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A Theoretical Interpretation of the Half-wave Reduction Potentials of Chloronitrobenzenes

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Synopsis. The half-wave reduction potential of chloronitrobenzenes has been studied with *ab initio* MO calculations. The relation between the energy of the lowest unoccupied MO and the reduction potential is given.

If the addition of the first electron to an aromatic hydrocarbon is the potential-determining step, there should be a relationship between the energy of the lowest unoccupied molecular orbital (LUMO) and the reduction potential.[1] We have carried out MO calculation in order to obtain possible relation between the half-wave reduction potentials ($E_{1/2}$'s) for a series of chloronitrobenzenes and the number and position of chlorine atoms attached to the benzene ring. The polarographic data are taken from the works of Fujinaga *et al.*,[2] and Kitagawa and Nakashima.[3] The MO calculation was made on the STO-3G minimal basis by use of the GAUSSIAN 70 program.[4] The coordinate and the geometrical parameters are shown in Fig. 1. For the sake of simplicity, all the bond angles in the X-Y plane are assumed to be 120° (sp^2 hybridization). The sole freedom of the geometrical change is the rotation (angle=θ°) of the nitro group around the C_1–N axis. According to X-ray analysis, pentachloronitrobenzene has $\theta=62°$.[5] In the present study, the MO calculation is restricted to four molecules, Nos. 1, 2, 3, and 7 which are sufficient to explain the trend of $E_{1/2}$ values (Table 1).

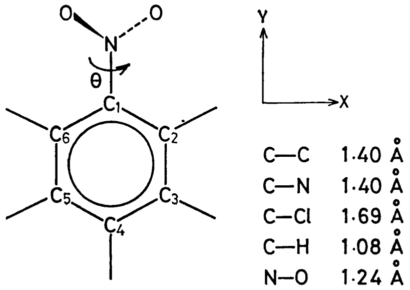

Fig. 1. The geometry taken for the MO calculation. All the bond angles are assumed to be 120°.

The values of $E_{1/2}$ are given for a variety of chloronitrobenzenes. We see a general tendency for the increase of chlorine substituents to give smaller negative values (easier reduction) except for *o*-dichloro-substituted nitrobenzenes (Nos. 7, 12, and 14). This is understandable in terms of the MO scheme, since the inclusion of hetero atoms lowers the LUMO of hydrocarbons.[1d] The greater the number of chlorine atoms attached to the benzene ring is, the more easily its anion radical is yielded through the acceptance of an electron into the LUMO. Of the three monochloronitrobenzenes 1, 2, and 3, the order of ease of one-electron reduction is *m*->*p*->*o*-chloronitrobenzene. In general, molecules with a greater amount of *meta*-Cl and a smaller amount of *ortho*-Cl are easily reduced. No. 9 (*m*-dichloro-substituted) is found to be most easily reduced among the series of dichloronitrobenzenes. The unfavorable role of the *ortho*-Cl against the easier reduction is observed typically in No. 7 with two Cl's. In spite of the inclusion of two hetero atoms, this molecule has a greater negative $E_{1/2}$ value (more difficult for reduction) than the parent nitrobenzene ($E_{1/2}=-1.09$). Such a trend holds also for the polychloronitrobenzenes.

TABLE 1. THE FIRST HALF-WAVE REDUCTION POTENTIAL ($E_{1/2}$) AND THE ORBITAL ENERGY OE THE LUMO (ε_{LUMO}) OF CHLORONITROBENZENES

No.	Substituents	$E_{1/2}$ (V *vs.* SCE)	ε_{LUMO} (a.u.)
1	*o*-Chloro	−1.06[2]	0.1708
2	*m*-Chloro	−0.93[2]	0.1472
3	*p*-Chloro	−0.99[2]	0.1473
4	2,3-Dichloro	−0.98	
5	2,4-Dichloro	−0.99	
6	2,5-Dichloro	−0.94	
7	2,6-Dichloro	−1.15[3]	0.1715
8	3,4-Dichloro	−0.89	
9	3,5-Dichloro	−0.86	
10	2,3,5-Trichloro	−0.87[a]	
11	2,4,5-Trichloro	−0.87	
12	2,4,6-Trichloro	−1.05	
13	2,3,4,5-Tetrachloro	−0.83[b]	
14	2,3,5,6-Tetrachloro	−1.01	
15	Pentachloro	−0.89	

a) Evaluated from cyclic voltammogram of No. 14.
b) Evaluated from cyclic voltammogram of No. 15.

The result given in Table 1 is interpreted theoretically in the MO scheme. First, the optimum θ of Nos. 1, 2, 3, and 7 is examined through a comparison of total energies. While No. 2 (*m*-Cl) and No. 3 (*p*-Cl) have a planar structure of $\theta=0°$ with the most widely spread π conjugation, No. 1 (*o*-Cl) and No. 7 (*o*-dichloro-substituted) have a nonplanar equilibrium structure with $\theta=54°$ and $\theta=71°$, respectively. The *ortho*-Cl thus has a remarkable effect of steric hindrance on the nitro group. The question arises as to how such a nonplanar structure is related to the above mentioned result of $E_{1/2}$ of *ortho*-substituted nitrobenzenes. As θ becomes greater, the levels of LUMO 1 and 7 ascend sharply. These LUMO's are the π^* orbital for $\theta=0°$. The effect of the *ortho*-Cl on the value of $E_{1/2}$ is explained as follows. The *ortho*-Cl causes twisting of the nitro group by steric hindrance. The subsequent nonplanar structure of the *o*-chloro-substituted nitrobenzenes raises the level of their LUMO's through the decrease of the extent of the π bonding between the benzene ring and the nitro group, resulting in the more difficult reduction, *i.e.*, a greater negative value of $E_{1/2}$. These molecules provide an interesting example of the "ortho effect" in their physical property *i.e.*, $E_{1/2}$.

Then, why does the *meta*-Cl make the reduction of nitrobenzene easier? In order to elucidate this effect, the mode of the π-MO interaction between the fragmental nitrobenzene and the chlorine atom is examined as to the planar monochloronitrobenzene. Of several π MO's of nitrobenzene, three unoccupied MO's, LUMO, (LU+1)MO, and (LU+2)MO are the most significant orbitals which contribute to the ascent or the descent of the LUMO of the monochloronitrobenzene. As for the chlorine atom, its $3p_z$ AO is the sole contributor to the LUMO of the monochloronitrobenzene. Figure 2a shows the nodal property of the π MO's of nitrobenzene and Fig. 2b the mode of the π-MO interaction between two fragmental sites. If only the LUMO of nitrobenzene interacts with the $3p_z$ AO, two kinds of orbitals, $\psi_{\mathrm{occ}}^{o,m,p}$ and $\psi_{\mathrm{uno}}^{o,m,p}$, are obtained. ψ_{occ} and ψ_{uno} indicate the occupied and unoccupied orbitals of the monochloronitrobenzene, respectively. The *o*, *m*, and *p* attached to the right shoulder denote the position, *ortho*, *meta*, and *para*, respectively, of the substituent. The (LUMO-$3p_z$) interaction causes the energy splitting between ψ_{occ} and ψ_{uno}, the degree of which depends entirely on the numerical value of the AO coefficients of the LUMO of nitrobenzene (Fig. 2a). Thus, the extent of energy splitting is *m*-Cl<*o*-Cl<*p*-Cl and the energy of the unoccupied level $\psi_{\mathrm{uno}}^{m}<\psi_{\mathrm{uno}}^{o}<\psi_{\mathrm{uno}}^{p}$ (ψ_{uno}^{p} is highest). The secondary effect coming from the (LU+1)MO and (LU+2)MO of nitrobenzene should also be taken into account.[6] The energy levels of ψ_{occ} and ψ_{uno} produced primarily by the (LUMO-$3p_z$) interaction are lowered (Fig. 2b) according to the extent of the secondary MO interaction of (LU+1)MO and (LU+2)MO. As a result of such MO interactions, the energy level of the LUMO of nitrobenzene and monochloronitrobenzenes would have the order, *m*-Cl<*o*-Cl<*p*-Cl<nitrobenzene with no steric hindrance.

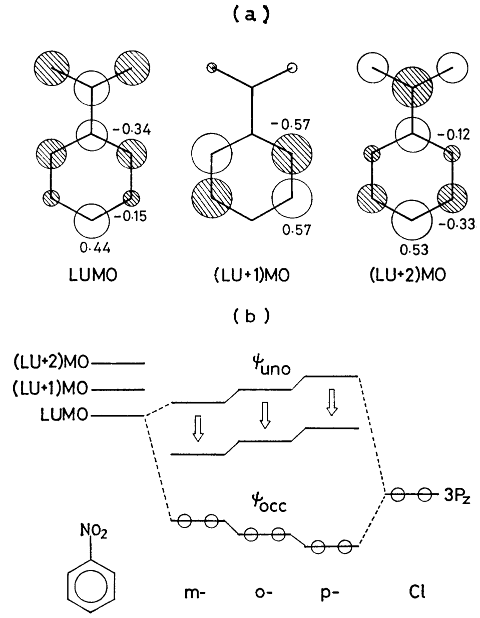

Fig. 2. (a); The AO coefficients of three π-type unoccupied MO's of nitrobenzene. (b); The mode of the orbital interaction between three unoccupied MO's of nitrobenzene and the $3p_z$ AO of Cl.

Thus, the correlation between the value of $E_{1/2}$, *i.e.*, the $\varepsilon_{\mathrm{LUMO}}$, and the position of the substituent Cl is interpreted in terms of two independent factors; (a) the degree of the orbital interaction between the LUMO of nitrobenzene and the $3p_z$ AO of Cl, which depends on the numerical value of AO coefficients of the former MO, and (b) the steric hindrance caused by the *ortho*-Cl, resulting in the nonplanar structure of the *o*-chloro-substituted nitrobenzenes. In fact, the order of the experimental $E_{1/2}$ values is satisfactorily in line with that of the calculated $\varepsilon_{\mathrm{LUMO}}$ values.

All LUMO's of the four molecules adopted for the MO calculation are π^* (or almost π-type) orbitals. It is conceivable that, even when these molecules are reduced in one-electron step and their LUMO's accepted one electron, no dechlorination takes place. The first one-electron wave of polarography is reported to represent the reversible reduction of these compounds and the first wave corresponds to the formation of the relatively stable anion radical.

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