for reading the manuscript of this paper. This work was supported by a grant from the U. S. Public Health Service No. C 1559 (C4).

Experimental

Potassium hypophosphite, KH_2PO_2, having a purity of more than 98%, was purchased from Oldbury Electrochemical Co. A 50% aqueous solution was prepared in distilled water and was cleaned with active charcoal, and the same solution was used both for the Raman and infrared measurements.

The Raman spectrum was obtained photographically using a Raman spectrograph[11] in the Department of Chemistry, University of Michigan, through the kindness of Dr. R. C. Taylor. The 4358 Å. Hg emission was used as the exciting light.

Depolarization measurements were made by the two exposure method using Polaroid cylinders in a manner similar to that described by Crawford and Horwitz.[12] Exposure times were monitored by an integrating photoelectric-counter and the intensities of the lines were compared by means of a Leeds and Northrup microphotometer. Since the collimating baffles were not as closely spaced as those of Crawford and Horwitz, an appreciable convergence error was present which resulted in the maximum value for the depolarization ratio being about 0.94 instead of 0.86. A correction for this was not made, but due allowance was made in interpreting the results.

In the infrared measurement of the aqueous solution of KH_2PO_2, the solution was kept between two AgCl plates.

Infrared absorption measurements in the 4000–700 cm.$^{-1}$ region for the KH_2PO_2 solution and all other samples described in this paper were made by a Perkin–Elmer 21 spectrometer with a NaCl prism, and in the 700–400 cm.$^{-1}$ region by a Perkin–Elmer 112 spectrometer with a CsBr prism.

A thin sheet of solid KH_2PO_2, in which thin pyramidal crystals were oriented with their axes practically in one direction, was prepared on an AgCl plate. For observing the dichroism of this crystal, the AgCl polarizers were put in both sample and reference beams. In order to change the direction of polarization of the incident radiation relative to the direction of orientation, the two polarizers were rotated, instead of rotating the sample.

Crystalline calcium hypophosphite, $Ca(H_2PO_2)_2$. was also purchased from Oldbury Electrochemical Co. and had a purity of not less than 98%.

The samples of potassium phosphite, K_2HPO_3, and barium phosphite, $BaHPO_3$, were prepared from phosphorous acid (with the purity of 99%, purchased from Oldbury Electrochemical Co.) by dissolving it in water and adding KOH or $Ba(OH)_2$ until the *p*H of the solution reached 8.

The samples of barium monomethyl phosphate, $BaCH_3$-OPO_3, and barium dimethyl phosphate, $Ba((CH_3O)_2PO_2)_2$, were obtained from commercial samples of roughly equimolar mixtures of mono- and dimethyl phosphate supplied by Oldbury Electrochemical Co. The two phosphates were separated from each other through solubility difference of the barium salts in water.[13]

---

[11] G. L. Vidale and R. C. Taylor, THIS JOURNAL, **78**, 294 (1956).

[12] B. L. Crawford and W. Horwitz, *J. Chem. Phys.*, **15**, 268 (1947).

[13] W. D. Kumler and J. J. Eiler, THIS JOURNAL, **65**, 2355 (1943).

ANN ARBOR, MICHIGAN

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF CALIFORNIA AT LOS ANGELES]

Polarography of Carbonyl Compounds. III. Semi-empirical and Empirical Relationships between Structures and Half-wave Potentials

BY DALE M. COULSON,[1] WILLIAM R. CROWELL AND S. KATHLEEN TENDICK

RECEIVED OCTOBER 18, 1956

New data are reported on the polarographic reduction of several *o*-, *m*- and *p*-substituted benzaldehydes and acetophenones in 50% dioxane solutions. Two series of empirical equations are derived expressing the relation between structures and half-wave potentials. The first series, based on the LCAO–MO theory, involve linear additive structural parameters and the second series employ Hammett's sigma constants. For each substituent the structural parameter and value of σ are calculated and tabulated. Experimentally determined half-wave potentials at zero *p*H ($E^0_{1/2}$) are compared with those obtained by use of these two series of equations and those based on the free-electron gas theory.

Recently there have been several attempts to develop theoretical or semi-empirical relationships between polarographic half-wave potentials and the structures of unsaturated carbonyl compounds. Progress has been limited by the lack of suitable experimental data. With the advent of the wide spread use of mixed aqueous–organic solvent systems, such as dioxane–water and ethanol–water, data not invalidated by adsorption effects are rapidly becoming available. Fields and Blout[2,3] studied the polyene aldehydes $CH_3(CH{=}CH)_jCHO$ with values of *j* from 1 through 5 in buffered 50% dioxane solutions. Coulson and Crowell[4,5] studied several additional compounds in similar supporting electrolyte solutions. These data were summarized in the first paper of this series.[4] Pasternak[6] and Schmid and Heilbronner[7] studied several aromatic carbonyl compounds in buffered 48% ethanol solutions, showing results that were very similar to those obtained in 50% dioxane solutions.

The present paper presents data for several *o*-, *m*- and *p*-substituted benzaldehydes and acetophenones in buffered 50% dioxane solutions. As indicated in the first paper of this series,[4] the half-wave potential, $E_{1/2}$, for the one-electron reduction of each carbonyl compound in acid solutions is a function of *p*H as indicated in equation 1

$$E_{1/2} = E_{1/2}^0 - p\text{H}(B) \qquad (1)$$

where $E_{1/2}^0$ is the half-wave potential at *p*H zero and *B* is the slope of the $E_{1/2}$ *vs.* *p*H plot. The slope of the $E_{1/2}$ *vs.* *p*H plot usually has a value of approximately 0.06 volt per *p*H unit and the electrode reaction mechanism is probably

---

[1] Stanford Research Institute, Menlo Park, California.

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

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

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

[5] D. M. Coulson and W. R. Crowell, *ibid.*, **74**, 1294 (1952).

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

[7] R. W. Schmid and E. Heilbronner, *ibid.*, **37**, 1453 (1954).

$$RCHO + H^+ + e^- \rightleftarrows R\dot{C}HOH \qquad (2)$$

which is the equivalent of

$$RCHO + {}^1/_2H_2 \rightleftarrows R\dot{C}HOH \qquad (3)$$

A more complete description of the electrode mechanism has been given elsewhere.[4,5]

In addition to reporting new data for several aldehydes and ketones, a discussion of the various empirical and semi-empirical relationships between the structures and half-wave potentials of unsaturated carbonyl compounds is given. The molecular orbital theories of Scrocco and Cappellina[8] and Schmid and Heilbronner[7] are reinterpreted, using a slightly different molecular orbital model for the product molecule resulting from the reduction of an unsaturated carbonyl compound according to equation 2. Following this discussion an empirical equation involving linearly additive structural parameters based on the general form of the linear combination of atomic orbitals–molecular orbital theory is developed. Results by this equation are compared with those by Pacault and Pointeau's[9] free-electron gas expression and those employing Hammett's equation.

Experimental

Polarograph.—The initial work was carried out with a Sargent manual type polarograph and the procedure was essentially the same as that described in our previous papers when a Fisher Elecdropode was used.[4,5] These runs are designated by the letter M in the table.

All subsequent work was performed with a recording polarograph constructed by the electronics shop of the University of California at Los Angeles chemistry department. Span voltages from 0.5 to 2 are applied to the dropping electrode system by means of dry cells connected to a helical potentiometer rotated by a synchronous motor. A Leeds and Northrop Micromax recorder modified into a self balancing potentiometer was adapted to record the currents delivered by the dropping electrode circuit at the different applied voltages. A series of shunts makes it possible to cover a wide range of currents and the resistances are such that currents can be read directly on the chart scale in microamperes. The recorder drum is rotated by a synchronous motor which can be started at the same time as the span motor. The chart speed is 60.0 seconds per large division of the chart. A standard cell can be connected into different portions of the circuit to standardize the span voltage, initial voltage and recorder slide wire before each run. In these operations the recorder pen is used as the null point indicator. The pen response is 3.6 seconds for full scale travel. Different capillaries were used, with drop times from 3.31 to 5.50 and capillary constants from 2.35 to 1.23.

Polarographic Cell and Polarographic Determinations.—The polarographic cell and method of making polarographic determinations were essentially the same as those described in the previous work. In the case of the recording polarograph, wave heights were measured from the top of the diffusion current wave at the mid-point of its inflection to the corresponding point at the top of the residual current wave.

The reference half-cell was a saturated calomel electrode, and all measurements were made in a thermostat regulated at 25.0 ± 0.1°.

***p*H Meter.**—Either a Beckman model G or model H *p*H meter was used. In comparing the glass electrode used with a hydrogen electrode in the 50% dioxane solutions, it was found that *p*H measurements agreed within 0.01 to 0.05 *p*H units.

50% Dioxane Solutions.—As in our previous measurements the buffer solutions were prepared by adding dioxane to an equal volume of an aqueous solution 0.2 *f* in potassium chloride, 0.2 *f* in acetic acid and 0.2 *f* in orthophosphoric acid. The various compounds were dissolved in this solution and the desired *p*H values obtained by the addition of concentrated ammonium hydroxide.

Reagents.—The dioxane was refluxed over sodium for at least 12 hours and distilled over sodium shortly before a run was to be made. In order to observe freedom from impurities, polarograms of the buffer solution were always obtained before the addition of the aldehyde or ketone.

The aldehydes and ketones were either freshly redistilled or recrystallized shortly before each run. Compounds not commercially available were prepared by student assistants using standard methods.

Results and Discussion

Half-wave potentials at a *p*H of zero in 50% dioxane solutions for several aryl-aldehydes and -ketones are given in column 4 of Table I. These values were obtained by extrapolating a plot of $E_{1/2}$ *versus* *p*H for each compound to a *p*H of zero, and are designated as $E_{1/2}^0$. The slope of the $E_{1/2}$ *versus* *p*H plot for each compound is given in column 5. For each compound, approximately 12 to 20 polarograms were run, with the *p*H varying from 2 to 4.5 and the carbonyl compound concentration varying from about 10^{-1} to 1 millimolar.

TABLE I

SUMMARY OF RESULTS OF POLAROGRAPHIC RUNS ON BENZALDEHYDE, ACETOPHENONE AND DERIVATIVES

Substituent	Compound	Concn., mmole/l.	$-E^1/_2{}^0$, v.	Slope, v./*p*H unit
None	Ald.(M)[a]	0.800	0.869	0.0638
None	Ket.	0.090–0.721	.993	.0604
p-Cl	Ald.	0.800	.808	.0637
	Ket.(M)	.730	.926	.0625
m-Cl	Ald.	0.111–0.667	.798	.0651
	Ket.	.098– .588	.925	.0712
o-Cl	Ald.	0.800	.729	.0637
	Ket.	.800	.964	.0632
p-Br	Ald.(M)	.900	.812	.066
	Ket.(M)	1.14 –1.78	.928	.064
m-Br	Ald.	0.181–0.800	.768	.0656
	Ket.	.148– .800	.899	.0642
o-Br	Ald.	.106– .496	.733	.0632
	Ket.	.0778–.453	.982	.0627
p-OH	Ald.	.100– .670	.991	.0623
	Ket.	.295– .600	1.101	.0608
m-OH	Ald.	0.595	0.870	.0633
	Ket.	.635	1.000	.0578
o-OH	Ald.	0.118–0.800	0.918	.0639
	Ket.(M)	1.04 –1.95	1.065	.066
p-CH_3O	Ald.	0.308–0.800	0.964	.0649
	Ket.	.352– .802	1.078	.0590
m-CH_3O	Ald.	.132– .616	0.845	.0658
	Ket.	.118– .600	.974	.0631
o-CH_3O	Ald.	.210– .624	.849	.0607
	Ket.	.102– .584	.959	.0675
p-CH_3	Ald.(M)	1.00 –1.06	.887	.064
	Ket.(M)	0.90 –0.92	1.019	.058
m-CH_3	Ket.	.274–0.392	1.009	.0585

[a] M, results by manual polarograph.

In our earlier work an apparent difference in the hydrogen electrode and glass electrode *p*H of 50% dioxane solutions was reported. Further study of this problem showed no discrepancy. As a result,

---

(8) F. Scrocco and F. Cappellina, *Boll. Sci. fac. chim. ind.*, *Bologna*, **12**, 101 (1954).

(9) A. Pacault and R. Pointeau, *Compt. rend.*, **236**, 2060 (1953).

the $E_{1/2}^0$ values reported earlier were all 14 millivolts more negative than the correct values.

The effect on half-wave potentials of substituents on an aromatic ring conjugated with a carbonyl group in both the benzaldehyde and acetophenone series is in qualitative agreement with effects observed for other reactions. Electron attracting groups facilitate reduction while electron donating groups make reduction more difficult.

The "*ortho*-effect" is apparently greater for the acetophenones than for the benzaldehydes. This undoubtedly is due to steric interference between the methyl group and the larger *ortho*-substituents such as Br– and Cl–, while CH_3–O–, and –OH groups show normal behavior.

Semi-empirical Relations between Half-wave Potentials and Structures.—Coulson and Crowell[5] proposed the use of an harmonic oscillator model to represent the behavior of the conjugated π-electrons in the reactant carbonyl compound. A free-electron gas model was applied to the product free-radical carbinol. The half-wave potential was assumed to be related to the difference between the energies of the π-electron systems of these two models. Pacault and Pointeau[9] pointed out some of the difficulties in this original treatment and employed a free-electron gas model for both reactant and product molecules. According to their treatment, the $E_{1/2}^0$ values for the polyene aldehydes, $CH_3–(CH{=}CH)_j–CHO$, are given by the equation

$$E_{1/2}^0 = 4.804 - 19.06\left[\frac{j+2}{2j+3.506}\right]^2 \qquad (4)$$

The calculated $E_{1/2}^0$ values by equation 4 are given in column 4 of Table II. The agreement with the experimentally determined values is probably within the experimental error.

Scrocco and Cappellina[8] applied a zero-order linear combination of atomic orbitals–molecular orbital theory, LCAO–MO, to relate the structures and half-wave potentials of the polyene aldehydes. In this theory it was assumed that the half-wave potential of each compound was related to the difference between the sum of the ground state π-electron energies of the product and reactant molecules. The pz orbital of the OH–group of the product molecule was assumed to be completely localized. In this case the agreement between the calculated and experimental half-wave potentials was only fair. Their values calculated by this theory and corrected by the addition of 14 millivolts are given in column 5 of Table II.

TABLE II

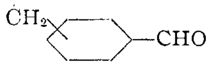
EXPERIMENTAL AND CALCULATED HALF-WAVE POTENTIALS OF POLYENE ALDEHYDES

	$-E_{1/2}^0$ v. *vs.* S.C.E.			
Compound	Exp.[2]	Eq. 14	Eq. 4[9]	S and C[8]
$CH_3–CH{=}CH–CHO$	0.853	0.853	0.854	0.773
$CH_3–(CH{=}CH)_2–CHO$	.622	.610	.609	.576
$CH_3–(CH{=}CH)_3–CHO$	.480	.473	.470	.476
$CH_3–(CH{=}CH)_4–CHO$	.379	.386	.379	.416
$CH_3–(CH{=}CH)_5–CHO$	.315	.325	.316	.375

Schmid and Heilbronner[7] carried out a more refined LCAO–MO treatment and obtained satisfactory agreement between the predicted and experimental data for several aryl aldehydes. In this theory models similar to those of Scrocco and Cappellina were used to represent the reactant and product molecules. However, a correction was applied for the heteroatom, oxygen, in the carbonyl group.

All of these theories must be considered semi-empirical since it was necessary to evaluate two or more constants in the equations relating half-wave potentials and structures on the basis of the experimental half-wave potentials involved.

We feel that the molecular orbital for the product molecule in equation 3 should include the oxygen pz one-electron orbit. By this model $2j + 3$ conjugated π-electrons occupy the $(j + 1)$ ground state energy levels, with one electron in the lowest excited state energy level. Using this model for the product free-radical and Scrocco and Cappellina's model for the reactant carbonyl compound, the difference between the sums of the π-electron energies of the product and reactant molecules is simply the energy required to place an electron in the lowest excited state of the reactant molecule. Scrocco and Cappellina have tabulated the β-coefficients for all of the levels, using the zero-order LCAO–MO approximation, for the polyene aldehydes, $CH_3–(CH{=}CH)_j–CHO$, with values of j from 0 to 5 inclusive. Our calculations for this model give identical results. Table III lists the coefficients to be multiplied by β, the exchange integral, for the 1st excited state for the polyene aldehydes, benzaldehyde, cinnamaldehyde and the hypothetical methylene *m*- and *p*-substituted benzaldehydes



If a methyl group is substituted for the carbonyl group hydrogen atom, the π-electron system remains essentially unchanged but the experimental half-wave potentials are all shifted to more negative values. Consequently, a correction must be applied to the LCAO–MO results to account for the effect of this substitution.

TABLE III

EXCHANGE INTEGRAL COEFFICIENTS FOR CERTAIN POLYENE, ARYL AND ARYL METHYLENE ALDEHYDES[a]

Compound	C_i (β-coef. of 1st unoccupied level)	Compound	C_i (β-coef. of 1st unoccupied level)
$CH_3–CH{=}CH–CHO$	0.618	Benzaldehyde	0.662
$CH_3–(CH{=}CH)_2–CHO$	.445	*m*-Methylene	
$CH_3–(CH{=}CH)_3–CHO$	.347	benzaldehyde	.674
$CH_3–(CH{=}CH)_4–CHO$	.285	*p*-Methylene	
$CH_3–(CH{=}CH)_5–CHO$	.241	benzaldehyde	.780
		Cinnamaldehyde	.474

[a] In forming a molecular orbital the carbonyl group is assumed to be equivalent to an ethylenic group.

The change in internal energy, represented in part by the change in π-electron energy, is only a fraction of the energy change accompanying the polarographic reduction of a carbonyl compound. To relate the structures and potentials it is also necessary to include enthalpy terms not determined by the π-electron energies and an entropy term. We, therefore, write

$$-nEf = \Delta F = \Delta H_I + \Delta H_E - T\Delta S \qquad (5)$$

where E equals $E_{1/2}^0 + E''$ in volts, E'' representing the reference electrode potential; ΔH_I is the difference between the π-electron energy terms for the product and reactant molecules; ΔH_E is the change in external energy terms including the OH bond energy minus one-half of the H_2 bond energy, and $T\Delta S$ is the entropy term. The ΔH_E and $T\Delta S$ terms are assumed to be essentially constant for the compounds being considered. These approximations lead to the approximate expression

$$E_{1/2}^0 = -E'' + \Delta H_I/nf + E''' \qquad (6)$$

where E''' takes the place of the $[\Delta H_E/nf - T\Delta S/nf]$ term.

Introducing the LCAO–MO results in units of β we have

$$E_{1/2}^0 = E' + C_i\beta \qquad (7)$$

where $E' = E''' - E''$, C_i is the β-coef. of the 1st unoccupied M.O. and $C_i\beta = \Delta H_I/nf$, with β expressed in electron-volts.

From plots of $E_{1/2}^0$ *versus* C_i for the aryl aldehydes, polyene aldehydes and aryl methyl ketone series, we find that β is -1.400 e.v. and E''' has the values $+0.307$, $+0.258$ and $+0.211$ v. *vs.* N.H.E., if E'' is the potential of the saturated calomel electrode. We assume that only one equation would be necessary to relate structures and potentials for these three series of compounds if a suitable correction term were applied for the effect of substituting one group for another, such as methyl for hydrogen in the LCAO–MO calculations. The effect of this kind of substitution seems to be relatively constant throughout a reaction series. Consequently, the energy level diagrams are merely displaced by a constant amount by this substitution. This indicates a predominantly inductive effect, with very little resonance contribution. The equations relating structures and potentials for the aryl aldehydes, polyene aldehydes and aryl methyl ketones are (8), (9) and (10), respectively

$$E_{1/2}^0(\text{aryl}) = +0.060 - 1.400C_i \qquad (8)$$

$$E_{1/2}^0(\text{polyene}) = +0.012 - 1.400C_i \qquad (9)$$

$$E_{1/2}^0(\text{aryl methyl}) = -0.063 - 1.400C_i \qquad (10)$$

Empirical Relationships

The application of quantum mechanics to the problem of relating structures and chemical reactivity has been limited by the complexity of the mathematical problems involved. We, therefore, have developed an empirical relationship between the LCAO–MO results and experimental potentials that has the same general form as equation 7 and relates the structures of complex molecules and their potentials in terms of linearly additive structural parameters. It was observed that the β-coef., C_i, for the lowest unoccupied energy level in the LCAO–MO method for the polyene aldehydes can be expressed as

$$C_i = \frac{3.158}{2j + 3.110} = \frac{3.158}{n + 1.110} \qquad (11)$$

where n is the number of one-electron orbitals combined to form the molecular orbital for the carbonyl compound. Now $n + 1.110$ is a linearly additive structural parameter which we will designate as having the relationship

$$n + 1.110 = \Sigma_i Z_i \qquad (12)$$

where Z_i is the structural parameter for the ith group in the molecule. Substituting $3.158/\Sigma_i Z_i$ for C_i in equations 8, 9 and 10, we obtain the equations

$$E_{1/2}^0(\text{aryl aldehyde}) = +0.060 - 4.421/\Sigma_i Z_i \qquad (13)$$

$$E_{1/2}^0(\text{polyene aldehyde}) = +0.012 - 4.421/\Sigma_i Z_i \qquad (14)$$

$$E_{1/2}^0(\text{aryl methyl ketone}) = -0.063 - 4.421/\Sigma_i Z_i \qquad (15)$$

Generalizing, we can relate $\Sigma_i Z_i$ to the experimentally determined half-wave potentials as

$$\Sigma_i Z_i = \frac{4.421}{(E' - E_{1/2}^0)} \qquad (16)$$

Structural parameters, Z_i, for various substituents on the benzene ring for benzaldehydes and acetophenones were determined by means of equation 16 and are shown in Table IV along with the average value. For purposes of comparison with results from other empirical relationships, these average substituent parameters were then used to calculate the predicted half-wave potentials by means of equations 13 and 15. These results are shown in column 4 of Table V. Values of $n + 1.110$ for the polyene aldehydes listed in Table II were calculated and equation 14 used to determine the $E_{1/2}^0$'s shown in column 3 of Table II.

TABLE IV

EMPIRICAL STRUCTURAL PARAMETERS FOR SUBSTITUENTS ON THE BENZENE RING OF BENZALDEHYDES AND ACETOPHENONES

Substituent	Constant Z_i Benzaldehyde[a]	 Acetophenone[a]	Av.
m-Br	0.572	0.521	0.547
m-Cl	.386	.362	.374
p-Br	.303	.344	.324
p-Cl	.326	.356	.341
m-CH_3O	.118	.086	.102
m-OH	− .018	− .049	− .034
m-CH_3		− .094	
p-CH_3	− .099	− .143	− .121
p-CH_3O	− .451	− .417	− .434
p-OH	− .561	− .508	− .535
o-OH	− .247	− .355	− .301
o-CH_3O	.097	.167	.132

[a] For unsubstituted compound $\Sigma_i Z_i = 4.767$.

We have also taken the liberty to apply the equation for the free-electron gas model of Pacault and Pointeau in a similar manner with equally satisfactory results. The substituted benzaldehyde equation used is

$$E_{1/2}^0 = 4.866 - 19.06\left[\frac{j+2}{2j+3.506}\right]^2 \qquad (17)$$

And the substituted acetophenone equation used is

$$E_{1/2}^0 = 4.743 - 19.06\left[\frac{j+2}{2j+3.506}\right]^2 \qquad (18)$$

Here the assumption was made that "j" in equation, 4, 17 and 18 could be taken as an empirically linearly additive structural parameter. The value of "j" is unity for the ethylenic group in the free-electron gas model. Other groups were then evaluated in terms of their ethylenic group equivalent. These results are shown in column 5 of Table V.

TABLE V

CORRELATION OF EXPERIMENTALLY AND EMPIRICALLY DETERMINED HALF-WAVE POTENTIALS FOR BENZALDEHYDES AND ACETOPHENONES

Compound	Substituent	$-E_{1/2}^0$, v. *vs.* S.C.E.			
		Expt.	Eq. 13 or 15 (M.O.)	Eq. 17 or 18 (free-electron gas)	Eq. 19 or 20 ($\rho\sigma$)
Aldehyde	None	0.869	0.867	0.870	0.875
Ketone		.993	.990	.993	.998
Aldehyde	*m*-Br	.768	.772	.772	.767
Ketone		.899	.895	.895	.890
Aldehyde	*m*-Cl	.798	.800	.802	.772
Ketone		.925	.923	.925	.895
Aldehyde	*p*-Br	.812	.808	.808	.811
Ketone		.928	.931	.931	.934
Aldehyde	*p*-Cl	.808	.806	.806	.812
Ketone		.926	.929	.929	.935
Aldehyde	*m*-CH_3O	.845	.848	.846	.843
Ketone		.974	.971	.969	.966
Aldehyde	*m*-OH	.870	.874	.873	.876
Ketone		1.000	.997	.996	.999
Aldehyde	*m*-CH_3		.886	.886	
Ketone		1.009			1.017
Aldehyde	*p*-CH_3	0.887	.892	.893	0.922
Ketone		1.019	1.015	1.016	1.035
Aldehyde	*p*-CH_3O	0.964	0.960	0.959	0.949
Ketone		1.078	1.083	1.082	1.062
Aldehyde	*p*-OH	0.991	0.985	0.984	0.973
Ketone		1.101	1.108	1.107	1.086
Aldehyde	*o*-OH	0.918	0.930	0.932	
Ketone		1.065	1.053	1.055	
Aldehyde	*o*-CH_3O	0.849	0.842	0.838	
Ketone		0.959	0.965	0.970	

Both of these approaches must be considered empirical due to the approximations and methods of application used. They do retain the approximate general form of the semi-empirical relationships from which they were borrowed. However, we can therefore expect their applicability to be somewhat wider in scope than a purely empirical relationship such as Hammett's well known $\rho\sigma$ equation[10] which is also applicable to the benzaldehydes and acetophenones. We have calculated σ-values for the various substituents for the benzaldehydes and acetophenones using equations 19 and 20

$$\sigma\text{, benzaldehydes} = (0.875 + E_{1/2}^0\text{ subs.})/0.275 \quad (19)$$

$$\sigma\text{, acetophenones} = (0.998 + E_{1/2}^0\text{ subs.})/0.275 \quad (20)$$

Table VI shows our results. The excellent agreement between the sigma values determined by equations 19 and 20 shown in Table VI indicates the applicability of Hammett's relation to polarographic reductions involving a free-radical product molecule. The half-wave potentials predicted by equations 19 and 20 using Hammett's σ-values derived from other reactions are given in column 6 of Table V. The agreement between experimental and predicted half-wave potentials is not as good as for the equations based on the LCAO-MO and free-electron gas models but is reasonably satisfactory.

TABLE VI

HAMMETT'S SIGMA CONSTANTS

Substituent	σ Values			
	Benzaldehyde eq. 19	Acetophenone eq. 20	Av.	Hammett[10]
m-Br	+0.389	+0.360	+0.375	+0.391
m-Cl	+ .280	+ .265	+ .273	+ .373
p-Br	+ .229	+ .254	+ .242	+ .232
p-Cl	+ .244	+ .262	+ .253	+ .227
m-CH_3O	+ .109	+ .087	+ .098	+ .115
m-OH	+ .018	− .007	+ .006	− .002
m-CH_3		− .040	− .040	− .069
p-CH_3	− .044	− .076	− .060	− .170
p-CH_3O	− .324	− .291	− .308	− .268
p-OH	− .422	− .374	− .398	− .357
H-	+ .022	+ .018	+ .020	.000

Acknowledgments.—The authors wish to thank Professors Theodore A. Geissman and William G. McMillan for their helpful advice during this investigation, and to express their appreciation to B. David Wilson, Roy R. Sakaida, James K. Brownlee, George F. Bajor, William H. Richardson and Wallace H. Pippin for their able assistance in the experimental work.

LOS ANGELES, CALIFORNIA

---

[10] H. H. Jaffe, *Chem. Revs.*, **53**, 222 (1953).