annelled rings is counterbalanced by another effect. The latter may be an effect of most suitable orientation at the electrode surface in the course of the electrode process, which the rigid carbazole derivative cannot achieve.

The value of pK_N for 3-indolecarboxaldehyde[14] has been shown to deviate from pK_N–σ plot, even when $\sigma^-_{p\text{-CHO}}$ was used. When the value of pK_N for 2-indolecarboxaldehyde (Table II) was correlated with $\sigma^-_{p\text{-CHO}}$, $\sigma_{m\text{-CHO}}$, or $(\sigma_p + \sigma_m)_{\text{CHO}}/2$, a small deviation in the same direction as for the 3-formyl derivative was observed. This clearly indicates a type of interaction between the formyl group and the indole ring, different from the interaction between the aniline ring and the aldehydic groups as expressed in the value of $\sigma^-_{p\text{-CHO}}$.

Specific interaction, not expressed by substituent constants, between the aldehydic group and the heterocycle is shown also by the comparison of the effect of an annelled benzene ring. Whereas pK_N value for the unsubstituted pyrrole is *0.54 units larger* than that for indole,[14] the effect of the annelled benzene ring on pK values of 2-carboxaldehydes is just opposite (Table II): the pK_N value for the pyrrole derivative is *0.35 units smaller* than that of the indole compound. In addition to the type of interaction observed for the 3-indolecarboxaldehyde[14] which would be in pyrrole even stronger than in indole (assuming comparable values of reaction constant ρ), it is impossible for the 2-carboxaldehydes to rule our direct interaction between the formyl group and the heterocyclic nitrogen.

The interaction between the formyl group and the indole ring, which increases the reactivity toward the OH^- attack on the NH group, seemingly decreases the reactivity of the formyl group to oxidation. This is shown by the absence of electroactivity of 3-indolecarboxaldehyde. Smaller interaction is shown by the 2-indolecarboxaldehyde, the electroactivity of which has not been impaired. Also the increase in the reactivity toward oxidation from pyrrole to indole derivative (Table II) is in the expected direction. Available data for these compounds do not allow us to distinguish if the changes in potentials are due to changes in formation of the electroactive geminal diol anion, in the electron transfer, or the hydrogen abstraction and more detailed analysis must be postponed.

All these results, nevertheless, indicate interaction between the formyl group and the indole ring, stronger for the 3 isomer than for the 2 isomer. Nevertheless, as such interaction operates not only in the 3 isomer, but also in the 2-carboxaldehyde it is indicated that the explanation by enol formation, offered for 3-carboxaldehyde,[14] might not be complete.

Presence of a unit negative charge on the heterocyclic ring decreases reactivity toward the hydroxide attack on the carbonyl group in a similar way as N-substitution. This follows from comparison of pK' values in Table II with values for N-substituted pyrrole derivatives (Table I).

For hydrated aldehydes the small effect of the annelled benzene ring in the thiazole derivatives as well as of *N*-methyl substitution in 2-imidazolecarboxaldehyde on values of pK_s (Table III) is probably due to the absence of conjugation in both the predominating geminal diol and its anion.

On the other hand, the ease of oxidation is increased by the added benzene ring in the 2-benzothiazolecarboxaldehyde and decreased by N-methylation in the imidazole derivative, as follows from comparison of polarographic half-wave potentials (Table III). As such change cannot reflect the position of the equilibrium yielding geminal diol anion, it must be caused by structural effects either on the electron transfer or hydrogen abstraction.

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Nucleophilic Additions to Aldehydes and Ketones. 3.[1] Reactions of Ortho-Substituted Benzaldehydes and Their Polarographic Oxidations

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Ortho-substituted benzaldehydes add in strongly alkaline media hydroxide ions in a reversible, rapidly established equilibrium reaction, in which an anion of the geminal diol [$ArCH(OH)O^-$] is formed. Extrapolation to zero ionic strength and use of acidity function J_- made it possible to determine thermodynamic equilibrium constants for benzaldehydes bearing both electropositive and electronegative substituents. Correlation of pK_a with $\sigma_{o\text{-X}}$ and dissociation constants of benzoic acids were explained by similarity in structures of the geminal diol anion and carboxylate ion or the transition state in ester hydrolysis. Structural effects on polarographic half-wave potentials of anodic waves indicated quantitative or qualitative changes in the heterogeneous portion of the electrode process, seemingly involving the hydrogen abstraction step [$ArCH(OH)O^- \rightleftharpoons ArCOOH + 2e + H^+$].

Previously[1,3] the acidity scale J_- for reactions involving addition of hydroxide ion in strongly alkaline media has been used for determination of thermodynamic values of equilibrium constants for additions to meta- and para-substituted benzaldehydes[3a] as well as to some heterocyclic aldehydes.[1] In this paper the study was extended to some ortho-substi-

Table I. Spectral Properties and Equilibrium Constants K for the Addition of Hydroxide Ions to Benzaldehydes Substituted in Ortho Position by X

No.	X	Registry no.	λ_{max}, nm	ϵ, l/mol cm	pK[a] (overlap)	p$\bar{K}$[d]	pK'[e] (overlap)	pK'[f] (J_- plots)	Δ[g]	pK_{COOH}[h]	σ_{p}-X[j]	σ_{o}-X[k]
1	OC_2H_5	613-69-4	257	9800	+1.18[b]		15.18[b]	15.30	0.12	4.21	−0.25	−0.35
2	COO^-	58502-59-3	255	7700	+1.14[b]		15.14[b]	15.31	0.17	5.51	+0.13	
3	$CH(CH_3)_2$	6502-22-3	262	14200	+0.99[b]		14.99[b]	15.21	0.22	3.64	−0.20	
4	OCH_3	135-02-4	257	10500	+0.96[b]		14.96[b]	15.15	0.19	4.09	−0.27	−0.39
5	H	100-52-7	250	12800	+0.90[b]		14.90[b]			4.19	0.00	0.00
6	CH_3	529-20-4	260	11700	+0.86[b]	+1.03	14.86[b]	15.10	0.24	3.92	−0.17	−0.17
7	I	26260-02-6	258	6700	−0.33[c]		13.67[c]	13.83	0.16	2.66	+0.27	+0.21
8	Cl	89-98-5	254	8800	−0.36[c]	−0.41	13.64[c]	13.81	0.17	2.92	+0.23	+0.20
9	Br	6630-33-7	256	8800	−0.41[c]		13.59[c]	13.80	0.21	2.85	+0.23	+0.21
10	F	446-52-6	246	12300	−0.44[c]		13.56[c]	13.78	0.22	3.27	+0.06	+0.24
11	CF_3	447-61-0	246	8800	−0.59[c]		13.41[c]	13.45	0.04		+0.55	
12	NO_2	552-89-6	260	12800	−1.11[c]	−1.03	12.89[c]	13.01	0.12	2.21	+0.78	+0.80

[a] $K = C_{ArCH(OH)O^-}/C_{ArCHO}C_{OH^-} \times y_{ArCH(OH)O^-}/y_{ArCHO}\,y_{OH^-}$. [b] Values obtained by overlap procedures using compounds 7–12 as reference. [c] Values obtained by extrapolation to zero ionic strength. [d] $\bar{K} = C_{ArCH(OH)O^-}/C_{ArCHO}C_{OH^-}$; nonthermodynamic values reported by Greenzaid.[4] [e] pK' = pK + pK_w. [f] Values of pK_a obtained by means of J_- acidity function. [g] Difference between values obtained by means of J_- and the overlap procedure. [h] Dissociation constants of corresponding benzoic acids in water at 25 °C. [j] Hammett substituent constants. [k] Taft substituent constants based on ester hydrolysis.

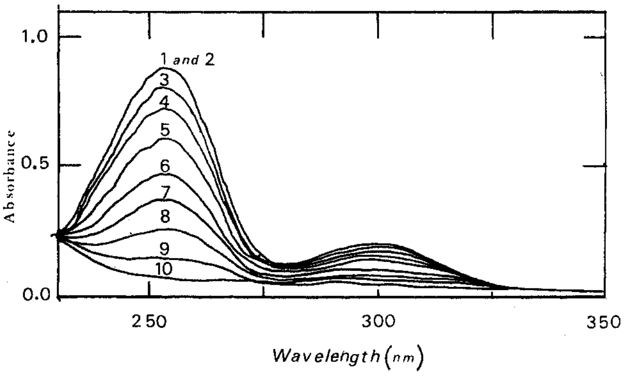

Figure 1. The uv spectra of 1 × 10^{-4} M o-chlorobenzaldehyde at 25 °C in aqueous (1% ethanol) sodium hydroxide solutions of the following molar concentrations: 2, 0.01; 3, 0.05; 4, 0.1; 5, 0.2; 6, 0.4; 7, 0.6; 8, 1.0; 9, 2.0; 10, 5.0. Curve 1 phosphate buffer, pH 10.

tuted benzaldehydes. Greenzaid[4] reported crude practical equilibrium constants for three monosubstituted ortho benzaldehydes. It was attempted to compare thermodynamic values of equilibrium constants with his data and to include a wider variety of both electropositive and electronegative substituents than could be studied by Greenzaid, whose treatment made it impossible to study solutions containing more than 1.5 M base.

As it has been proved[5] that the geminal diol anion is the reactive species in electrooxidation of benzaldehydes in alkaline media and a linear relationship between the polarographic half-wave potentials[6] and Hammett substituent constants σ has been confirmed for meta- and para-substituted benzaldehydes, the electrooxidation of ortho-substituted benzaldehydes and the effect of the nature of the substituent have been investigated as well.

Experimental Section

Chemicals. Benzaldehydes used were commercial products (Aldrich Chemical Co., Milwaukee, Wis.), freshly redistilled or recrystallized. Their purity was checked by gas–liquid chromatography. Stock solutions (0.01 M) of these aldehydes were prepared freshly each day in 96% ethanol. The origin of sodium hydroxide and preparation of solutions was the same as in part 2 of this series.[1]

Apparatus. Spectrophotometric and polarographic equipment used was the same as in part 2.[1] The capillary used had in 1 M potassium chloride at 0.0 V (vs. SCE), rate of flow m = 2.2 mg s^{-1} and drop time t_1 = 3.1 s at height of mercury column h = 65 cm.

Procedures. Recording of the uv spectra, polarographic curves, and measurement of half-wave potential was carried out as described in part 2.[1] The logarithmic analysis of polarographic curves was carried out by current measurement obtained with curves recorded at a slow rate of scanning (1 mV/s) to prevent hysteresis effects.

Evaluation of Equilibrium Constants. To determine the value of equilibrium constant K for reaction 1

$$ArCHO + OH^- \rightleftharpoons ArCH(OH)O^- \qquad (1)$$

absorbance in the region between 250 and 280 mn was measured. The anions of the geminal diols formed in reaction 1 are for the majority of benzaldehydes studied practically transparent in this wavelength region (Figure 1), with the exception of o-nitrobenzaldehyde. Absorbance in this wavelength region is thus for most aldehydes a linear function of the concentration of the free aldehydic form. Molar absorptivity coefficients of these forms were obtained in buffers pH 10 where formation of the anion can be neglected (Figure 1). For o-nitrobenzaldehyde the decrease of the absorption band at 260 nm was accompanied by an increase of a band at 335 nm corresponding to the absorption of the nitrobenzene portion of the geminal diol anion with a resulting isosbestic point at 311 nm. As no change in the absorbance at 260 nm in 5 and 10 M sodium hydroxide was observed, this value was taken for the residual absorbance.

Values of the ratio $C_{ArCH(OH)O^-}/C_{ArCHO}$ were obtained by means of eq 2

$$C_{ArCH(OH)O^-}/C_{ArCHO} = (A_0 - A)/(A - A_r) \qquad (2)$$

where A_0 is the absorbance of the aldehyde form ArCHO, A_r the residual absorbance of the anion $ArCH(OH)O^-$ (practically zero for all derivatives except o-nitro), and A the absorbance of the solution at any given sodium hydroxide concentration (all measured at a given wavelength).

Results

Thermodynamic values of equilibrium constants of reaction 1 were obtained in three different ways.

For compounds 7–12 (Table I) where the value of pK is less than zero, values of log $(C_{ArCH(OH)O^-}/C_{ArCHO})$ − log C_{OH^-} were plotted against C_{OH^-}. Extrapolation of such linear plots to zero ionic strength (i.e., to $C_{OH^-} = 0$) gave thermodynamic values of K (Table I).

For benzaldehydes 1–6 with pK values greater than zero the overlap procedure[8] was used. Because of the large gap between pK values of compounds 7–12 and 1–6, pK values for the latter were used successively as a reference value pK for each of the compounds 7–12. Averages of these values are reported in Table I.

To convert measured equilibrium constants (K) for hydroxide ion addition to a more conventional scale for hydrogen

Table II. Polarographic Half-Wave Potentials[a] (vs. SCE) of Benzaldehydes Substituted in Ortho Position by X in Sodium Hydroxide Solutions of Varying Molarity

X	0.01 M	0.03 M	0.1 M	0.3 M	1.0 M	3.0 M	5.0 M	7.0 M	pK'[b] (overlap)	d$E_{1/2}$/ dJ_-[c]
F	−0.146	−0.156	−0.192	−0.251	−0.275	−0.327	−0.342		13.56	−0.068
Cl	−0.130	−0.162	−0.213	−0.251	−0.291	−0.339	−0.330		13.64	−0.077
Br	−0.154	−0.183	−0.221	−0.257	−0.305	−0.348	−0.346		13.59	−0.071
I	−0.140	−0.186	−0.208	−0.273	−0.273	−0.300	−0.327		13.67	−0.076
CF_3						−0.147	−0.227		13.41	
NO_2	−0.176	−0.191	−0.216	−0.243	−0.269	−0.271	−0.304	−0.298	12.89	−0.044
OCH_3		−0.129	−0.146	−0.166	−0.202	−0.219	−0.274	−0.286	14.96	−0.050
OC_2H_5			−0.125	−0.145	−0.178	−0.192	−0.257	−0.274	15.18	−0.054
CH_3			−0.134	−0.157	−0.214	−0.287	−0.343	−0.357	14.86	−0.096
$CH(CH_3)_2$			−0.150	−0.189	−0.253	−0.325	−0.432		14.99	−0.101
COO^-						−0.150	−0.180	−0.217	15.14	−0.103
H			−0.193	−0.230	−0.295	−0.393	−0.454	−0.450	14.90	−0.114

[a] Half-wave potentials measured against a carbon rod cathode, expressed relative to the half-wave potential of the unsubstituted benzaldehyde for which the values vs. SCE have been reported.[5] [b] pK' values determined by the overlap procedure (Table I). [c] Slope of the linear portion of the $E_{1/2}$–J_- plot in the J_- region where the half-wave potentials are shifted to more negative values with increasing J_- (Table III).

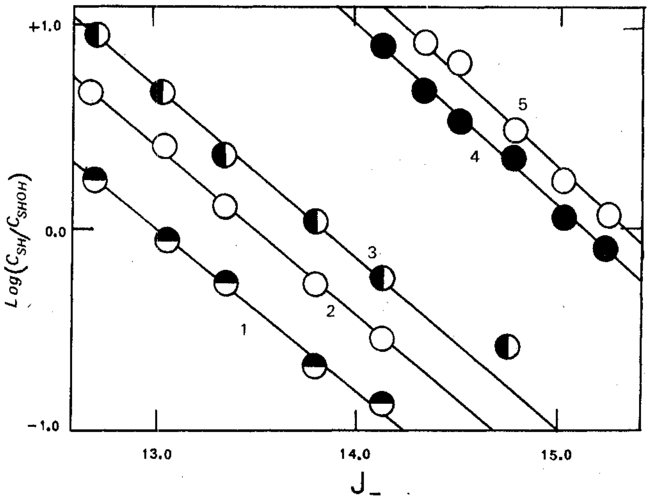

Figure 2. Values of log (C_{SH}/C_{SHOH^-}) determined from spectrophotometric results plotted against the J_- scale: 1, o-nitrobenzaldehyde; 2, o-trifluoromethylbenzaldehyde; 3, o-iodobenzaldehyde; 4, o-tolualdehyde; 5, o-ethoxybenzaldehyde.

ion abstraction (pK'), the expression pK' = pK + pK_w was used.

Alternatively, it was possible to use acidity function J_- established by means of meta- and para-substituted benzaldehydes[3b] using eq 3.

$$pK' = J_- - \log (C_{ArCH(OH)O^-}/C_{ArCHO}) \quad (3)$$

Systems which follow eq 3 must show a linear dependence of log ($C_{ArCH(OH)O^-}/C_{ArCHO}$) on J_- with a unit slope. Experimental values for ortho benzaldehydes gave linear plots (Figure 2) with slopes varying between 0.92 and 1.07. From the intercept of these linear plots at 50% conversion when pK' = J_- values of pK' were obtained and are given in Table I.

The fulfillment of eq 3 indicates that all compared ortho-substituted benzaldehydes undergo the same type of nucleophilic addition (or acid/base) reaction as the meta- and para-substituted ones. No time change of spectra which would indicate a consecutive or side reaction was observed. The reversibility of the interaction with hydroxide ions was confirmed by partial acidification of the alkaline solution which produced the spectrum of the free aldehyde.

Polarographic anodic waves of the 12 ortho-substituted benzaldehydes studied corresponded to a two-electron oxidation process.[5,9] The limiting currents of these waves when corrected for the changes in viscosity ($i_{corr} = i_{meas} \times \eta^{1/2}$) were independent of sodium hydroxide concentration in the range 0.01 to 7 M. Half-wave potentials (Table II) were a function of pH and J_-. The $E_{1/2}$ − J_- (pH) plot shows two linear sections (Figure 3), shift at lower J_- and independence at higher J_- values. The intersection of the two linear parts was observed at J_- values somewhat larger than the pK' value. The slope d$E_{1/2}$/dJ_- depends considerably on the nature of the substituent (Table II). Waves of o-carboxybenzaldehyde were measurable only at concentrations of sodium hydroxide higher than about 3 M; in the same region of strongly alkaline solutions the oxidation of o-trifluoromethyl derivative was also indicated, but the resulting wave was too indistinct for measurement.

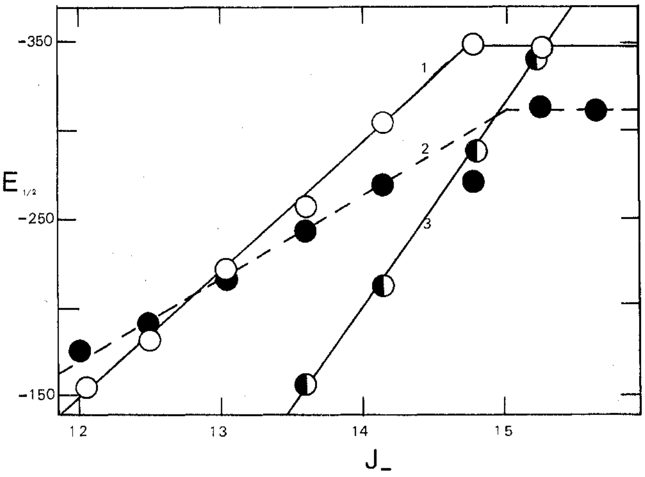

Figure 3. Dependence of half-wave potentials (mV vs. SCE) of substituted benzaldehydes on pH and acidity function J_-: 1, o-bromobenzaldehyde; 2, o-nitrobenzaldehyde; 3, o-tolualdehyde.

Logarithmic analysis of the wave shape (Figure 4) gave linear plots of varying slope (Table III). No attempts have been made to study the anodic waves of ortho benzaldehydes at lower pH values by means of pulse polarography so that no information is available on shifts of half-wave potentials or the change in wave height in this pH region.

Discussion

Equilibria. Attempts to correlate quantitatively structural effects of ortho substituents on rates and equilibria can be

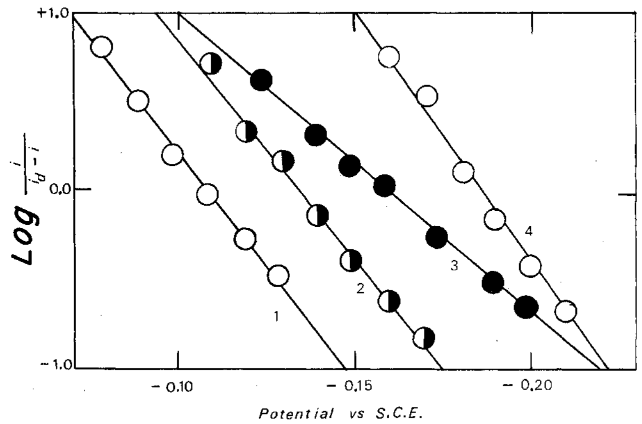

Figure 4. The logarithmic analysis of the rising portion of the anodic wave of ortho-substituted benzaldehydes. The value of log $(i/i_d - i)$ plotted against potential in volts: 1, *o*-tolualdehyde; 2, *o*-bromobenzaldehyde; 3, *o*-fluorobenzaldehyde; 4, *o*-iodobenzaldehyde.

Table III. Electrochemical Data for Oxidation of Benzaldehydes Substituted in Ortho Position by X Obtained in Alkaline Solutions

X	$dE_{1/2}/dJ_-$, V	$\beta n_a{}^a$ (0.058)/ $dE_{1/2}/dJ_-$	$dE/d\log(i/i_d - i)$, V	$\beta n_a{}^b$ (0.058)/ $dE/d\log(i/i_d - i)$
F	0.068	0.85	0.060	0.97
Cl	0.077	0.75	0.046	1.26
Br	0.071	0.82	0.039	1.49
I	0.076	0.76	0.036	1.61
NO_2	0.044	1.32	0.032	1.81
OCH_3	0.050	1.16	0.038	1.53
OC_2H_5	0.054	1.07	0.035	1.66
CH_3	0.096	0.60	0.041	1.41
$CH(CH_3)_2$	0.101	0.57	0.037	1.56
COO^-	0.103	0.56		
H	0.114	0.51	0.059	0.98

[a] Values obtained from shifts of half-wave potentials with sodium hydroxide concentration. [b] Values obtained from the slope of current–voltage curves.

classified into four categories: (a) attempts to correlate the rate or equilibrium constants of ortho-substituted compounds with Hammett substituent constants for corresponding para substituents ($\sigma_{p\text{-X}}$); (b) attempts to correlate such constants with a multiparameter equation, treating the ortho effects as additive to the polar effects; (c) attempts to correlate such constants with a special set of ortho-substituent constants ($\sigma_{o\text{-X}}$); (d) attempts to correlate them with equilibrium or rate constants for another reaction of ortho-substituted compounds.

The first approach is based on the qualitative assumption that electronic effects in para and ortho positions are not substantially different. The small difference between the role of the inductive effect in various positions on the benzene ring relative to the reactive center has been demonstrated,[10] so that the above assumption seems to equal the plausible conclusion that the resonance effect in para and ortho positions are not substantially different. Deviations from the $\log K_{o\text{-X}}$–$\sigma_{p\text{-X}}$ plot can then be interpreted as one of the proximity effects due to steric hindrance of coplanarity, direct field effect, or effect of the large steric requirements of the ortho substituent.

The second approach assumes the additivity of steric effects and is thought to be confirmed by apparently improved correlation resulting from the introduction of a second term in a linear free energy relationship. It seems that even statisticians have problems with deciding what is a measure of better correlation when a further adjustable parameter is included, and hence, even when a statistical proof was offered,[11] it does not seem to be possible to decide with certainty whether the improvement of the correlation is apparent or real. Moreover, the assumption of general additivity of steric effects does not seem to be plausible, as direct interactions of adjacent groups will depend also on the size, steric requirements, polarizability, and charge of the reactive center—not only of the substituent.

The same type of arguments apply also to the introduction of a special set of ortho-substituent constants. This presumes that the inductive, resonance, and polar effects of the ortho group are additive and that the relative size of the steric group will be independent of the reaction series and analogous to the steric effect operating in the series chosen as reference.

The limitation of the fourth type of application is that correlation between equilibrium constants is restricted to reaction series where both the structures of the starting materials and of the products (and hence also of the transition states) were similar in both series compared. The similarity in structures in starting materials *and* products in both series is the key to the limits of such application. It seems that the differences in structures of the starting material and product may be relatively small for this application to be successful. It seems difficult to predict how small these differences can be, but even when such $\log K^1_{o\text{-X}}$–$\log K^2_{o\text{-X}}$ correlations are successful, their use will be restricted to a narrow range of reactions and universality—one of the main advantages of the linear free energy treatments—will be lost.

The values of pK' for reaction 1 (Table I) show acceptable correlation with $\sigma_{p\text{-X}}$ constants for $\rho = 3.50$ ($r = 0.92$ for 11 compounds). This indicates that steric effects in the addition of hydroxide ions to benzaldehydes are not predominant when compared with electronic effects. The only substantial deviation from the linear pK'–$\sigma_{p\text{-X}}$ plot was observed for the COO^- grouping, which shows a pK' value 1.5 larger than predicted by the pK'–$\sigma_{p\text{-X}}$ plot and similar to values obtained for branched *o*-alkyl or alkoxy derivatives. As even branched alkyl groups do not show any substantial steric effect on the pK' values, it can be concluded that the deviation results from the effect of aldehydic group on the carboxylate group rather than vice versa. Assumption of steric hindrance of coplanarity of the phenyl and carboxylate groups resulting in a loss of resonance interaction would explain why the change in pK' value due to an *o*-COO^- group is comparable to that caused by *o*-$CH(CH_3)_2$ or *o*-OR groups. Nevertheless, the competing effect of the negative unit charge cannot be excluded.

The correlation of pK' with $\sigma_{o\text{-X}}$ constants derived from the study of ester hydrolysis is comparable, with $\rho = 2.1$ and $r = 0.93$. This might indicate that the steric requirements in the transition state in ester hydrolysis [e.g., in $ArC(O^-)(OH)OR$] are comparable with those in the addition product [Ar-$C(O^-)(OH)H$].

Best correlation has been nevertheless obtained for comparison of pK' values of benzaldehydes with pK_{COOH} of ortho-substituted benzoic acids (Figure 5). Slope 1.25, $r = 0.96$, was obtained for ten compounds (for *o*-CF_3 no pK_{COOH} was found). The value for the ortho-carboxylate derivative was again observed to deviate. The pK' value was about one pK unit smaller than predicted by the pK'–pK_{COOH} plot. In this case it is nevertheless impossible to distinguish whether the deviation is caused predominantly by the steric hindrance in the benzaldehyde or by specific mutual interaction of the carboxylate groups in the second dissociation step of the *o*-phthalic acid. When the values for polysubstituted benzaldehydes reported by Greenzaid[4] (except for the 2,6-disubstituted ones) were included (Figure 5) the slope 1.34 and $r = 0.97$ were obtained. The effect of 2,6 disubstitution mentioned by Greenzaid[4] is probably due to a steric hindrance to coplanarity of the aldehydic group with the phenyl ring.

Greenzaid[4] first reported the linearity of the log K'–log

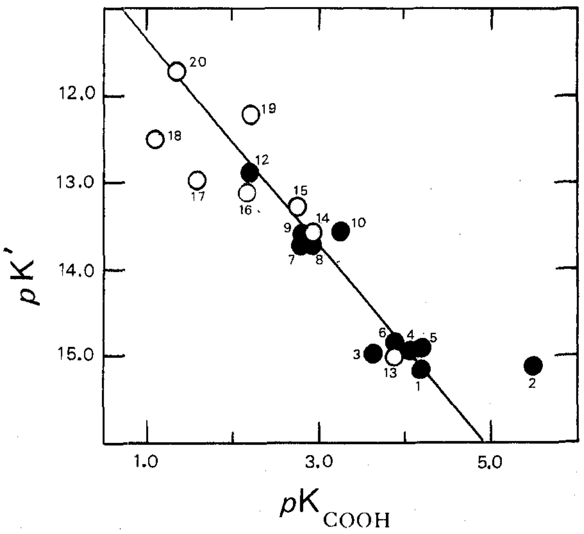

Figure 5. Dependence of pK' values for the addition of hydroxide ions to benzaldehydes on pK_{COOH} values for the corresponding benzoic acids. No. 1–12: our measurements, monosubstituted benzaldehydes, numbering see Table I; no. 13–20, values reported by Greenzaid[4] for 13, *o*-tolualdehyde; 14, *o*-chlorobenzaldehyde; 15, 2,4 dichlorobenzaldehyde; 16, *o*-nitrobenzaldehyde; 17, 2,6-dichlorobenzaldehyde; 18, 2-chloro-4-nitrobenzaldehyde; 19, 2-chloro-5-nitrobenzaldehyde; 20, 2,4 dinitrobenzaldehyde.

K_{COOH} plot for a limited range of substituents, but did not attempt to offer an explanation of the reasons for this correlation. We assume that the basis is the similarity in the steric requirements of the acid [ArC(=O)OH and ArC(=O)H] and the conjugate base [ArC(=O)O$^-$ and ArCH(O$^-$)OH] forms. Any future correlation can be expected only for structurally closely related series.

The differences between our values and the three values reported for monosubstituted ortho derivatives by Greenzaid (Table I) are small for the strongly electronegative, somewhat larger for the more electropositive substituents. This reflects the narrower range of hydroxide concentration over which Greenzaid[4] was able to carry out measurements.

Differences between our values obtained by the overlap procedure and based on J_- function reflect differences in the choice of "anchoring" compounds, which were compounds 7–12 in the overlap procedure, *m*- and *p*-nitro- and cyanobenzaldehydes in the definition of J_- acidity function. Even when the relative values are reliable to ±0.03 pK units, the absolute accuracy is not better than ±0.1 pK unit.

Electrooxidation. Based on a wide range of reaction series it was possible to prove repeatedly[6] that shifts of polarographic half-wave potentials with structure can be correlated with empirical substituent constants in a way analogous to treatments of rate or equilibrium constants. Conditions necessary for such treatment is that mechanism of all compared processes remains identical, that the transfer coefficient obtained from the shape of waves is either the same for all compounds compared or a linear function of the substituent constant involved. Furthermore, all the half-wave potentials compared must be either pH independent, the slope $dE_{1/2}/$dpH must be practically the same, or the slope must be a linear function of the particular substituent constant.

All these conditions are well fulfilled for half-wave potentials of meta- and para-substituted benzaldehydes. Consequently, a linear $E_{1/2}$–$\sigma_{m,p}$-X plot was observed.[5] For ortho-substituted benzaldehydes the values of the transfer coefficient β obtained either from the wave shape or from the $E_{1/2}$–J_- plots varied widely for the substituents studied and were not a simple function of substituent constants $\sigma_{p\text{-X}}$ or $\sigma_{o\text{-X}}$. It is thus not surprising that no linear relationship has been found between the half-wave potentials and either $\sigma_{p\text{-X}}$, $\sigma_{o\text{-X}}$, or pK_{COOH} values.

The overall number of electrons transferred, the region of potentials in which the anodic waves were observed, and the shape of the $E_{1/2}$–pH(J_-) plots for ortho-substituted compounds were similar to those observed for meta- and para-substituted benzaldehydes. It is thus possible to conclude that the overall reaction scheme of the electrooxidation is in both cases similar and that the anion of the geminal diol [ArCH(OH)O$^-$] is the electroactive form.

Nevertheless, the considerable differences in the values of transfer coefficients indicate differences in the electrode process proper. The values of βn_a (Table III) not only vary according to the procedure used in obtaining them, but show variations even inside each group. These differences are smaller for values of βn_a obtained by logarithmic analysis of polarographic waves (Table III), where the majority of the compounds gives βn_a between 1.49 and 1.66, the exception being the unsubstituted compound (βn_a = 0.98), *o*-F (0.97), *o*-Cl (1.26), and *o*-NO$_2$ (1.81). Larger variability of the value of βn_a obtained from shifts of $E_{1/2}$ with J_- seems to indicate formation of three groups: ortho halogens (βn_a = 0.75–0.85), ortho-alkyl substituted compounds together with unsubstituted benzaldehyde (0.51–0.60), and *o*-COO$^-$ and the remaining *o*-OCH$_3$, *o*-OC$_2$H$_5$, and *o*-NO$_2$ (1.07–1.32). The greater sensitivity of the values obtained from $E_{1/2}$–J_- plots seems to indicate that the difference among the ortho derivatives and between the ortho and meta/para derivatives is probably in the hydrogen abstraction step[5] [ArCH(OH)O$^-$ $\rightleftharpoons$ ArCOOH + 2e + H$^+$). Nevertheless, until it is better understood why for some electrode processes the values of βn_a (or αn_a) obtained from shape and half-wave potential shifts are identical whereas for others (like benzaldehyde oxidations) different,[12] such conclusions must remain tentative.

Conclusions

The good structural correlations found for pK_a values and the hydroxide addition reaction and the poor ones found for half-wave potentials of ortho-substituted benzaldehydes indicate that the complication is in the heterogeneous rather than homogeneous component of the electrode process. The indication that steric effects can affect a heterogeneous process at the electrode surface more deeply than a homogeneous process in the solution (even when in a layer adjacent to the electrode) can contribute to investigations of heterogeneous electrode processes.

References and Notes

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