If we let the subscripts "r" and "p" represent reactant and product molecules, then the difference in polarographic half-wave potentials, $\Delta E_{1/2}$, for aqueous and 50% dioxane solutions is

$$\Delta E_{1/2} = \frac{-0.059}{n}\left(\log \frac{A_p}{A_r}\text{ aq.} - \log \frac{A_p}{A_r}\text{ diox.}\right) \quad (11)$$

Substituting C/S values for activities in equation (11) for aqueous solutions and assuming that the solubilities of both reactant and product molecules are large and approximately equal in 50% dioxane solutions, the following expression results

$$\Delta E_{1/2} = -0.059\left(\log \frac{0.3}{4}\text{ aq.} - \log 1\text{ diox.}\right) = 0.07\text{ volt} \quad (12)$$

The experimental value is approximately 0.07 volt in the *p*H range of 2 to 5.

In the case of crotonaldehyde and crotonyl alcohol, the solubilities are 15 g. and 16.6 g. per 100 g. of water, respectively. Thus, the half-wave potentials in 50% dioxane and water should be approximately the same. Experimentally, this was found to be the case.

Relation between Structure and Half-wave Potential.—The second paper in this series[6] deals with the quantitative relation between structure and polarographic half-wave potential, thus only a few qualitative remarks will be made here.

The half-wave potential is dependent only on the structure of the reactant molecule and is independent of the product molecule.[6] Knowing this to be the case, we make the following observations: (1) A positive inductive or permanent polar effect, such as is demonstrated by the methyl group in acetophenone, benzalacetone and crotylideneacetone makes reduction more difficult. (2) Resonance or tautomeric effects in general make reduction easier. This effect is demonstrated by the polyene aldehyde series, CH_3-$(CH{=}CH)_jCHO$, where j is 1 through 5. These compounds and their $E^0_{1/2}$ values are listed in Table I as compounds 3, 8, 9, 10 and 11. It will be noted that the $E^0_{1/2}$ value becomes less negative as j increases from 1 to 5. (3) Some electron rich groups, such as phenyl, when adjacent to the carbonyl group, may be polarized in such a manner that reduction is more difficult than would be predicted on the basis of the tautomeric effect alone. As would be expected from a consideration of the distances involved, this effect is much more pronounced in benzaldehyde than in cinnamaldehyde.

LOS ANGELES, CALIF. RECEIVED JUNE 9, 1951

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENTS OF THE UNIVERSITY OF CALIFORNIA AT LOS ANGELES AND THE UNIVERSITY OF WISCONSIN]

Polarography of Carbonyl Compounds. II. A Theoretical Relationship between the Polarographic Half-wave Potentials and Structures of Carbonyl Compounds

BY DALE M. COULSON AND WILLIAM R. CROWELL

A quantum mechanical relation between the structures and polarographic half-wave potentials of carbonyl compounds is presented.

The previous paper[1] in this series presented polarographic data for a number of conjugated unsaturated carbonyl compounds. In that paper, the effects on the half-wave potential of *p*H, solvent and structure in the carbonyl compound were discussed. The present paper presents a quantum mechanical theory showing the quantitative relationship between the structures and half-wave potentials for the compounds in Table I.

As a starting point, the assumption is made that carbonyl compounds of type I are reduced at the dropping mercury cathode by a one-electron, one-proton process. The evidence for this mechanism

$$\underset{\text{I}}{CH_3{-}(CH{=}CH)_j{-}CHO} + H^+ + e^- \rightleftarrows \underset{\text{II}}{CH_3{-}(CH{=}CH)_j{-}\dot{C}HOH} \quad (1)$$

was presented in the previous paper.[1] At a given *p*H value the half-wave potential for Equation (1) is a function of the structures of the reactant and product molecules only, if all other factors are held constant. For convenience in the previous paper, the $E_{1/2}$ *vs.* *p*H curve for each compound for 50% dioxane solutions was extrapolated to a *p*H of zero. The half-wave potential at a *p*H of zero is designated as $E^0_{1/2}$ in Table I.

In the following discussion, the reactant molecule, I, is treated as an approximately linear harmonic oscillator as Lewis and Calvin[2] did for the prediction of the absorption spectra for the diphenylpolyenes. The product molecule, II, is treated as a free-electron gas model similar to that presented by Kuhn[3] in his prediction of absorption spectra of certain cyanines.

The Reactant Molecule.—The polyene aldehyde I is considered to be composed of $j + 1$ harmonic oscillator units, each unit oscillator being composed of the two π-electrons of the double bond. It is also assumed that the sigma bonding electrons do not make a significant contribution to the oscillator. For the best coupling of these unit oscillators to form an approximately linear oscillator throughout the length of the compound, the configuration should be all *trans*.

As a first approximation, it is assumed that all of the unit oscillators are identical. That is, the ethylenic and carbonyl groups are assumed to act as identical oscillator units. According to Lewis and Calvin,[2] it takes very little perturbation to

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[1] D. M. Coulson and W. R. Crowell, THIS JOURNAL, **74**, 1290 (1952).

[2] G. N. Lewis and M. Calvin, *Chem. Revs.*, **25**, 272 (1939).

[3] H. Kuhn, *Helv. Chim. Acta*, **31**, 1441 (1948); **32**, 2247 (1949).

TABLE I

EXPERIMENTAL AND CALCULATED $E^{\circ}_{1/2}$ VALUES

	Compound	$-E^{\circ}_{1/2}$ *vs.* S.C.E., volts Expt.	$-E^{\circ}_{1/2}$ *vs.* S.C.E., volts Calcd. Eq. (16)	$\Delta E^{\circ}_{1/2}$,[a] volt	Resonance energy,[b] kcal.
1	CH_3—$(CH{=}CH)_1$—CHO	0.867[1,c]	0.866	−0.001	12.1
2	CH_3—$(CH{=}CH)_2$—CHO	.636[c]	.635	− .001	17.4
3	CH_3—$(CH{=}CH)_3$—CHO	.494[e]	.495	.001	20.7
4	CH_3—$(CH{=}CH)_4$—CHO	.393[c]	.398	.005	23.0
5	CH_3—$(CH{=}CH)_5$—CHO	.329[c]	.329	.000	24.5
6	$CH_2{=}CH$—CHOt	.753[1]	(CH_3- = −0.41)	.....	8.2
7	CH_3—$(CH{=}CH)_2$—CO—CH_3	.710[1]	0.713	0.003	15.7
8	Benzaldehyde[d]	.882[1]	(phenyl_1 = 0.54)	.....	5.2
9	Acetophenone	1.011[1]	1.044	0.033	8.8
10	Cinnamaldehyde[d]	0.598[1]	(phenyl_2 = 0.80)	.....	11.7
11	Benzalacetone	.665[1]	0.670	0.005	16.8
12	Mesityl oxide	.96[e]	1.02	0.06	10
13	Acetaldehyde	....	1.394[f]	.....	..
14	Formaldehyde	....	1.109[f]	.....	..

[a] $E^{\circ}_{1/2}$ expt. − $E^{\circ}_{1/2}$ calcd. [b] Consult the paragraph dealing with resonance energies for the meaning of this term. [c] Data of Blout and Fields, private communication and THIS JOURNAL, **70**, 930 (1948). [d] Model compound for a group constant determination. [e] Estimated from Pasternak's data.[4] [f] Not experimentally determinable.

cause all of the units to oscillate in phase. Thus, the classical law

$$\nu_0 = \frac{1}{2\pi}\sqrt{\frac{f}{M}} \qquad (2)$$

is obeyed by the reactant molecule I. In Equation (2), ν_0 is the frequency, f is the restoring force constant and M is the mass of the oscillator. Since

$$\nu_0 = 2E/h \qquad (3)$$

where E is the energy of the π-electron system and h is Planck's constant.

$$E = \frac{h}{4\pi}\sqrt{\frac{f}{M}} \qquad (4)$$

The assumption is made that the restoring force constant, f, along the length of the unsaturated chain is the same as that for each unit of the coupled oscillator. The mass, M, of the whole oscillator is $(2j + 2)m$, where m is the mass of the electron. Thus, the energy of the π-electron system of a polyene aldehyde, as an approximately linear harmonic oscillator, is

$$E = \frac{h}{4\pi}\sqrt{\frac{f}{2m}}\sqrt{\frac{1}{j+1}} \qquad (5)$$

Substituting k for the quantity $\frac{h}{4\pi}\sqrt{\frac{f}{2m}}$

$$E_{n'} = k\sqrt{\frac{1}{j+1}} = k\sqrt{\frac{1}{n'}} \qquad (6)$$

where n' is the total number of double bonds in the polyene aldehyde molecule. Each double bond is considered to be a unit oscillator rather than the individual electron, since in the ground state of the molecule the electrons have paired spins in accordance with the Pauli exclusion principle. Thus, they act in pairs and each pair occupies a given quantum level.

The Product Molecule.—The product molecule, II, resulting from the polarographic reduction of I, has an odd number of π-electrons and is therefore a free-radical. It was found by Kuhn[3] that certain dye molecules containing chains of π-electrons could be treated as though the π-electrons constituted a "free-electron-gas" in a "one-dimensional box." It is reasonable to assume that the "odd" (unpaired electron) may be found any place along the unsaturated chain, a condition that makes the analogy between the free radical and a free-electron gas quite reasonable. The "one-dimensional box" is the atomic skeleton of the molecule. The π-electrons occupy the lowest available N quantum levels, one in each level.

For a particle in a one-dimensional box the potential function

$$V(x) = 0 \text{ if } 0 < x < a \qquad (7)$$

and

$$V(x) = \infty \text{ if } x < 0 \text{ or } x > a \qquad (8)$$

where a is the length of the box and x is the position of the particle along the length of the box. The Schroedinger wave equation for the particle in a one-dimensional box is

$$\frac{d^2\psi}{dx^2} + 8\frac{\pi^2 m}{h^2}[E - V(x)]\psi = 0 \qquad (9)$$

where m is the mass of the particle, h is Planck's constant, and E is the energy of the particle. In the region $0<x<a$, the general solution of equation (9) is a sine wave with an integral number of nodes in the box. Introducing the quantum number, N, as the number of nodes, the wave length becomes $2a/N$. The normalized ψ-function is given by

$$\psi = \sqrt{\frac{2}{a}}\sin\frac{\pi N x}{a} \qquad (10)$$

where $N = 1, 2, 3, \ldots$, and the energy of the N'th quantum level, E_N, is given by

$$E_N = \left[\frac{h^2}{8M}\right]\frac{N^2}{a^2} = k'\frac{N^2}{a^2} \qquad (11)$$

If we let M represent the mass of an electron and a the length of the unsaturated chain we have

$$E_N = k'\frac{N^2}{L^2(2j+3)^2} = k'\frac{N^2}{N^2L^2} = \frac{k'}{L^2} \qquad (12)$$

where k' is equal to $h^2/8M$, a is equal to $(2j + 3)L$, $2j + 3$ is equal to N and L is the length of a methine group. The total length of the unsaturated chain is one bond length greater than the number of atoms in it. Likewise there are $2j + 3$ electrons in the free-electron gas since two nonbonding oxygen electrons are included. Thus the ratio $N^2/(2j + 3)^2$ is unity.

Calculation of the Half-wave Potential.—The difference between the energy levels of the product and reactant molecules at unit hydrogen ion activity is equal to the polarographic half-wave potential on an "absolute" potential scale $E^\circ_{1/2}$ for the carbonyl compounds under consideration. Thus

$$E^\circ_{1/2}{}'' = E_N - E_{n'} = k'/L^2 - k\sqrt{1/n'} \qquad (13)$$

There are constant terms in equation (13) that are unknown, therefore this equation is not useful as such. However, if an arbitrary zero point on the potential scale is chosen, this equation may be used to calculate the half-wave potentials referred to this arbitrary zero point. For convenience the potential of the S.C.E. will be taken as the zero point. The half-wave potential with reference to the S.C.E. becomes

$$E^\circ_{1/2} = k'' - k\sqrt{1/n'} \qquad (14)$$

where k'' is the constant term in equation (13) plus the "absolute" potential of the S.C.E. Figure 1 is a graph of $E^\circ_{1/2}$ values *vs.* n' or $\sqrt{1/n'}$ for the first five compounds in Table I. The values of k'' and k from the $E^\circ_{1/2}$ *vs.* $\sqrt{1/n'}$ plot are $+0.406$ and $+1.800$, respectively. Thus, the relation between $E^\circ_{1/2}$ and n' becomes

$$E^\circ_{1/2} = (0.406 - 1.800/\sqrt{n'}) \text{ volts } vs. \text{ S.C.E.} \qquad (15)$$

for compounds 1 through 5 in Table I. The disagreement between the calculated and experimental $E^\circ_{1/2}$ values is $\Delta E^\circ_{1/2}$ in Table I.

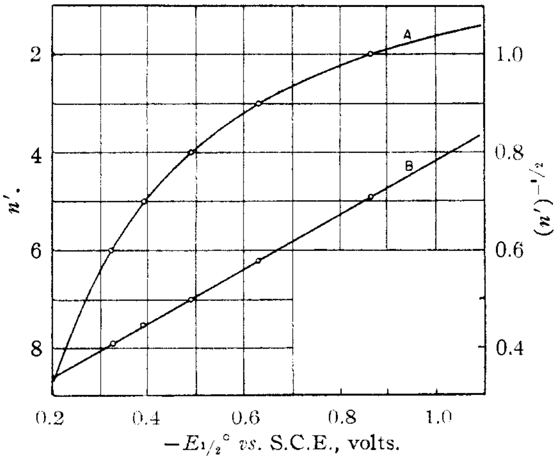


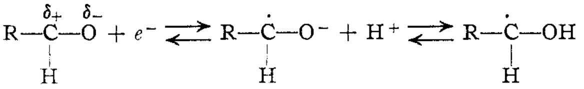
Fig. 1.—A, $E_{1/2}{}^\circ$ *vs.* n'; B, $E_{1/2}{}^\circ$ *vs.* $(n')^{-1/2}$.

Generalization of the Theory.—Equation (15) is applicable only to the polyene aldehydes. However, if $\sum_{i}^{0} C_i$ is substituted for n', the equation becomes quite general.

$$E^\circ_{1/2} = (0.406 - 1.800/\sqrt{\Sigma C_i}) \text{ volt } vs. \text{ S.C.E.} \qquad (16)$$

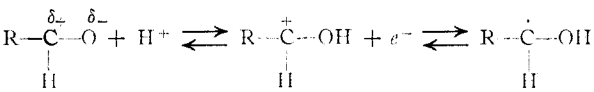
where C_i is a group constant representative of the i'th group in the molecule. Equation (16) is generally applicable to carbonyl compounds reduced by the one-electron, one-proton process.

The reduction mechanism involves the addition of a proton to a negatively charged oxygen atom and an electron to a positively charged hydrocarbon part of the molecule. This process may be formulated as a stepwise process



$$\underset{\text{III}}{\mathrm{R{-}\underset{\underset{H}{|}}{\overset{\delta_+}{C}}{-}\overset{\delta_-}{O}}} + e^- \rightleftharpoons \underset{\text{IV}}{\mathrm{R{-}\underset{\underset{H}{|}}{\dot{C}}{-}O^-}} + \mathrm{H^+} \rightleftharpoons \underset{\text{V}}{\mathrm{R{-}\underset{\underset{H}{|}}{\dot{C}}{-}OH}} \qquad (17)$$

or



$$\underset{\text{III}}{\mathrm{R{-}\underset{\underset{H}{|}}{\overset{\delta_+}{C}}{-}\overset{\delta_-}{O}}} + \mathrm{H^+} \rightleftharpoons \underset{\text{VI}}{\mathrm{R{-}\underset{\underset{H}{|}}{\overset{+}{C}}{-}OH}} + e^- \rightleftharpoons \underset{\text{V}}{\mathrm{R{-}\underset{\underset{H}{|}}{\dot{C}}{-}OH}} \qquad (18)$$

which may be summarized by Equation (1).

On the basis of Equations (17) and (18) it is obvious that the reduction potential depends on two factors: (1) the relative ease with which an electron may be added to the hydrocarbon part of the molecule; (2) the relative ease with which the oxygen atom may be protonated. These two steps must, however, be considered as a concerted process. The first step in Equation (18) is merely an acid–base reaction which can be studied independently. Such an investigation is being carried on at present and will be reported in a later paper. The potential associated with the second step in reaction (18) shows the relative electron density on the hydrocarbon portion of the protonated molecule and is also subject to independent measurements. Assuming that the free-electron gas picture is representative of the product molecule, V, the potential of the second step in reaction (18) is a measure of the sum of the inductive effects and independent of the tautomeric effects. This was shown to be the case by Equation (12), in which the N'th energy level was not a function of the length of the unsaturated portion of the molecule.

In the present paper no attempt will be made to delineate between I- and T-effects. The manner in which the group effects and group constants were derived is not in itself sensitive to the type of effect, but rather merely integrates all of the effects into a single constant characteristic of the group for Equation (1) at a given pH value. However, it is quite clear that the effect of a methyl group is primarily inductive.

Determination of Group Constants.—The summation of group constants for a given molecule may be determined graphically or by the use of Equation (19).

$$\Sigma C_i = \left[\frac{1.800}{0.406 - E^\circ_{1/2}}\right]^2 \qquad (19)$$

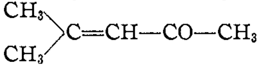
On this basis the ΣC_i for crotonaldehyde is 2.00 by definition. The ΣC_i for acrolein with a $E^\circ_{1/2}$ of -0.753 volt is 2.41. Thus if hydrogen is assigned a value of zero the methyl group constant becomes -0.41 and the carbonyl group constant becomes $+1.41$. From Fig. 1 or Equation (19) the ΣC_i for benzaldehyde is 1.95 and C_{phenyl} is $+0.54$. Due to the polarizability of the phenyl group, the

T-effect is partially canceled in benzaldehyde. Thus, C_{phenyl} is different in cinnamaldehyde than in benzaldehyde. The ΣC_i for cinnamaldehyde is 3.21. Therefore, the C_{phenyl} not adjacent to carbonyl is +0.80. Using the group constants summarized in Table II, $E^\circ_{1/2}$ values may be calculated for other compounds composed of the groups for which C_i values are known. For acetophenone the ΣC_i is 0.54 for the phenyl group plus 1.41 for the carbonyl group minus 0.41 for the methyl group or 1.54. Substituting this value in Equation (16) or consulting Fig. 1, $E^\circ_{1/2}$ calcd. is −1.044 volt *vs.* S.C.E. Similar calculations were made for the remainder of the compounds in Table I. The excellent agreement between the experimental and calculated $E^\circ_{1/2}$ values is shown in the fourth column of Table I and may be taken as evidence that the theory is essentially correct.

TABLE II

GROUP CONSTANTS

—CH=CH—	1.000
>C=O	1.41
H—	0.000
CH_3—	−0.41
Phenyl₁ adjacent to carbonyl	0.54
Phenyl₂ removed from carbonyl by one double bond	0.80

Mesityl oxide,  $(CH_3)_2C{=}CH{-}CO{-}CH_3$ has two methyl groups on a single carbon atom, thus the inductive effect of each one is partially canceled out by the other. Assuming bond angles of 120°, the vectorial effect of the two methyl groups is simply

$$2(-0.41 \sin 30°) = 2(-0.41 \times 1/2) = -0.41 \quad (20)$$

This is probably too large since the bond angle between the methyl groups is probably somewhat greater than 120° due to electrostatic repulsion between the methyl groups and attraction between the more electronegative oxygen atom and each of the methyl groups. On the basis of this oversimplified picture, the calculated $E^\circ_{1/2}$ for mesityl oxide is −1.02 volts. The experimental value is −0.96 volt on the basis of Pasternak's[4] data for 48% ethanol. This agreement is undoubtedly within the uncertainty of the experimental value. If the group constants are simply added without considering this cross-conjugation effect, the predicted $E^\circ_{1/2}$ value is −1.24 volts.

Resonance Energies.—Formaldehyde and acetaldehyde are taken as reference compounds since they are the first members of the aldehyde and methyl ketone series. If a phenyl group is substituted for one of the hydrogen atoms in formaldehyde, benzaldehyde results. The difference between the formaldehyde and benzaldehyde half-wave potentials is 0.227 volt, which corresponds to an energy of 5.2 kcal. Therefore there is 5.2 kcal. resonance energy between the benzene ring and the carbonyl group. Similar calculations for the other compounds give the resonance energies listed in the last column of Table I. The polyene aldehydes, crotylideneacetone, acetophenone, benzalacetone and mesityl oxide are considered to be derivatives of acetaldehyde. The remainder of the compounds in Table I are taken as derivatives of formaldehyde.

These resonance energies were derived from the data for polarographic reductions in 50% dioxane solutions and may not be exact for the gaseous, pure liquid, or solid state of the compound. As noted in the previous paper,[1] different results are obtained for pure aqueous solutions due to the low solubilities of some of the organic compounds.

[4] R. Pasternak, *Helv. chim. Acta*, **31**, 753 (1948).

LOS ANGELES, CALIF. RECEIVED JUNE 9, 1951

[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE SPRAGUE ELECTRIC COMPANY]

Neighboring Group Interaction in the Reduction of 2,2'-Dinitro-4,4'-bis-(trifluoromethyl)-biphenyl

BY SIDNEY D. ROSS AND IRVING KUNTZ

The sodium sulfide reduction of 2,2'-dinitro-4,4'-bis-(trifluoromethyl)-biphenyl proceeds stepwise to yield 2,2'-dinitroso-4,4'-bis-(trifluoromethyl)-biphenyl, 3,8-bis-(trifluoromethyl)-benzo(c)cinnoline-5-oxide and 3,8-bis-(trifluoromethyl)-benzo(c)cinnoline. Catalytic hydrogenation results in a mixture containing 2,2'-diamino-4,4'-bis-(trifluoromethyl)-biphenyl in addition to the above benzo(c)cinnoline and benzo(c)cinnoline oxide. The mechanisms of these reductions are discussed. The deamination reaction on 2,2'-diamino-4,4'-bis-(trifluoromethyl)-biphenyl yields either the benzo(c)cinnoline or a mixture of the benzo(c)cinnoline and 4,4'-bis-(trifluoromethyl)-biphenyl, depending on the reaction conditions.

In a series of excellent papers Winstein, *et al.*,[1] have thoroughly dealt with the role of neighboring groups in replacement reactions. On low temperature catalytic hydrogenation of 2,2'-dinitro-4,4'-bis-(trifluoromethyl)-biphenyl, I, we obtained products which indicated a comparable interaction of either the 2,2'-nitro groups or of reduction products derived therefrom. To elucidate the nature of this interaction, we have studied both the catalytic and chemical reduction of I.

With tin and hydrochloric acid, I, prepared by modification of the procedure of Bradsher and Bond,[2] is smoothly reduced to 2,2'-diamino-4,4'-bis-(trifluoromethyl)-biphenyl (II). With sodium sulfide and alkali the major products formed are 3,8-bis-(trifluoromethyl)-benzo(c)cinnoline (III), 3,8-bis(trifluoromethyl)-benzo(c)cinnoline-5-oxide (IV) and 3,8-bis-(trifluoromethyl)-benzo(c)cinno-

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[1] S. Winstein and E. Grunwald, THIS JOURNAL, **70**, 828 (1948). This paper presents a general theory of neighboring groups and reactivity and contains extensive references to the detailed work in this field.

[2] C. K. Bradsher and J. B. Bond, *ibid.*, **71**, 2659 (1949).