The Higher Ionization Potentials of Chlorobenzene

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THE photoelectron spectra excited by helium resonance radiation[1] in a number of substituted benzenes[2] have indicated a broadening and in some cases a splitting into two of the first band (due to the e_{1g} orbital level in benzene). The form of the spectra obtained from the coaxial-grid energy analyser used in this work allowed only adiabatic ionization potentials to be measured. On repeating some of these measurements with a 180° magnetic sector analyser[3] we have obtained spectra which show this splitting more clearly and from which it is possible to measure vertical ionization potentials directly and thus to allow direct comparison with the results of molecular-orbital calculations. Though the splitting is largest in some disubstituted compounds the spectrum of chlorobenzene (see Figure 2) is especially interesting since it shows in addition to a clear division in the highest energy band (*cf.* benzene, Figure 1) with a peak separation of 0·33 *ev* a pair of comparatively sharp bands for which the I.P. (11·44, 11·79 *ev*) is in the range expected for the chlorine $3p$ lone-pair electrons (*cf.* CH_3Cl, I.P. 11·22 *ev*). This assignment is based on the observation that these bands are considerably sharper than any other feature in the spectrum, indicating their non-bonding character and that a sharp band is formed with about this ionization potential in the spectrum of all chlorine containing compounds so far examined. The splitting can perhaps be equated to the energy difference between the chlorine $3p$ orbitals ($3p_y$ in the molecular plane perpendicular to the C–Cl bond and $3p_x$ parallel to the ring-carbon $2p_x$ orbital).

Though the first vertical I.P. for chlorobenzene is less than that for benzene (9·35 and 9·39 *ev* respectively—adiabatic values 8·99 and 9·248 *ev*) indicative of electron release from chlorine to the benzene ring, this is now seen to be offset by an increased second I.P. The overall effect of chlorine has thus been not only to split the degenerate upper π-level of benzene but also to increase the mean $\pi_{2,3}$ I.P. (from 9·39 to 9·51 *ev*) indicative of electron withdrawal from the ring. It is apparent that the $+M$-effect of the chlorine is practically balanced by its $-I$-effect.

The ionization process is one which should call in to play the mesomeric release of suitably placed lone-pair electrons. The present results which indicate the importance of an electron-withdrawing inductive effect, suggest that the latter should be relatively more important in the ground state of the molecule. They are thus in better accord with the generally accepted view[4] based upon rate-constant data for aromatic substitution reactions than with the more recent proposals originating in absorption spectroscopy and theoretical calculations[5,6] which have suggested a positive inductive effect of chlorine upon π-electrons of aromatic systems (I_π positive). The bands in the spectra of chlorobenzene which seem to be associated with the σ-electrons also show a general shift to lower energies compared with benzene as expected if I_σ is negative.

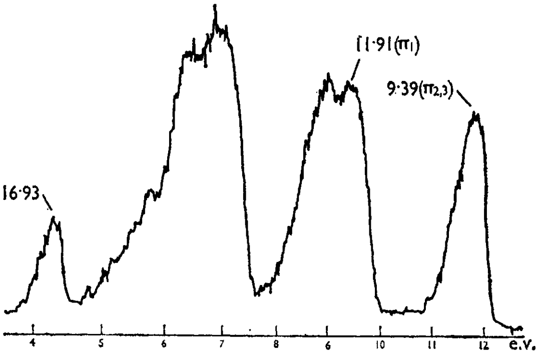

FIGURE 1

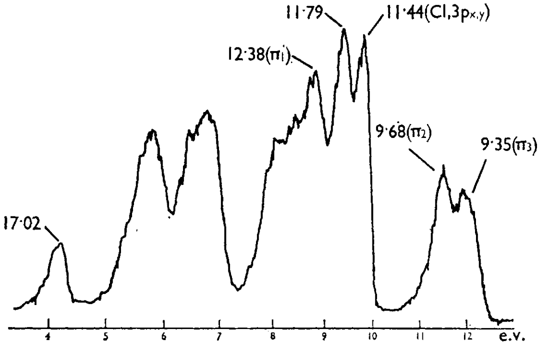

FIGURE 2

Photoelectron spectra of benzene (Figure 1) *and chlorobenzene (Figure* 2) *using a* 180° *magnetic electron-velocity analyser (see text). Electron energy increases from left to right (abscissa scale in* ev). *Ordinate, electron count rate to arbitrary scale. Vertical ionization potentials and proposed assignments indicated over each spectrum.*

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