while the same is not true in series α.

A plot of the IEs *versus* the pK_a values of 5- and 4-substituted pyrrole-2-carboxylic acids[11] was also linear (*r* 0.98 and 0.97, respectively).

A correlation of the ^{1}H n.m.r. chemical shifts of the methyl groups in the α- and β-positions *versus* IEs shows reasonable but not satisfactory results; the best fit is that of π_3^{-1} *versus* δ of β-CH_3 (*r* 0.90). The influence of α-substituents on the chemical shifts of α'-CH_3 is obviously negligible.

EXPERIMENTAL

5-R-3-Ethoxycarbonyl-2,4-dimethylpyrroles (1α),[1] (2α),[12] (3α),[13] (4),[2] (5α),[14] and (7α) [15] and 4-R-2-ethoxycarbonyl-3,5-dimethylpyrroles (2β),[2] (3β),[16] (5β),[2] (6β),[2] and (7β) [15] were prepared as reported. 2-Ethoxycarbonyl-3,5-dimethylpyrrole was obtained by protiodecarboxylation of 5-ethoxycarbonyl-2,4-dimethylpyrrole-3-carboxylic acid as in ref. 1. The compounds were purified by recrystallisation or chromatography on silica gel (Merck) and resublimed *in vacuo*.

^{1}H N.m.r. spectra were obtained in $CDCl_3$ on a JEOL JNM-C60 HL instrument with tetramethylsilane as internal standard.

The u.p. spectra were run on a Perkin-Elmer PS18 spectrometer at temperatures ranging from 60 to 130 °C. Calibration was performed using CH_3I and Ar as internal standards.

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* The conversion of the slopes into dimensionless values yields ρ −16.7 and −16.6, respectively, for π_3^{-1} and π_2^{-1} *versus* σ_p in series β and ρ −15.8 and −12.6, respectively, for π_3^{-1} and π_2^{-1} *versus* σ_p for series α.

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