A Molecular Orbital Consideration on the Polarographic Reduction Potentials of Aromatic Ketones

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A linear relationship was found between the polarographic half-wave reduction potentials of aromatic ketones in an alkaline medium and their lowest vacant π-electronic energies calculated according to the LCAO MO method. The height of the lowest vacant level of a ketone seems to be very much dependent on the scale of its π-conjugation framework itself as well as on the polar nature of the carbonyl group involved.

INTRODUCTION

It is well established[1~6] that the polarographic half-wave reduction potentials of unsaturated hydrocarbons are linearly correlated to their lowest vacant π-orbital energies calculated according to the molecular orbital theory. Regarding carbonyl compounds, however, little discussion has been made in terms of this theory, although a voluminous literature is available on their polarography. The only paper has been published by Schmid and Heilbronner,[7] who showed that the half-wave potentials of several aromatic aldehydes determined in an alkaline medium were in a good linear relation with the corresponding lowest vacant levels.

It is from the above aspect that the present writers are interested in the data on half-wave potentials of aromatic ketones investigated by Pasternak.[8] We could verify a satisfactory linear relationship to hold between the potentials of these ketones and their lowest vacant π-orbital enegies calculated on the basis of the simple molecular orbital method. The heights of these energy levels seem to be very much dependent on the scales of the π-conjugation frameworks concerned.

METHOD OF CALCULATION

The lowest vacant π-electronic level, ε_{lv}, of an unsaturated ketone will be represented as

$$\varepsilon_{lv} = \alpha + x_{lv}\beta,$$

where α and β are the Coulomb integral of a carbon atom and the reasonance integral of a carbon—carbon π-bond in benzene. The coefficient, x_{lv}, was obtained by solving the simple molecular orbital secular equation (neglecting overlap integrals). The energy parameters empolyed for carbonyl groups were as follows:

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$$a_C = a, \quad a_O = a + 2\beta \text{ and } \beta_{CO} = \sqrt{2}\beta$$

Similar coefficients, $x_{lv}{}^0$, for unsaturated hydrocarbon analogues of the ketones were calculated in order to clarify the feature of the polar effect of carbonyl groups upon the lowest vacant π-orbital energy. In either case, hyperconjugation of methyl groups was not taken into account.

RESULTS AND DISCUSSION

Table 1 summarizes the calculated results of the lowest vacant π-orbital energies of aromatic ketones together with their data on half-wave reduction

Table 1. Data on half-wave potentials and lowest vacant π-orbital energies of aromatic ketones.

No.	Aromatic Ketone	Formula	$-E_{1/2}{}^a$ (V.vs.N.C.E.)	$-x_{lv}$	$-x_{lv}{}^0$
1	Dibenzoylethane	$C_6H_5COCH_2CH_2COC_6H_5$	1.67	0.4315	0.6622
2	Acetophenone	$C_6H_5COCH_3$	1.64	0.4315	0.6612
3	Benzoin	$C_6H_5COCH(OH)C_6H_5$	1.55	0.4315	0.6612
4	Benzophenone	$C_6H_5COC_6H_5$	1.42	0.3235	0.5645
5	Benazalacetone	$C_6H_5CH=CHCOCH_3$	1.36	0.2817	0.4736
6	Dibenzoylmethane	$C_6H_5COCH_2COC_6H_5$	1.34	0.4315	——
7	Ethylideneacetophenone	$C_6H_5COCH=CHCH_3$	1.28	0.2985	0.5471
8	Benzalacetophenone	$C_6H_5CH=CHCOC_6H_5$	1.19	0.2365	0.4456
9	Dibenzalacetone	$C_6H_5CH=CHCOCH=CHC_6H_5$	0.97	0.1899	0.3972
10	Benzil	$C_6H_5COCOC_6H_5$	0.79	0.0000	0.4286
11	trans-Dibenzoylethylene	$C_6H_5COCH=CHCOC_6H_5$	0.63	0.0000	0.4073

a. In alcohol-water mixture containig boric acid (0.2 M), potassium hydroxide (0.17 M) and potassium chloride (0.3 M); pH, 11.3.[8]
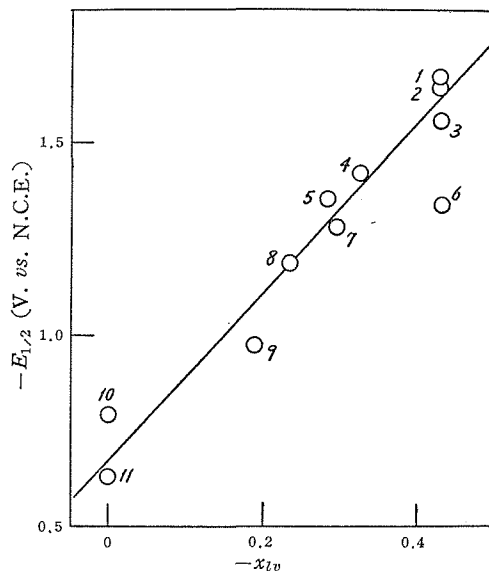

Fig. 1 Linear relationship between $E_{1/2}$ and x_{lv} of aromatic ketones. As to the numbering, see Table 1.

potentials, $E_{1/2}$, determined by Pasternak.[8] Inspection of Table 1 indicates that, as a broad generality, the value of $-x_{lv}$ decreases with the decreasing magnitude of $-E_{1/2}$ i. e., the ketones are more subject to reduction as their lowest vacant levels lie lower. Between $-x_{lv}$ and $-E_{1/2}$ there exists a linear relationship, as shown in Fig. 1.

The plot for dibenzoylmethane, however, deviates largely from the straight line. This will partly be due to that, in the present calculation, the hyperconjugation effect of methylenic group is not taken into account. Dibenzoylmethane is the unique ketone in Table 1 that has a methylenic group intervening between two conjugating groups, i. e. benzoyl groups. Since it is recognized in Table 1 that the calculated value of $-x_{lv}$ becomes smaller as a larger number of π-electrons are concerned with the conjugation, inclusion of pseudo-π-electrons of the methylenic group into calculation will lead us to the smaller value of $-x_{lv}$.* In this sense we recalculated x_{lv} of this compound to obtain the following results:

α_H	β_{OH}	$-x_{lv}$
$\alpha-0.2\beta$	2β	0.3932
$\alpha-0.2\beta$	$\sqrt{3}\beta$	0.3827
$\alpha-0.1\beta$	2β	0.3759
$\alpha-0.1\beta$	$\sqrt{3}\beta$	0.3604

It will thus be apparent that the lowest vacant level of dibenzoylmenthane may lie lower than the height of $\alpha-0.4315\beta$ which was originally obtained with neglect of hyperconjugation effect of the methylenic group, although any quantitative estimation of the energy level may be impossible because of the uncertainty of the energy parameter** concerned with the methylenic group.

In dibenzoylethane, however, such a hyperconjugation effect of the group —CH_2CH_2— would be insignificant; if the two methylenic groups should be incorporated into the π-conjugation, the half-wave potential of the ethane would be far less negative than -1.67 V.

By use of the least square method, $E_{1/2}$ of aromatic ketones listed in Table 1 was related to the value of x_{lv} by the linear equation:

$$E_{1/2}=2.15x_{lv}-0.68 \tag{1}$$

with the correlation coefficient of 0.979, where the data on dibenzoylmethane was not included.

The reduction mechanism of these aromotic was also proposed by Paster-

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* An alternative interpretation may be possible in terms of the *keto-enol* tautomomerism in dibenzoylmethane. A tentative calculation of the value for x_{lv} corresponding to the *enol* form
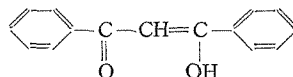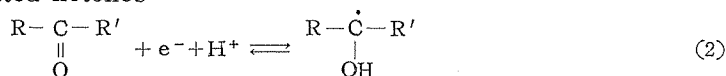
gave -0.4080, which is less negative than -0.4315 listed in Table 1. The integral parameters concerned with the hydroxy-group were assumed as $\alpha_{OH}=\alpha+\beta$ and $\beta_{C-OH}=\beta$.

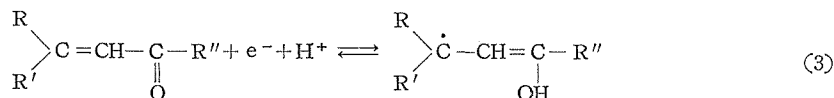** According to Pullman *et al.*[2], the following energy parameters are recommendable for a methylenic group: $\alpha_C=\alpha-0.1\beta$, $\alpha_H=\alpha-0.2\beta$ and $\beta_{OH}=2\beta$.

nak[8] in which the potential-determining step was represented as follows:

i. For saturated ketones

$$R-\underset{\underset{O}{\|}}{C}-R' + e^- + H^+ \rightleftharpoons R-\underset{\underset{OH}{|}}{\overset{\bullet}{C}}-R' \tag{2}$$

ii. For α,β-unsaturated ketones

$$\underset{R'}{\overset{R}{>}}C=CH-\underset{\underset{O}{\|}}{C}-R'' + e^- + H^+ \rightleftharpoons \underset{R'}{\overset{R}{>}}\overset{\bullet}{C}-CH=\underset{\underset{OH}{|}}{C}-R'' \tag{3}$$

However, considering the pH-independency of the reduction potentials at high pH, the potential-determining step of the ketone reduction in an alkalkine medium is possibly represented in general as

$$R-\underset{\underset{O}{\|}}{C}-R' + e^- \rightleftharpoons \left[R-\underset{\underset{O}{\|}}{C}-R' \right]^- , \tag{4}$$

whever R and R' denote either of saturated and unsaturated groups. It may be considered as another possible evidence in support of this mechanism that $E_{1/2}$ of the ketones proved to be linearly related to their x_{lv}, i. e., the relative magnitude of the total π-electronic energy difference between $RR'C=O$ and $[RR'C=O]^-$. Thus, from Equation (1), the empirical parameter β is evaluated* as -2.15 eV, which is in reasonable agreement with -2.23 eV and -2.27 eV obtained in a similar manner regarding unsaturated hydrocarbons[5] and stilbene derivatives,[9] respectively.

From studies on the polarographic reduction of ketones and substituted nitrobenzenes, Shikata and Tachi[10] concluded that organic compounds are more easily reduced as more electronegative groups are substituted. However, the term "electronegative" is not necessarily related to the electron-withdrawing nature of the substituents. As an exmple for this, it may be cited that the half-wave potentials of aromatic hydrocarbons are distributed within a considerable range of voltage despite of the non-existence of polar substituents.[1~6] Thus, a possibility is to be expected that the electrochemical reducibility of the aromatic ketones treated here might be dependent on the nature of their π-conjugation framework itself as well as on the polar effect of the carbonyl groups involved.

In order to make the above situation clear, were calculated the lowest vacant π-electronic energies, x_{lv}^0, belonging to the hydrocarbon analogues of the ketones listed in Table 1. The results are plotted against the corresponding value of x_{lv} in Fig. 2, where it is seen that, aside from benzil and dibenzoylethylene, a linear relationship holds between the two sets of the calculated quantities. It is thus apparent that, as far as the two ketones are put aside from consideration, x_{lv}^0's will also be in a linear correlation with the half-wave reduction potentials of the ketones.**

The magnitude of the polar effect of carbonyl groups in a ketone upon

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* For the one-electron reductions of conjugated compounds, would generally hold the rolationship: $\partial E_{1/2}/\partial x_{lv} = -\beta$ where β is expressed in eV. See, ref. 3.

** The value for $|x_{lv}^0|$ may be regarded as an index for the degree of π-conjugation nature of the molecular frameworks, the degree being larger as the index diminishes.
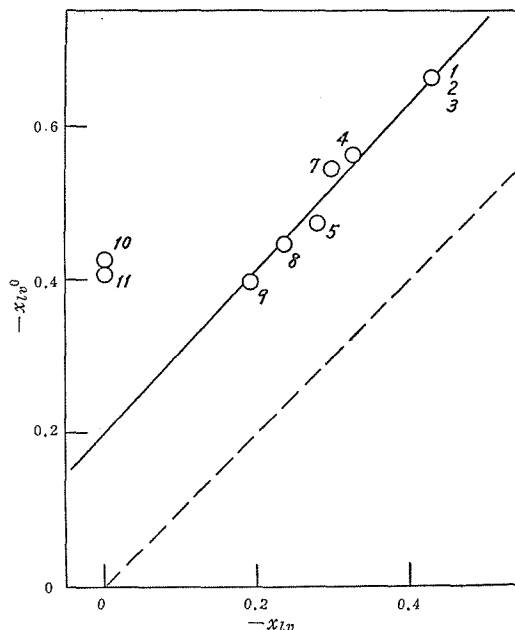
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Fig. 2. Relation between x_{lv} and $x_{lv}{}^0$ of aromatic ketones. The broken line represents the relationship: $x_{lv}=x_{lv}{}^0$. As to the numbering, see Table 1.

the lowest vacant level may be represented by the vertical* distance of the corresponding plot from the broken line: $x_{lv}=x_{lv}{}^0$. The magnitude of the effect in monoketones seems to be essentially constant (0.20 in units of β), while in benzil and dibenzoylethylene, both of which are diketones, the effect is nearly twice as large as $0.20\,\beta$. It will be interesting to note that the polar effects of carbonyl groups have an additive property.

From these findings it is generally suggested that the half-wave potentials of a series of conjugated compounds having the same numbers of equivaent polar groups would simply be related to the value $x_{lv}{}^0$ (conjugative effect) and that the effects of polar groups in conjugated molecules upon their half-wave potentials (polar effect) would be regard as additive in nature. The latter statement coinides with the line of our perturbation calculations of the lowest vacant levels of stilbene derivatives[9] and vinyl monomers.[11]

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* Parallel to the ordinate.