due to van der Waals forces or to specific valency forces such as hydrogen bonding, E^*_A might be expected to be of greater magnitude than E^*_B for a liquid B in which a lesser degree of ordering obtains. Since entropy is related to structural order, the differential entropies of dilution ($\bar{S}_1 - \bar{S}_1^0$) may be interpreted as indicating the strengthening or weakening effects of solute amino acids on the quasi-solid structure of water. $\bar{S}_1 - \bar{S}_1^0$ as a function of molality concentration may be expressed by an equation of the form[13]

$$\bar{S}_1 - \bar{S}_1^0 = km^2$$

Only in the case of glycine does k in the above expression have a positive value, *i.e.*, glycine weakens the structure of water.

Lyons and Thomas[27] have discussed a number of properties of aqueous solutions of glycine in terms of the structure-weakening effect of glycine on the solvent.

If the assumption is made that the Arrhenius equation is valid over a short temperature range, say 25–35°, $E^*_{H_2O}$ may be calculated providing that reliable values are known for the viscosities of water at these temperatures. In view of the discussion above

$$\Delta E^* = E^*_{H_2O} - E^*_{soln}$$

should parallel in sign the differential entropies of dilution.

Values for the calculated quantity ΔE^*, the differential activation energy for viscous flow, are tabulated in Table V for the concentration range for which the differential entropies of dilution have been computed, and are shown plotted in Fig. 1. Of the five amino acids investigated in this work, only for glycine has ΔE^* been found to have a positive value.

The quantity ΔE^* is fairly well expressed as a function of concentration by the equation

$$\Delta E^* = Am + Bm^2 + Cm^3 + \ldots$$

Values for the constants in the above expression are given in Table VI.

TABLE VI

CONSTANTS FOR THE EQUATION: $\Delta E^* = Am + Bm^2 + Cm^3 + \ldots$

Amino acid	*A*	*B*	*C*	*D*
Glycine	47.4	12.92	0.288	0
α-Alanine	−285.6	43.15	0.876	0
β-Alanine	−147.8	64.78	−17.05	1.30
α-Amino-*i*-butyric	−616	137	0	0
α-Amino-*n*-valeric	−544	−1.62	0	0

In Fig. 1 it will be noted that the relative positions of the curves representing ΔE^* correspond to the relative positions of the curves representing $\bar{S}_1 - \bar{S}_1^0$; *e.g.*, at the higher concentrations the curves for β-alanine lie above those for α-alanine, and both curves for these two acids lie intermediate between the corresponding curves for glycine and the curves for both α-amino-*i*-butyric acid and α-amino-*n*-valeric acid. Aside from the agreement in sign, strict parallelism between ΔE^* and $\bar{S}_1 - \bar{S}_1^0$ does not exist for the entire range of concentration considered. It will be noted, for example, that for concentrations up to slightly beyond 0.4 molal, $\bar{S}_1 - \bar{S}_1^0$ for α-alanine is greater than for β-alanine whereas the opposite is true for ΔE^*. It will also be noted that at all concentrations the spread between ΔE^* for α- and β-alanine is much greater than the spread between ΔE^* for α-amino-*i*-butyric acid and α-amino-*n*-valeric acid whereas again the opposite is true for $\bar{S}_1 - \bar{S}_1^0$. In general, however, Fig. 1 indicates the existence of the correlation suggested.

Correlation of ΔE^* with $\bar{S}_1 - \bar{S}_1^0$ calculated from heats of dilution at 25° might be more demonstrable if viscosity data were available at 20 and 30°, and if, for amino acids as yet uninvestigated, both ΔE^* and $\bar{S}_1 - \bar{S}_1^0$ be found to have positive values.

PITTSBURGH, PENNA. RECEIVED AUGUST 13, 1951

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

Polarography of Carbonyl Compounds. I. Linear Unsaturated Conjugated Molecules

BY DALE M. COULSON[1] AND WILLIAM R. CROWELL

Polarographic data for benzaldehyde, acetophenone, crotonaldehyde, acrolein, cinnamaldehyde, benzalacetone and crotylidene acetone in well buffered aqueous and 50% dioxane solution are summarized in this paper.[2] The effects of *p*H, solvent, liquid junction potentials and ionic strength on the half-wave potentials are discussed. A qualitative statement of the effect of structure in the organic molecule on the half-wave potential is made.

Recently considerable interest has been shown in the relation between the structures and polarographic half-wave potentials of unsaturated aldehydes and ketones. Fields and Blout[3,4] made an extensive study of the polyene aldehydes, CH_3—$(CH{=}CH)_j$—CHO, where "*j*" was 1 through 5. They used 50% dioxane as the solvent and several buffers that give effective buffering in the *p*H ranges for which each buffer was used. A summary of their data is included in Table I. Pasternak[5] studied a number of aryl- and alkyl-unsaturated aldehydes and ketones using 48% ethanol as the solvent. He also used buffering systems that were effective in their respective *p*H ranges. Since these two sets of data were for different solvents, in order to correlate these data

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[1] Shell Oil Company, Martinez, California. Most of the data on which this paper is based were taken from a thesis presented by Dale M. Coulson for the degree of Ph.D. at the University of California at Los Angeles, June 1, 1950.

[2] For more complete experimental data order Document 3407 from American Documentation Institute, 1719 N Street, N.W., Washington 6, D. C., remitting $1.00 for microfilm (images 1 inch high on standard 35 mm. motion picture film) or $1.20 for photocopies (6 × 8 inches) readable without optical aid.

[3] M. Fields and E. R. Blout, THIS JOURNAL, **70**, 930 (1948).

[4] M. Fields and E. R. Blout, private communication.

[5] R. Pasternak, *Helv. Chim. Acta*, **31**, 753 (1948).

TABLE I

SUMMARY OF POLAROGRAPHIC DATA

Compound	Solvent	$-E^{\circ}_{1/2}$ *vs.* S.C.E., volt	Slope. B	$i_d/Cm^{2/3}t^{1/6}$
Benzaldehyde	H_2O	0.800	0.066	1.75
Benzaldehyde	48% alc.[a]	0.86	0.06	..
Benzaldehyde	50% diox.	0.882	.063	1.43
Acetophenone	H_2O	0.949	.065	1.63
Acetophenone	48% alc.[a]	1.00	.06	..
Acetophenone	50% diox.	1.011	.054	1.27
Crotonaldehyde	H_2O	0.867	.062	1.78
	50% diox.[b]	.867	.059	1.43
Acrolein	H_2O	.743	.061	1.3
Acrolein	50% diox.	.753	.061	1.3
Cinnamaldehyde	H_2O	.470[c]	.065	1.64
Cinnamaldehyde	50% diox.	.598	.064	1.32
Benzalacetone	H_2O	.539[c]	.070	2.0
	48% alc.[a]	.64	.06	..
	50% diox.	.665	.064	1.42
Crotylidene acetone	50% diox.	.710	.059	1.0
2,4-Hexadienal[b]	50% diox.	.636	.06	1.39[d]
2,4,6-Octatrienal[b]	50% diox.	.494	.06	1.37[d]
2,4,6,8-Decatetraenal[b]	50% diox.	.393	.06	1.25[d]
2,4,6,8,10-Dodecapentaenal[b]	50% diox.	.329	.06	1.24[d]

[a] Data of Pasternak, ref. (5). [b] The $E^{\circ}_{1/2}$ value based on Fields and Blout's data for crotonaldehyde was 0.029 volt more positive than on the basis of the present work. Thus a correction of −0.029 volt was added to each of the $E^{\circ}_{1/2}$ values based on the data of Fields and Blout for the last four compounds in Table I. [c] $E^{\circ}_{1/2}$ values at 8×10^{-5} M or less. [d] Calculated from diffusion coefficients based on Fields and Blout's work.

it was felt that the effect of solvent on the half-wave potential should be studied.

The present paper reports polarographic results for benzaldehyde, acetophenone, crotonaldehyde, cinnamaldehyde, acrolein and benzalacetone in both aqueous and 50% dioxane solutions and crotylidene acetone in 50% dioxane. It is limited to a critical discussion of the experimental method and results, and a few qualitative observations on the effect of structure in the carbonyl compound and solvent on the polarographic half-wave potential. In the next paper[6] of this series a quantum mechanical theory will be presented showing a quantitative relationship between the structures and half-wave potentials of a number of carbonyl compounds.

Experimental Part

Polarograph.—The polarographic measurements were made with a Fisher Elecdropode, the current and voltage scales of which were calibrated by means of a Leeds and Northrup Student's Potentiometer. In order to make the current scales read directly in multiples or submultiples of microamperes per division, suitable resistances were added in series with the galvanometer such that each scale read directly in microamperes. The resistances in the potentiometer circuit of the Elecdropode were so adjusted that no calibration corrections were necessary. The polarograms were obtained by plotting the average current readings in microamperes *vs.* the potential at 25 millivolt increments. The capillary constant, m, the mass of mercury flowing through the capillary per second was 1.295 mg. The drop time was recorded at the top of each wave.

***p*H Meter.**—A Beckman model H *p*H meter was used to determine the *p*H of the solutions in the polarographic cell. For a few of the 50% dioxane solutions, *p*H measurements were made with both the glass and hydrogen electrodes. In both cases, the reference electrode was an aqueous saturated calomel electrode.

Polarographic Cell.—The polarographic cell was a 25 ml. cylindrical vessel with a side arm through which a glass electrode was inserted. Thus, *p*H measurements could be made without removing the dropping electrode assembly from the cell. The dropping electrode, a salt bridge leading to a large saturated calomel electrode, a gas inlet, a gas outlet and the tip of a 10-ml. ammonium hydroxide buret were inserted through holes in a rubber stopper in the cell. A Beckman saturated calomel electrode dipping into the large saturated calomel electrode was used to check the potential of the latter and for the *p*H measurements. The salt bridge consisted of an inverted U-shaped glass tube with a separatory funnel at the top in the middle of the bend and sintered glass filters at each end. The arm making connection with the saturated calomel electrode was filled with a 2% agar–agar solution saturated with potassium chloride. The other arm which made contact with the solution in the cell was filled with a saturated solution of potassium chloride as was the separatory funnel. After each series of determinations, the solution in this arm was replaced with fresh solution from the separatory funnel. The purpose of this procedure was to prevent the saturated calomel electrode from becoming poisoned with organic materials diffusing over from the polarographic cell.

Hydrogen Electrode.—The hydrogen electrode consisted of a large platinized platinum foil immersed in the aqueous or 50% dioxane buffer solution with hydrogen gas bubbling through it. In the polarographic measurements using the hydrogen electrode as a reference electrode, the other side of the cell, in which the dropping electrode was inserted, contained a solution of the carbonyl compound in the same buffer solution as was in the hydrogen electrode. The agar plug between the two half-cells was saturated with potassium chloride

Aqueous Buffer Solutions.—A stock buffer solution 0.1 *f* in potassium chloride, 0.1 *f* in acetic acid and 0.1 *f* in orthophosphoric acid was used. This solution has a *p*H value of 1.6. Solutions of the carbonyl compounds in this medium were placed in the polarographic cell and the desired *p*H values were obtained by adding 15 *f* ammonium hydroxide dropwise from the buret.

50% Dioxane Solutions.—A stock aqueous buffer solution that was 0.2 *f* in potassium chloride, 0.2 *f* in acetic acid and 0.2 *f* in orthophosphoric acid was added to an equal volume of dioxane. Solutions of carbonyl compounds in this medium were placed in the polarographic cell and the desired *p*H values were obtained by dropwise addition of concentrated ammonium hydroxide solution that contained equal volumes of water and dioxane.

Polarographic Determinations.—The temperature of the solutions was maintained at 25.0 ± 0.1° by means of a thermostatically controlled water-bath. In each case, oxygen was removed from the solution by bubbling nitrogen through it for 15 to 20 minutes. The *p*H was measured, the polarograms recorded and the *p*H rechecked. A few drops of concentrated ammonia solution was added, nitrogen bubbled again for 15 to 20 minutes, and the *p*H again measured. The procedure was repeated until sufficient data were obtained over a range of *p*H values to determine the effect of *p*H on the polarographic half-wave potential.

Reagents.—The dioxane was refluxed over sodium for several hours and then distilled from sodium. This procedure yielded a product that was polarographically inactive in the range of potentials studied. The carbonyl compounds had the following boiling or melting points in °C.

Benzaldehyde,	26.3 (1 mm.)
Crotonaldehyde,	100 (1 atm.)
Cinnamaldehyde,	128.5 (26 mm.)
Crotylidene acetone	58–60 (6 mm.)
Acetophenone	27 (1 mm.)
Acrolein	52 (1 atm.)
Benzalacetone	41–42

The inorganic reagents were all C.P. grade.

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(6) D. M. Coulson and W. R. Crowell, THIS JOURNAL, **74**, 1294 (1952).

Results and Discussion

***p*H Measurements and Liquid Junction Potentials.**—If the liquid junction potential between aqueous saturated potassium chloride solution and 0.1 *M* potassium chloride in 50% dioxane is greater than a few millivolts, both hydrogen and glass electrode *p*H values may be somewhat in error.

The potential of the cell

$$\text{Hg}|\text{Hg}_2\text{Cl}_2\text{, KCl (sat. aq.)}|\text{KCl (sat., 50\% diox.) Hg}_2\text{Cl}_2|\text{Hg} \quad (1)$$

was found to be zero, therefore the liquid junction potential of this cell is zero. A saturated solution of potassium chloride in 50% dioxane is 1.2 *M*. The junction potential for the liquid junction

$$\text{KCl (sat., 50\% diox.)}|\text{KCl (0.1 } M\text{, 50\% diox.)} \quad (2)$$

must then be practically the same as for the liquid junction

$$\text{KCl (sat., aq.)}|\text{KCl (0.1 } M\text{, 50 diox.)} \quad (3)$$

The junction potential for the liquid junction

$$\text{KCl (1 } M\text{, aq.)}|\text{KCl (0.1 } M\text{, aq.)} \quad (4)$$

is less than 0.002 volt.[7] The junction potential for (3) is therefore probably less than 0.002 volt also. Thus, the *p*H values measured with a hydrogen electrode and an aqueous saturated calomel electrode are representative of the hydrogen ion activities. The hydrogen electrode is well behaved in 50% dioxane solutions. The potentials become constant as soon as the electrode becomes saturated with hydrogen gas and are reproducible within 0.001 volt.

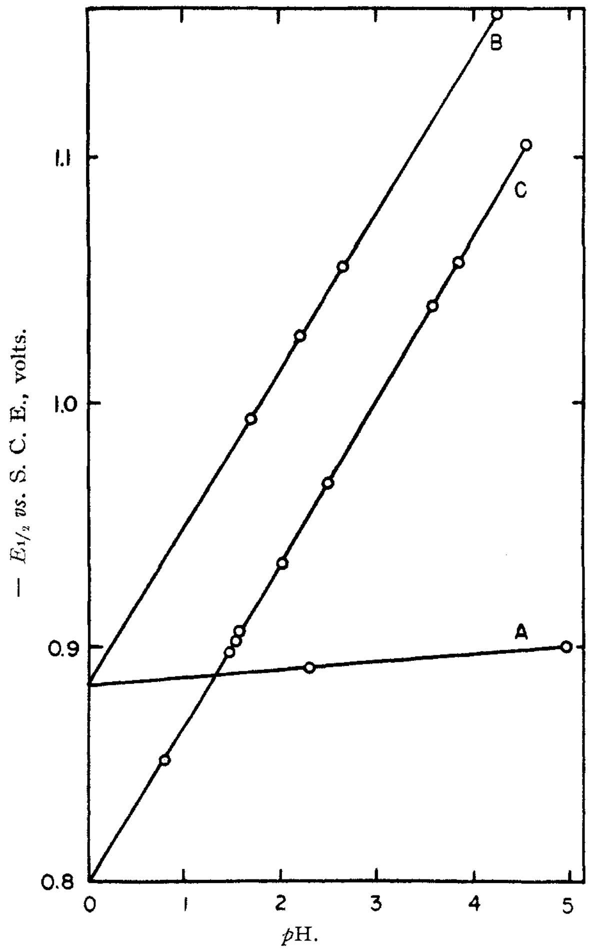

Fig. 1.—Benzaldehyde—$E_{1/2}$ *vs.* *p*H curves: A, $E_{1/2}$ *vs.* hydrogen electrode −0.246 volt, 50% dioxane; B, $E_{1/2}$ *vs.* S.C.E., 50% dioxane; C, $E_{1/2}$ *vs.* S.C.E., aqueous solutions.

In the *p*H range of 2 to 5, the glass electrode values were 0.23 *p*H unit higher than the hydrogen electrode values. When polarograms on crotonaldehyde, acrolein and benzaldehyde were run using a hydrogen electrode as the reference electrode, the half-wave potentials at the various *p*H values were essentially the same for each compound. This was to be expected since both electrode reactions involve equal numbers of electrons and protons. Thus, a small error in the measurement of *p*H would not measurably affect the half-wave potential, since the hydrogen ion activities in the hydrogen electrode and the dropping mercury cathode compartment were identical in each experiment. For benzaldehyde, the curve formed by plotting the hydrogen electrode half-wave potential minus 0.246 v.[8] *vs.* *p*H measured with the hydrogen electrode is the A-curve in Fig. 1. Curve B, formed by plotting half-wave potentials *vs.* S.C.E. against corrected glass electrode *p*H values for the 50% dioxane solutions, intersects the A-curve at a *p*H value of zero. If the correction had not been made the intersection would be at a *p*H value of 0.23, but at essentially the same potential. Similar results are obtained for crotonaldehyde, acrolein and acetophenone. Thus, it is obvious that there was an error of 0.23 *p*H unit in the glass electrode *p*H values, that the liquid junction potentials are negligible, and that the hydrogen electrode *p*H values are correct.

Buffers.—In order that a buffer be effective, the *p*H or *p*OH of the solution should be within the range of *pK* ± 1 for acids or bases, respectively. The supporting electrolyte used in the present work contained phosphoric acid which has *pK* values of 2 and 7, acetic acid, *pK* 5 and ammonium hydroxide, *pK* 5. This system adequately covers the *p*H range of 1.3 to 10 in aqueous solutions and 2 to 10 in 50% dioxane solutions.

Crowell and Kelley[9] report that changing the ionic strength from 0.1 to 1.0 in the *p*H range of 2 to 5 has no appreciable effect on the half-wave potential of benzaldehyde. This fact lends support to the free-radical reduction mechanism, discussed elsewhere in this paper, since the activity coefficients of both reactant and product molecules would be affected in the same manner if they are both uncharged molecules. However, if the product molecule were an ion, and the reactant molecule uncharged, the half-wave potential would undoubtedly shift appreciably with changing ionic strength as is the case with cadmium.[10] Thus, the fact that the ionic strength increases with *p*H

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[7] G. N. Lewis and M. Randall, "Thermodynamics," McGraw-Hill Book Co., Inc., New York, N. Y., 1923, p. 406.

[8] The −0.246 volt is the potential difference between the normal hydrogen and saturated calomel electrodes.

[9] W. R. Crowell and K. Kelley, private communication.

[10] D. D. DeFord and D. L. Anderson, THIS JOURNAL, **72**, 3918 (1950).

has no appreciable effect on the half-wave potentials of the compounds mentioned in the present paper.

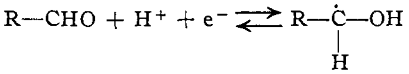
Polarographic Results

Table I is a summary[2] of polarographic data for a number of carbonyl compounds studied in this Laboratory and by others in three different solvents. Only data taken under ideal conditions of buffering have been considered. The half-wave potential of the first one-electron wave at any pH value at which it is observed is given by equation (5).

$$E_{1/2} = E^{\circ}_{1/2} - p\mathrm{H}\,(B) \qquad (5)$$

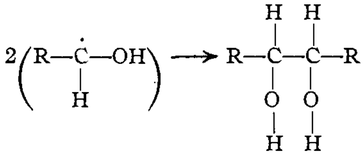
By substituting the appropriate $E^{\circ}_{1/2}$, pH and B values from Table I, the $E_{1/2}$ value may be calculated. The letter "B" in equation (5) is the slope of the $E_{1/2}$ *vs.* pH curve for the individual compounds. Equation (5) is applicable only in the pH range within which the one-electron, one-proton process is observed. For all of the compounds in the present study, it is applicable for pH values of 5 or less. In some cases the pH range may extend as high as 10.

The number of equivalents per mole, n, determined by plotting $\log i/(i_d - i)$ *vs.* $E_{d.e.}$ was found to be 1.0 ± 0.1 for each of the compounds in solutions with pH values of 5 or less. On the basis of these data and the work of Pasternak,[5] the electrode reaction is assumed to be a reversible one-electron, one-proton process which may be formulated



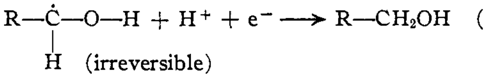
$$\mathrm{R{-}CHO} + \mathrm{H^+} + e^- \rightleftarrows \mathrm{R{-}\underset{H}{\overset{\cdot}{C}}{-}OH} \qquad (6)$$

This may be followed by the irreversible process



$$2\left(\mathrm{R{-}\underset{H}{\overset{\cdot}{C}}{-}OH}\right) \longrightarrow \mathrm{R{-}\underset{\underset{H}{O}}{\overset{H}{C}}{-}\underset{\underset{H}{O}}{\overset{H}{C}}{-}R} \qquad (7)$$

Pasternak[5] found that benzaldehyde, reduced at a large pool of mercury at considerably higher concentrations than were used in this work, gave the product shown in equation (7). The electrode process for the second wave is



$$\mathrm{R{-}\underset{H}{\overset{\cdot}{C}}{-}O{-}H} + \mathrm{H^+} + e^- \longrightarrow \mathrm{R{-}CH_2OH} \qquad (8)$$

(irreversible)

For benzaldehyde in solutions with pH values of 5 or less, the $E_{1/2}$ value of the second one-electron wave is nearly constant at −1.20 volts *vs.* S.C.E. Since the half-wave potential for the second wave is independent of pH, the process is probably one in which the electron enters first, followed by an irreversible extraction of a proton from the solvent. At pH values greater than 5 only one apparently irreversible wave appears. It is approximately twice as high as each of the waves previously described and is the result of the two-electron, two-proton process

$$\mathrm{R{-}CHO} + 2\mathrm{H^+} + 2e^- \longrightarrow \mathrm{RCH_2OH} \qquad (9)$$

The slope of the $E_{1/2}$ *vs.* pH curve is 0.043 ± 0.002 volt per pH unit between the pH values of 5 and 10. The $E_{1/2}$ value for this two-electron wave in aqueous solutions with a pH value of 6.33 at 2.0×10^{-4} M in benzaldehyde is −1.237 volt *vs.* S.C.E. The corresponding diffusion current constant is 3.50.

The general characteristics of the polarograms of the other compounds in this study are similar to those of benzaldehyde with the following exceptions. No second wave was observed in the case of crotonaldehyde. For cinnamaldehyde and benzalacetone in aqueous solutions at concentrations greater than 8×10^{-5} molar, the shapes of the curves indicate that the reactions are apparently irreversible and there is considerable shift in the half-wave potential with concentration changes. The cause for the shift in half-wave potentials is undoubtedly due to an adsorption phenomenon at the mercury-water interface. It is possible that a unimolecular layer of reactant or product molecules is adsorbed on the surface of the drop of mercury at concentrations greater than 8×10^{-5} M. The diffusion current corresponding to this "adsorption" wave is approximately 0.2 microampere under the conditions of these experiments. This small wave is apparently reversible when the concentration is 8×10^{-5} M or lower. It gives an n-value of unity and at a given pH value the half-wave potential does not change with concentration.

At concentrations greater than 8×10^{-5} M, a second wave appears directly after the first. The height of this second wave is proportional to the concentration in excess of 8×10^{-5} M. Thus, the sum of the two waves constitutes a one-electron reaction. The diffusion current constants in the table refer to the sum of these two waves.

The behavior of cinnamaldehyde in 50% dioxane solutions is similar to that of benzaldehyde. The "adsorption" phenomenon was not observed and the shapes of the waves indicate an apparently reversible one-electron electrode process. In 50% dioxane solutions there is a shift in half-wave potential with concentration for benzalacetone and the waves are not symmetrical. Thus, the fact that the n-values have an average value of 1.1 based on seven determinations is not proof of a one-electron electrode process. However, the diffusion current constant is approximately the same as that of cinnamaldehyde; therefore, both electrode processes probably involve the same number of electrons.

The Effect of Solvent.—In general aldehydes and ketones are less soluble in water than are the corresponding carbinols (the solubility of the free-radical carbinol is assumed to be the same as that of the corresponding alcohol). In 48% ethanol and 50% dioxane the solubilities of both reactant and product molecules are assumed to be comparatively large. The half-wave potentials in these solvents should be approximately the same at a given pH value for a given compound.

The solubilities of benzaldehyde and benzyl alcohol in water at 17° are 0.3 g. and 4 g. per 100 g. of water, respectively. If we take the pure substance as the reference state, the activity, A, is nearly unity in a saturated solution. At any given concentration, C, activity and solubility S, the following approximation is probably valid

$$AS = C \qquad (10)$$

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 pH 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-$(CH{=}CH)_j$CHO, 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 pH, 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

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

was presented in the previous paper.[1] At a given pH 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.* pH curve for each compound for 50% dioxane solutions was extrapolated to a pH of zero. The half-wave potential at a pH 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).

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