The Polarographic Reduction and Electronic Structures of Organic Halides

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In the last fifteen years the polarographic reduction of a number of conjugated hydrocarbons has been extensively studied, both experimentally and theoretically. Their pH-independent reversible half-wave reduction potentials, $E_{1/2}$, have been found to be linearly related to the energy, $\varepsilon_{1v}{}^{\pi}$, of their lowest unoccupied π orbital[1,2], the energy which would be needed in order to bring an electron to the orbital, as follows:

$$-E_{1/2}=\lambda_{1v}{}^{\pi}\beta_{\pi}+C$$

where $\lambda_{1v}{}^{\pi}$ is the coefficient of the energy of the level $\varepsilon_{1v}{}^{\pi}=\alpha_{\pi}+\lambda_{1v}{}^{\pi}\beta_{\pi}$ and α_{π} and β_{π} are the standard Coulomb and the standard resonance integrals of the π orbitals. From the inclination of the line the value of the resonance integral, β_{π}, was estimated to be -2.23 eV., which seemed to be reasonable in comparison with the value estimated from other physicochemical sources. The higher the energy of the level, that is, the smaller the value of $\lambda_{1v}{}^{\pi}$, the less reducible the hydrocarbon and, therefore, the more negative the half-wave reduction potential. A similar linear relationship between the lowest unoccupied π levels and the reduction potentials and a similar value of the integral β_{π} have been found for a variety of compounds, such as substituted stilbenes, substituted nitrobenzenes, aromatic ketones and vinyl compounds[3].

Furthermore, the structures of the products of the corresponding controlled potential electrolysis of hydrocarbons have been examined in terms of the π electron distribution of the hydrocarbon anions[2], in which an excess electron is accepted in the lowest unoccupied π levels and from which products will be yielded by protonation. Protons add to those positions which have a large electron density, and a product results in which a double bound or more is reduced. For instance, naphthalene is reduced to give 1, 2-dihydronaphthalene and 1, 4-dihydronaphthalene.

On the other hand, it has been elucidated that halogenated, saturated hydrocarbons are polarographically reducible, showing half-wave potential independent of the pH value and giving products in which carbon-halogen bonds are reduced to carbon-hydrogen bonds[4]. For instance, the half-wave reduction potential of methyl iodide is -1.63 V. vs. S. C. E. (saturated calomel electrode), and it is converted into methane when reduction is performed at that voltage. Further, it is interesting to notice that some of the halogenated, unsaturated hydrocarbons are reduced at a potential less negative than the potential at which the mother hydrocarbons are reducible, and carbon-halogen bonds are reduced in these compounds as well as in saturated halides[4].

With respect to the problems of the polarographic reduction of saturated compounds which have no π conjugated system, theoretical studies have never been carried out in relation to their electronic structure.

The present authors have established a simple molecular orbital method for calculating the σ electronic structure of saturated hydrocarbons and their derivatives[5,6] and have applied this method further to discussing the electronic structure of the σ skeleton in conjugated compounds[7,8]. By the aid of this method, one can calculate the energy levels and charge distribution of σ electrons.

In the present paper, the relations between the half-wave reduction potentials of saturated halides and their lowest unoccupied σ levels, and the connection between the distribution of the lowest unoccupied level and the structures of the reduction products will be discussed first. Then, similar discussions will be made for unsaturated halides and, at the end, a possibility that in polyhalogenated compound the lowest unoccupied σ level may creep below the lowest unoccupied π level will be suggested.

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[1] A. Maccoll, *Nature*, **163**, 178 (1949).

[2] G. J. Hoijtink and J. v. Schooten, *Rec. trav. chim.*, **71**, 1089 (1952).

[3] S. Koide and I. Tachi, *J. Electrochem. Soc. Japan*, **23**, 522 (1955); T. Fueno, K. Asada, K. Morokuma and J. Furukawa, *J. Polymer Sci.*, **40**, 511 (1959); T. Fueno, K. Morokuma and J. Furukawa, *Bull. Inst. Chem. Research, Kyoto Univ.*, **36**, 87, 96 (1958).

[4] M. v. Stackeberg and W. Stracke, *Z. Elektrochem.*, **53**, 118 (1949).

[5] K. Fukui, H. Kato and T. Yonezawa, This Bulletin, **34**, 1111 (1961).

[6] K. Fukui, H. Kato, H. Saito and T. Yonezawa, ibid., **35**, 1814 (1962).

[7] K. Fukui, T. Yonezawa, H. Kato, K. Morokuma, A, Imamura and C. Nagata, ibid. , **35**, 38 (1962).

[8] K. Morokuma, K. Fukui, T. Yonezawa and H. Kato, ibid., **36**, 47 (1963).

Method of Calculation

The electronic structures of π and σ electron systems have been calculated by using a simple LCAO MO (linear-combination-of-atomic-orbital molecular orbital) method, disregarding overlap integrals and electronic interactions.

In saturated compounds in which carbon atoms are sp^3-hybridized, molecular orbitals are written as linear combinations of all σ atomic orbitals—hydrogen 1s orbitals, sp^3-hybridized orbitals of carbons, and σ atomic orbitals of halogens. The energy, ε_i, of the ith molecular orbital is expressed as:

$$\varepsilon_i = \alpha_{sp^3} + \lambda_i^{sp^3}\beta_{sp^3-sp^3} \tag{2}$$

where α_{sp^3} and $\beta_{sp^3-sp^3}$ indicate the Coulomb intergral of a sp^3-hydbridized orbital of carbon and the resonance integral between sp^3 orbitals, making a standard σ bond. The larger value of $\lambda_i^{sp^3}$ corresponds to the lower energy since the resonance integrals is minus in sign. The Coulomb and the resonance integrals of each atom and bond adopted in the calculation are the same as were employed previously[5,6], they will not be repeated for the sake of brevity.

The method can be extended to the calculation of the σ electronic structures of conjugated compounds if, in this case, one regards the π electrons as making a field where σ electrons move. Then the energy of the ith σ molecular orbital, ε_i^{σ}, may be written as:

$$\varepsilon_i^{\sigma} = \alpha_{sp^2} + \lambda_i^{sp^2}\beta_{sp^2-sp^2} \tag{3}$$

where α_{sp^2} and $\beta_{sp^2-sp^2}$ are the standard Coulomb and the standard resonance integrals of the sp^2 σ orbitals. Similarly, the energy of the jth π molecular orbital calculated by the simple LCAO MO method is given as:

$$\varepsilon_j^{\pi} = \alpha_{\pi} + \lambda_j^{\pi}\beta^{\pi} \tag{4}$$

Calculated σ electron densities could clearly explain the experimental results of physicochemical properties — for instance, dipole moments, halogen coupling constants in PQR spectra, and proton chemical shifts in NMR spectra — as has been reported previously[7,8].

A no table finding of the calculation in halogenated compounds is that the substitution of hydrogens by halogens, while it does not change the energy of σ occupied levels very seriously, does give rise to a remarkable change in the energy of σ unoccupied levels. There occurs especially a considerable lowering of the lowest unoccupied σ level; this lowering becomes larger as the number of halogen atoms increases.

The Polarographic Reduction and σ Electronic Structures of Haloalkanes

Haloalkanes belong to one of the few groups of compounds which include no conjugated system but which can nevertheless be reduced polarographically. As was pointed out in the previous section, halogen substitution causes a lowering of the lowest unoccupied σ levels.

Imitating Eq. 1, we compared the first half-wave reduction potential of halomethanes with the energy of their lowest unoccupied σ level, obtaining the following relation:

$$-E_{1/2} = \lambda_{1v}^{sp^3}\beta_{sp^3-sp^3} + C' \tag{5}$$

TABLE I. FIRST HALF-WAVE REDUCTION POTENTIAL AND ENERGY AND ELECTRON DISTRIBUTION OF THE LOWEST UNOCCUPIED LEVEL OF HALOMETHANES

Compound	Half-wave reduction potential[4],*, $E^{1/2}$ V. vs. SCE	Energy of the lowest unoccupied level, $\lambda_{1v}^{sp^3}$	Partial bond order of the lowest unoccupied level on C–X bond	Sum of the distribution of the lowest unoccupied level on C–X bonds
CH_4	NW	−0.848	—	0
CH_3Cl	−2.23	−0.400	−0.369	0.78
CH_2Cl_2	−2.33	−0.229	−0.204	0.82
$CHCl_3$	−1.67	−0.081	−0.147	0.89
CCl_4	−0.78	+0.059	−0.116	1.00
CH_3Br	−1.63	−0.366	−0.375	0.79
CH_2Br_2	−1.48	−0.190	−0.208	0.83
$CHBr_3$	−0.64	−0.045	−0.144	0.87
CBr_4	−0.3	+0.089	−0.112	1.00
CH_3I	−1.63	−0.337	−0.381	0.80
CH_2I_2	−1.12	−0.167	−0.208	0.83
CHI_3	−0.49	−0.027	−0.146	0.90
CI_4	—	+0.095	−0.108	1.00

* NW indicates that the compound gives no reduction wave.

As can be seen in Table I, a parallelism between them was obtained for each series of halomethanes. A similar relation is obtained also in haloethanes. The discrepancy which is observed in comparing bromo- and iodomethanes is probably due to an inappropriate choice of energy parameters for halogen atomic orbitals which have never strictly tested nor improved; it is also perhaps due to the effect of disregarding the overlap integrals.

Although the linear relation represented by Eq. 5 was not precisely adopted to the values in Table I, we roughly estimated the magnitude of $\beta_{sp^3-sp^3}$ by means of Eq. 3 and so obtained a value of ca. -5 eV. This value is very close to that of $\beta_{sp^3-sp^3}$ obtained in the discussion of the NMR chemical shifts of halides (-5.7 eV.)[11] and also in that of the ionization potentials of halides (ca. -5 eV.)[11]. Furthermore, this would be rather rational in comparison with the above cited value of β_π, -2.23 eV.

From these correspondences between $E_{1/2}$ and $\lambda_{1v}{}^{sp^3}$, it can safely be said that the potential-determining step in the polarographic reduction of haloalkanes is the electron transfer from the electrode to their lowest unoccupied σ level. The fact that methane and other saturated hydrocarbons do not give a reduction wave is clearly because of the high energy of their lowest unoccupied σ levels.

The electron distribution of the lowest unoccupied level is greatly localized on the carbon-halogen bonds, and the bond order of the level on the bond is negative and large in absolute value, as may be seen in the fourth and fifth columns in Table I and Fig. 1. These calculated results suggest that, in a state which has an electron in that level, the carbon-halogen bonds are very easy to break down. The anion, which might be produced at the first step of the polarographic reduction of halides, corresponds to this case. One may consider a second process in which a carbon-halogen bond of the anion breaks and in which the resultant anion, or radical, reacts with a proton, or with a proton and an electron, in the solution (a 75% dioxane and 25% water solution was used as the solvent), as was suggested by Stackelberg and Stracke:

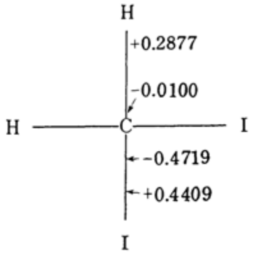

Fig. 1. Coefficient of atomic orbitals in the lowest unoccupied σ MO of diiodomethane.

$$\left.\begin{aligned} &R-X + e^- \rightarrow (R-X)^- \\ &(R-X)^- \rightarrow R\cdot + X^- \\ &R\cdot + e^- + H^+ \rightarrow RH \end{aligned}\right\} \quad (6)$$

or

$$\left.\begin{aligned} &R-X + e^- \rightarrow (R-X)^- \\ &(R-X)^- \rightarrow R^- + X\cdot \\ &R^- + H^+ \rightarrow RH \\ &X\cdot + e^- \rightarrow X^- \end{aligned}\right\} \quad (7)$$

Thus, one may clearly explain theoretically such a result of controlled potential reduction as that, for instance, methyl bromide was reduced to give methane, while ethyl bromide gave ethane. This connection seems to support the conclusion derived above that the first reduction potential of saturated halides corresponds to the electron transfer to the lowest unoccupied σ level. It has not yet been decided in which one of the two mechanisms, Eq. 6 or 7 the real breakdown of carbon-halogen bonds occurs. On the basis of the electron affinities of halogen and carbon atoms, however, the first mechanism, Eq. 6, seems to be more probable than the second one. If so, one who carried out the controlled potential electrolysis of halides in an aprotic solvent could observe the ESR spectra of the radical.

The Polarographic Reduction and σ and π Electronic Structures of Conjugated Halides

In this section relations between the half-wave reduction potential and the energy of the lowest σ and the lowest π unoccupied levels will be investigated. The experimental $E_{1/2}$ and the calculated height of the lowest unoccupied levels, $\lambda_{1v}{}^{sp^2}$ and $\lambda_{1v}{}^{\pi}$, of chlorobenzenes and chloroethylenes, as examples, are tabulated in Table II.

The height of the lowest unoccupied π level hardly varies in these series and seems to have no connection with their half-wave reduction potential, $E_{1/2}$. Even if one forcibly applies Eq. 1 to their relation, one is led to the irrational finding that the absolute value of β must exceed 20 eV. On the other hand, the height of the lowest unoccupied σ levels of these compounds is shown to be parallel to the half-wave potential, as in haloalkanes:

$$-E_{1/2} = \lambda_{1v}{}^{sp^2}\beta_{sp^2-sp^2} + C'' \quad (8)$$

From the parallelism the magnitude of $\beta_{sp^2-sp^2}$ is estimated to be -6.88 eV. (in the case of chlorobenzene), a value which seems to be appropriate in view of these of β_π and $\beta_{sp^3-sp^3}$.

TABLE II. FIRST HALF-WAVE REDUCTION POTENTIAL AND ENERGY AND ELECTRON DISTRIBUTION OF THE LOWEST UNOCCUPIED σ AND THE π LEVELS OF HALOGENOBENZENES AND HALOGENOETHYLENES

Substituents	Half-wave reduction potential[4)]* $E_{1/2}$, V.	Energy of the lowest unoccupied σ level, $\lambda_{1v}^{sp^2}$	Energy of the lowest unoccupied π level, λ_{1v}^{π}	Partial bond order of the lowest unoccupied σ level on C–X	Sum of the distribution of the lowest unoccupied σ level on C–X bonds
1. Chlorobenzenes					
no	NW	−0.501	−1.000	—	0
Cl	NW	−0.345	−0.983	−0.280	0.56
p-diCl	−2.49	−0.313	−0.967	−0.134	0.53
m-diCl	−2.48	−0.305	−0.991	−0.138	0.55
o-diCl	−2.51	−0.274	−0.973	−0.152	0.61
pentaCl	—	−0.187	−0.967	−0.048 −0.070 −0.079	0.64
hexaCl	−1.44	−0.158	−0.951	−0.054	0.67
2. Chloroethylenes					
no	NW	−0.664	−1.000	—	0
Cl	NW	−0.390	−0.975	−0.345	0.70
1,2-diCl	NW	−0.319	−0.951	−0.175	0.70
1,1-diCl	ca. −2.4	−0.229	−0.952	−0.207	0.84
triCl	−2.14	−0.196	−0.928	−0.173 −0.062	0.83
tetraCl	−1.88	−0.129	−0.906	−0.105	0.89

* NW indicates that the compound gives no reduction wave.

Furthermore, as to the reduction products, for instance, naphthalene from α-bromonaphthalene and ethylene from 1,2-diiodoethylene, an explanation similar to that in the case of haloalkanes would be possible based on the localizing and anti-bonding nature of the carbon-halogen bonds of the lowest unoccupied σ level, as is shown in Table II and Fig. 2.

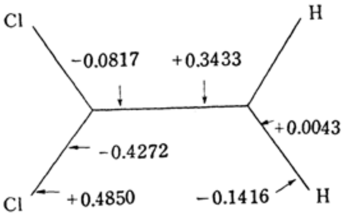

Fig. 2. Coefficient of atomic orbitals in the lowest unoccupied σ MO of 1,1-dichloroethylene.

Thus, the polarographic reduction of conjugated halides would represent the electron transfer process from the cathode to the lowest unoccupied σ, not π, level, in contrast with the case of other conjugated compounds, in which an electron runs into the lowest unoccupied π level, satisfying Eq. 1.

As the entropy change will not be very different between the both processes, that in which the electron transfers to the σ unoccupied level and that in which it transfers to the π unoccupied level, it may be said that the lowest unoccupied σ level would be lower than the lowest unoccupied π level. This conclusion is more certain as the number of halogen atoms in the molecule increases or as the halogen changes in the order F → Cl → Br → I.

One may raise the objection that the lowest unoccupied σ level into which an electron jumps may not be the lowest level of all, for, if the selective adsorption of carbon-halogen bonds occurs, an electron will have to run into the level which is localized in the bonds. However, the experimental finding that α-bromonaphthalene is reduced at a voltage (−1.96 V.) less negative than that at which naphthalene can first be reduced (−2.50 V.) renders the objection invalid.

In Fig. 3 is shown the energy diagram of lowest unoccupied levels, which is mainly deduced from the linear relationship (cf. Eqs. 1 and 8) between λ_{1v} and $E_{1/2}$. The value of the energies of the levels might include errors of the order 0.1 to 0.2 eV. The origin of the energy is arbitrary. One can see the inversion of the π and σ lowest unoccupied levels.

It is well-known that the nucleophilic substitution of unsaturated halides takes place exclusively at the halogen atom as follows:

$$\mathrm{Ar{-}X} + \mathrm{Y}^- \rightarrow \mathrm{Ar{-}Y} + \mathrm{X}^- \qquad (9)$$

where Y^- is a nucleophilic reagent. It seems very interesting to connect this fact with the

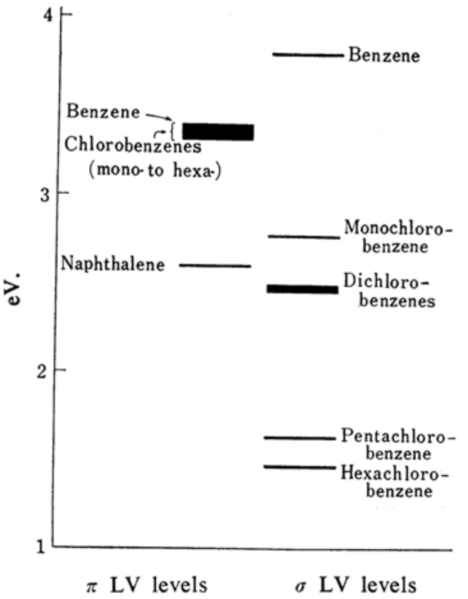

Fig. 3. Estimated lowest vacant π and σ levels.

inversion of energy levels. That is to say, when the reagent comes near the substrate, for instance, electrons on the substrate easily delocalize to the lowest unoccupied level, that is, the lowest unoccupied σ level, which causes a weakening of the carbon-halogen bonds, and so substitution occurs. Therefore, the mechanism of the nucleophilic substitution of unsaturated halides might differ from that of the ordinary substitution reactions of conjugated compounds in which π levels play a dominant role.

Furthermore, the inversion of the lowest unoccupied levels in unsaturated halides would result in a weak and broad transition from the highest occupied π level (the highest occupied of all) to the lowest unoccupied σ level (the lowest unoccupied of all), which would be seen in the range of larger wavelengths; this may be named the $\pi \rightarrow \sigma^*$ transition. An $n \rightarrow \sigma^*$ transition wave observed in saturated halides by Mulliken⁹⁾, but the $\pi \rightarrow \sigma^*$ transition in conjugated halides has not yet been observed nor even suggested. A more precise calculation by the LCAO ASMO CI method, which confirms our present conclusion, will be published elsewhere¹⁰⁾.

The Polarographic Reduction of Other Saturated Compounds

It is worth noticing that haloalkanes and alkylperoxides are the only saturated compounds that can be polarographically reduced. Alkylperoxide gives an almost pH value-independent wave at a much less negative potential; for instance, methyl hydroperoxide is reduced at −0.25 V. both in 0.01 N hydrochloric acid and 0.01 N sodium hydroxide. The lowest calculated unoccupied σ level in alkylperoxides, as well as in haloalkanes, is very low. For instance¹¹⁾,

$$\mathrm{CH_3OOH} \qquad \lambda_{1v}{}^{sp^3} = -0.0956^*$$

$$\mathrm{C_2H_5OOH} \qquad \lambda_{1v}{}^{sp^3} = -0.0940$$

$$\mathrm{(CH_3)_3COOH} \qquad \lambda_{1v}{}^{sp^3} = -0.0898$$

The lowering of the lowest unoccupied σ level in peroxides would have an intimate connection with their polarographic reduction, as one might except from the discussion on saturated halides.

The distribution of the lowest unoccupied level is also very localizing on the oxygen-oxygen bond, and the partial bond order on the bond is negative and large in absolute value (Fig. 4). Thus, after the electron transfer to the level, the breakdown of the bond will follow.

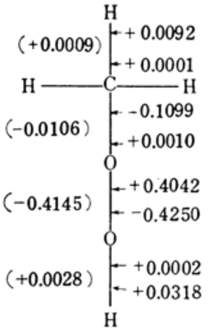

Fig. 4. Coefficient of atomic orbitals and partial bond order (in parentheses) of the lowest unoccupied MO.

Generally speaking, the lowering of the lowest unoccupied level is to be expected if a compound has one or more bonds whose resonance integrals are relatively small and, at the same time, one or both of the atoms constructing it are relatively electronegative. Peroxides and halides are typical examples.

Inversion of the lowest unoccupied σ and the lowest unoccupied π level may occur in the case where the lowering of the lowest unoccupied σ level is large, as has been stated above, and where the lowest unoccupied π level remains rather high. An electronegative atom in the compound necessarily causes a

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* The parameters used in the calculation will be published elsewhere¹¹⁾.

9) R. S. Mulliken., *J. Chem. Phys.*, **8**, 234, 382 (1940).

10) Presented partly at the International Symposium on Molecular Structure and Spectroscopy, Tokyo, September, 1961.

11) K. Fukui and H. Kato, to be published.

lowering of all levels, but when the atom has a lone pair to conjugate with neighboring atoms, the lowest unoccupied π level stays relatively high. The conjugated halides discussed in this paper and some conjugated peroxides seem to be the only examples where inversion may be expected.

Summary

The polarographic reduction potential of haloalkanes is connected with the energy of their lowest unoccupied σ level. Moreover, the reduction products are well explained in terms of the anti-bonding nature of the carbon halogen bond of the level. The polarographic reduction potential of conjugated halides is also correlated to their lowest unoccupied σ, not π, level. It has also been suggested that, in conjugated halides, the lowest unoccupied σ level might be lower than the lowest unoccupied π level and that the $\pi \rightarrow \sigma^*$ transition might be observed.

Most of the calculations have been carried out on the KDC-I digital computer of Kyoto University.

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