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IONIZATION EFFICIENCY CURVES OF SOME DI-SUBSTITUTED BENZENES

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Recently, Dewar and Kelemen[1] have calculated the energy levels of four fluorinated benzenes by SCF-MO method and have reported that the second ionization potentials of these compounds do not correspond to π-electron ionization, but correspond to σ-electron ionization.

Bonnier, Gelus and Nounou[2], and Nounou[3] have indicated that ionization potentials of methylated naphthalenes, methylated anthracenes and methylated phenanthrenes have linear relation with Hückel Molecular Orbital (H.M.O.) coefficients of π-electron.

Eland and Danby[4] have measured the ionization potentials of indene, naphthalene, azulene, biphenyl, isoquinoline and quinoline by photoelectron spectrometry. To relate the observed ionization potentials to H.M.O. theory they have plotted the first three ionization potentials of these compounds against the H.M.O. coefficient (a) of β, and have found that the points lie close to a straight line for which least squares analysis gives

$$\text{I.P.} = 6.22 + (2.77 \pm 0.15)a$$

From the result they identified the first three inner ionization potentials of these compounds studied with π-electron loss. More recently, Eland[5] has extended the method to 14 conjugated hydrocarbons and heteromolecules and reported that there is a linear relation between the vertical ionization potentials observed and H.M.O. coefficients for some compounds containing nitrogen or oxygen atoms.

In order to scrutinize the nature of the electron removed in successive ionization, we have measured the ionization potentials of o-,m-chloroaniline and o-,m-anisidine by electron impact method and compared them with the result obtained by simple LCAO MO calculation for these molecules.

The parameters used in the calculation were obtained from appropriate sources[6,7]. The ionization efficiency curve was measured with a CEC 21-103C mass spectrometer and treated by the E.D.D. method[8]. The constant b used in the E.D.D. calculation was 0.67. The distribution of electron energy in the mass spectrometer was measured by the Morrison's method[9], and was found to take approximately a form of Maxwellian distribution. Xenon was used for calibrating the energy scale. The sample were guaranteed reagents obtained from Tokyo Kasei Co. Ltd.. The chloroanilines were distilled once, anisidines were used without further purification. Details of the experiment, for instance, the effect of repeller voltage on the appearance potentials observed, will be reported elsewhere.

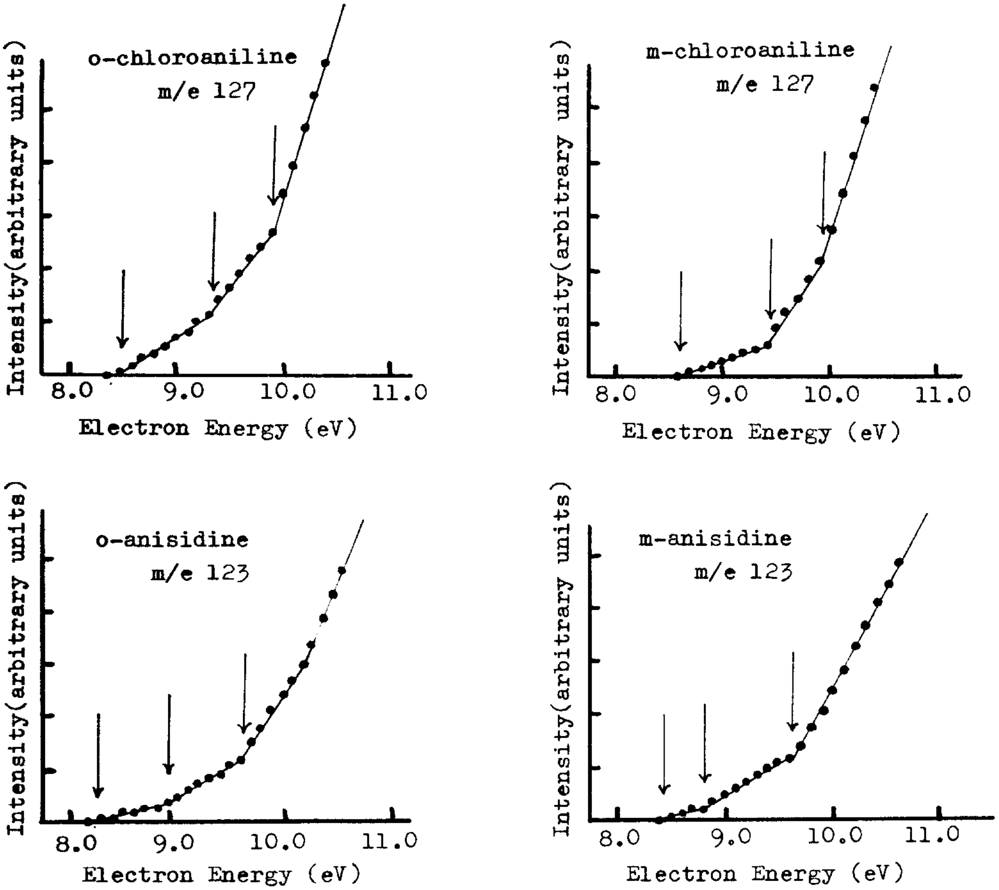

Fig. 1

The ionization efficiency curves for molecular ions are shown in Fig. 1. The electron energies corresponding to the onset point and the first and the second breaks of an ionization efficiency curve were assumed to be the successive vertical ionization potentials of the compounds. The vertical ionization potentials observed and H.M.O. coefficient of each of the first three occupied energy levels of π-electron calculated by simple LCAO MO method are shown in Table 1. The ionization potentials given in Table 1 are mean values of five measurements, and the given errors are maximum deviations.

	o-chloroaniline	m-chloroaniline	o-anisidine	m-anisidine
Observed Vertical Ionization Potentials. (eV)	8.48 ± 0.02 9.31 ± 0.13 9.91 ± 0.10	8.60 ± 0.10 9.41 ± 0.18 9.93 ± 0.15	8.21 ± 0.08 8.92 ± 0.12 9.58 ± 0.10	8.37 ± 0.05 8.81 ± 0.13 9.60 ± 0.10
Calculated H.M.O. Coefficient (a).	0.289 0.878 1.148	0.308 0.860 1.129	0.201 0.503 1.111	0.302 0.393 1.086

Table 1

To relate the observed vertical ionization potential to that of π-electron, we have plotted the first three ionization potentials observed of these compounds against the H.M.O. coefficient (a) of β (Fig. 2), as were done by authors cited[2~5]. The points lie close to a straight line,

$$I.P. = 8.0 + 1.7a$$

The ionization potential of o-chloroaniline have been reported as 7.9 eV by U.V. measurement[10]. Accepting this value as adiabatic ionization potential and comparing this with the value given in Table 1, we obtain 0.6 eV for the difference between the observed vertical ionization potential and the adiabatic ionization potential for the compound. Hence, the linear relation shown in Fig. 2 suggests there are about the same amount of differences between the vertical ionization potentials observed by electron impact method and the adiabatic ionization potentials for these compounds studied. The parallel line obtained by transferring 0.6 eV the line in Fig. 2 downward gives 7.4 eV for α, the Coulomb integral, and 1.7 eV for β, the resonance integral, which are compatible with those values accepted.

Simple LCAO MO theory with parameters accepted provides good predictions for the first and the inner π-electron ionization potentials of these aromatic compounds studied. The correlation found is close and the identification of the first three ionization potentials of the substances studied with π-electron loss is legitimate.

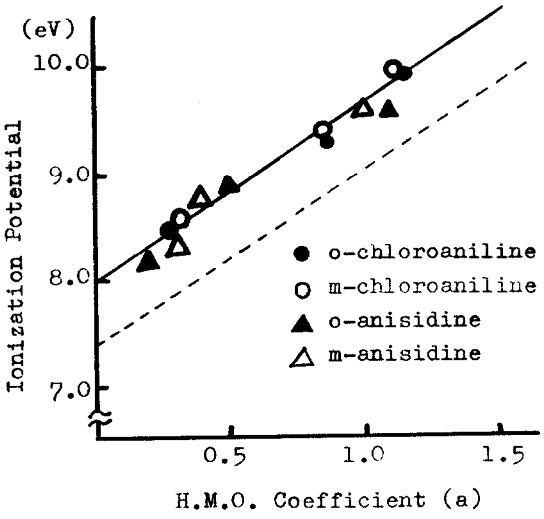

Fig. 2

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