130. *Mechanism of Aromatic Side-chain Reactions, with Special Reference to the Polar Effects of Substituents. Part X. Depolarisation Potentials of* p-*Substituted Benzaldehydes in Acid, Neutral, and Alkaline Media at the Dropping-mercury Cathode.*

By JOHN W. BAKER, W. CULE DAVIES, and (MISS) M. L. HEMMING.

The depolarisation potentials of *p*-R·C_6H_4·CHO (R = H, Me, Et, Pr^{β}, Bu^{γ}, Cl, OMe, NMe_2) in media of various p_H values have been measured polarographically. The order of the depolarisation potentials of the alkyl-substituted benzaldehydes amongst themselves and relative to unsubstituted benzaldehyde is different at different values of p_H.

An explanation of these results is attempted on the basis of the relative magnitudes and importance of the inductive and tautomeric electron-release effects of the alkyl substituents in both the ground and the activated states, Hughes, Ingold, Masterman, and MacNulty's treatment of the energy level being used in a manner similar to that previously applied to other problems (Baker, J., 1939, 1150).

In a recent communication (Baker, J., 1939, 1150) suggestions were advanced which indicated the general lines along which an explanation of the effects of alkyl groups on various aromatic side-chain reactions might be sought. This explanation, made possible by the energy-level treatment of Hughes, Ingold, Masterman, and MacNulty,[*] was based essentially on the possession, by alkyl substituents, of combined polarisation ($+I$, $+M$) and polarisability ($+E$) effects, the relative magnitudes and importance of which are largely dependent upon the intimate requirements of the particular reaction mechanism.

It was accordingly considered to be of interest and importance to investigate the depolarisation potentials of *p*-alkylbenzaldehydes by the polarographic method recently employed by one of us (Davies and Evans, J., 1939, 546) in the study of acetophenone derivatives. It was anticipated that such data would throw light on the effects of distant alkyl substitution on the direct, irreversible addition of hydrogen to the carbonyl double bond. The results of such an investigation are described in this communication and include a study of the effect of the p_H of the medium on the relative ease of electroreduction of various *p*-substituted benzaldehydes.

As before, depolarisation potentials are corrected for the anode potential and finally referred to the datum $E^0_h = 0$. Retention of the method of measurement of the polarograms adopted by Davies and Evans (*loc. cit.*), as opposed to the determination of "half-wave potentials" (Heyrovský and Ilkovič, *Coll. Czech. Chem. Comm.*, 1935, **7**, 198), has been preferred because of the occurrence of adsorption maxima and because its simplicity is advantageous in comparative work. A strictly standardised technique was maintained throughout the whole series of measurements.

Two capillaries were employed as dropping-mercury cathodes: one, which was used in taking measurements only in the ground electrolyte of tetramethylammonium bromide, had a drop speed of 2·8 secs. (in N/10-salt solution); the other, which was used in all other solutions, had a drop speed of 2·0 secs. The temperature was 21° ± 1° throughout.

Table I gives the depolarisation potentials of benzaldehyde in various media, the alcohol content of which was kept as low as possible. Some of the substituted benzaldehydes are not sufficiently soluble in such a medium and the depolarisation potentials of all the aldehydes recorded in Table II were measured in media containing approximately 33% (by volume) of alcohol.

TABLE I.

Depolarisation Potentials of Benzaldehyde.

Vol. of 0·04M-Ph·CHO in alcohol added; c.c.	Ground electrolyte, 20 c.c.	Cell potential, volts.*	Anode potential, volts.		Corrected depolarisation potential, volts.
			Obs.†	Corr.	
4	Buffer, p_H 1·4	− 0·94	0·000	0·336	− 0·60
4	Buffer, p_H 4	(*a*) − 1·33 (*b*) − 1·60	0·062	0·398	− 0·93 − 1·20
4	Buffer, p_H 7	− 1·47	0·058	0·394	− 1·08
4	Buffer, p_H 8	− 1·47	0·036	0·372	− 1·10
2	N/10-KCl	− 1·51	0·000	0·336	− 1·17
2	N/10-NMe_4Br	(*a*) − 1·37 (*b*) − 1·94	− 0·133	0·203	− 1·17 − 1·74
2	N/10-LiOH	− 1·30	− 0·203	0·133	− 1·17

* (*a*) First wave, (*b*) second wave.

† Measured against the N/10-calomel electrode.

An average anode potential, which does not depend appreciably on the particular aldehyde present, is recorded for each medium, and each result is a mean of two or more

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[*] The exigences of the present national emergency have further delayed the publication of this paper, but the present authors are greatly indebted to Prof. C. K. Ingold for his permission to extend the application of his method of treatment to the present results, completed just before the outbreak of war.

TABLE II.

Depolarisation Potentials of p-*Substituted Benzaldehydes*, R·C_6H_4·CHO.

Ground electrolyte.	R =	Cl.	H.	Me.	Et.	Pr$^\beta$.	Bu$^\gamma$.	OMe.	NMe_2.	Anode potential, volts. Obs.*	Anode potential, volts. Corr.
Buffer, p_H 1·4		−0·59	−0·64	−0·66	−0·66	−0·70	−0·67	−0·72	−0·63	−0·008	0·328
Buffer, p_H 4	(*a*)	−0·95	−1·02	−1·035	−1·02	−1·075	−1·05	−1·09	−1·07	0·031	0·367
	(*b*)	−1·24	−1·27	−1·31	−1·315	−1·40	−1·48	−1·39	—		
Buffer, p_H 7		−1·05	−1·14	−1·155	−1·14	−1·115	−1·11	−1·22	−1·175	0·044	0·380
Buffer, p_H 8		−1·11	−1·19	−1·24	−1·22	−1·22	−1·22	—	—	0·034	0·370
N/10-NMe_4Br	(*a*)	−1·12	−1·19	−1·25	−1·24	−1·24	−1·25	−1·31	−1·38	−0·139	0·197
	(*b*)	−1·66	−1·74	−1·96	−1·99	−2·095	−2·11	−2·16	−2·18		
N/10-KCl		−1·14	−1·20	−1·25	−1·26	−1·25	−1·25	−1·30	−1·40	−0·008	0·328

(*a*) First wave, (*b*) second wave.

* Measured against the N/10-calomel electrode.

independent determinations concordant to ± 0·005—0·01 volt. Wave heights are given in Table III (accurate to within 2%).

TABLE III.

Wave Heights (*mm.*) *of* p-R·C_6H_4·CHO *referred to a Galvanometer Sensitivity of* 1/100.

Ground electrolyte.	R =	Cl.	H.	Me.	Et.	Pr$^\beta$.	Bu$^\gamma$.	OMe.	NMe_2.
Buffer, p_H 1·4		57	54	54	50	47	48	65	102
Buffer, p_H 4	(*a*)	58	58	54	51	50	51	63	108
	(*b*)	47	52	50	52	46	43	49	
Buffer, p_H 7		96	96	90	93	87	82	90	(See Fig. 2)
Buffer, p_H 8		67	78	74	67	61	54	88	—
N/10-NMe_4Br	(*a*)	48	47	48	46	44	41	53	52
	(*b*)	48	29	33	35	36	34	27	50
N/10-KCl		52	55	55	50	47	42	58	59

In every case solutions were made by adding 10 c.c. of M/50-aldehyde in alcohol to 20 c.c. of the aqueous ground electrolyte, and about 5 c.c. of the resulting mixture used in taking a polarogram. The buffer solution of p_H 1·4 was a Clark and Lubs standard made by diluting a mixture of 250 c.c. of 0·2M-potassium chloride and 207·5 c.c. of 0·2N-hydrochloric acid to 1 litre. The others were McIlvaine's standards made by mixing the following quantities of the components:

	p_H 4.	p_H 7.	p_H 8.
0·2M-Na_2HPO_4, c.c.	96·4	205·9	243·1
0·1M-Citric acid, c.c.	153·6	44·1	6·9

Rapidity of measurement was essential in the aqueous-alcoholic mixture containing the p_H 8 buffer, since early salt crystallisation set in.

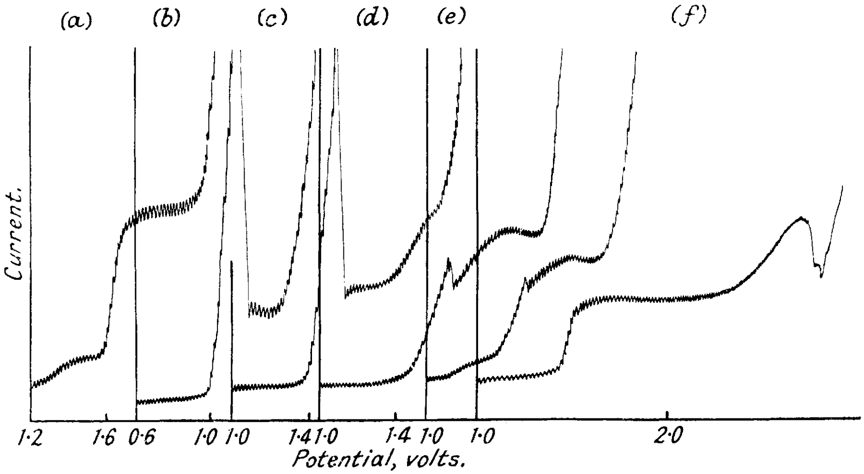
Immediately after the aldehyde from a sealed tube had been weighed out and its solution in alcohol prepared, the mixtures in the various ground electrolytes were made up, and the polarograms taken, and completed within 1—1·5 hours of opening the tube of aldehyde. The solutions were electrolysed exposed to the air. The quantity of aldehydic oxidation product present was, therefore, likely to be very small. Its presence, however, can sometimes be detected [see Fig. I (*e*), small wave immediately before the aldehyde wave].

The general appearance of the polarograms of the aldehydes is clear from Fig. 1. In strongly acid solution, buffered at p_H 1·4, a single wave is obtained. In a buffer of p_H 4, two waves of almost equal height, and of total height approximately twice that of the single wave observed in the buffer of p_H 1·4, are obtained. In the buffer solutions of p_H 7 and 8 single waves of height a little less than the total height of the double wave obtained in the solution of p_H 4 are given. A single wave, of height equal to that of the single wave in the strongly acid solution, is obtained in potassium chloride solution. In tetramethylammonium bromide solution a double wave is obtained: the first wave is a little shorter than the first waves of the other solutions, but the second wave is distinctly shorter. This decrease is possibly due to the increase in drop speed of the mercury from the capillary, which occurs when the voltage applied across the cell is proceeding beyond 2 volts; it seems unlikely that it indicates some change in the quantity of electricity required in the second stage of the reduction of the aldehyde. In spite of the very rapid drop rate above 2 volts, the polarograms obtained were accurately reproducible.

Aromatic aldehydes are, therefore, reduced electrically in two stages, and each stage requires 1 faraday per mol. (Tokuoka, *Coll. Czech. Chem. Comm.*, 1935, **7**, 392; and Table III). The non-occurrence of the second waves in the solutions of the aldehydes in potassium chloride and in a medium of p_{H} 1·4 is explained by the proximity of the potentials characterising the second stage of the aldehyde reduction and those of the deposition of potassium or hydrogen ion, respectively, in these solutions. The waves due to the deposition of the latter elements are, therefore, coincident with the wave due to the second stage of the reduction of the aldehyde. The single wave obtained in the solutions of p_{H} 7 and 8 is due to the small difference in the depolarisation potentials of the two stages of reduction of the aldehyde in these solutions; no separation of the waves, therefore, results.

FIG. 1.

Polarograms of p-tert.-*Butylbenzaldehyde.*



10 *C.c. of* M/50-p-tert.-*butylbenzaldehyde (in alcohol) in* 20 *c.c. of ground electrolyte. Ground electrolyte:* (*a*) N/10-*potassium chloride,* (*b*) *buffer* p_{H} 1·4, (*c*) *buffer* p_{H} 4, (*d*) *buffer* p_{H} 7, (*e*) *buffer* p_{H} 8, (*f*) N/10-*tetramethylammonium bromide. Galvanometer sensitivity,* 1/200, *except in* (*a*), *where it is* 1/100.

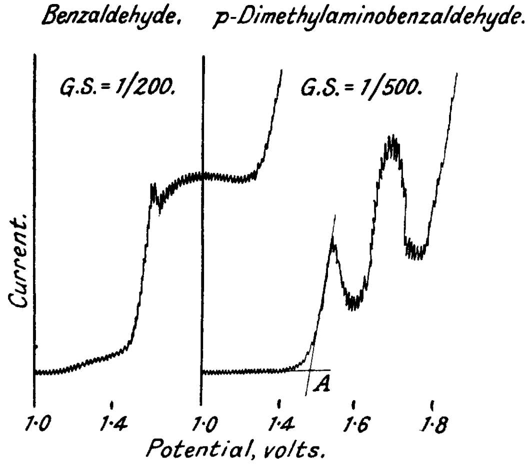
Adsorption Maxima.—No adsorption maxima occur in the polarograms of solutions of *p*-chlorobenzaldehyde, or with any of the aldehydes in neutral salt solutions. In the buffer solutions of p_{H} 7 and 8 (see Fig. 1) small maxima are produced. *p*-*iso*Propylbenzaldehyde gives a large maximum in the solution of p_{H} 1·4 and a slightly smaller one on the head of the first wave in the solution of p_{H} 4. *p*-*tert.*-Butylbenzaldehyde behaves similarly, but the maxima are still greater. The addition of a small amount of aqueous sodium methyl-red satisfactorily suppresses the maxima, and the depolarisation potentials are unaffected.

p-Dimethylaminobenzaldehyde gave slightly different polarograms from those of the other aldehydes in certain of the media. In the solution of p_{H} 1·4, the wave obtained (there is some indication of separation into two waves) is twice the height of that given by the other aldehydes, which suggests that the potentials at which the two stages of electrolytic reduction of this aldehyde occur are almost identical and less negative than the deposition potential of hydrogen ion. In the medium of p_{H} 4 the separation of the two waves is indistinct. The polarogram of the aldehyde in a medium of p_{H} 7 (Fig. 2) cannot be readily explained. The maxima are not suppressed by the addition of sodium methyl-red. The potential at A was taken as that at which the normal first stage of reduction takes place.

Polarograms of the type obtained by Tachi (*Mem. Coll. Agric. Kyoto*, 1938, No. 42, 16) with weak bases (*e.g.*, pyridine) were not obtained here.

Buffering.—When investigating the influence of p_H of the medium on the electroreduction of an organic compound, it is of great importance that the buffering should be adequate, in order that the p_H–depolarisation potential curves should be smooth, and not show peculiar inflections in the neighbourhood of neutrality (Müller, *Chem. Reviews*, 1939, **24**, 107). The proportion of buffer to aldehyde used in the present work is not as great as Müller suggests is generally desirable, but it is felt that it is adequate for the reduction of benzaldehyde and its derivatives. The actual amount of aldehyde reduced, and hence the amount of H$^+$ used or OH$^-$ produced at the cathode during the electrolysis, is exceedingly small. Therefore, if we only consider changes produced by the actual electrolysis, the buffer capacity employed by us is exceptionally high. The possibility of some change in the organic compound in solution, irrespective of the electrolysis, cannot be excluded and might demand still further buffering, but such complications are not expected to be important with the aldehydes studied.

FIG. 2.



10 *C.c. of* M/50-*benzaldehyde or* p-*dimethylaminobenzaldehyde in alcohol and* 20 *c.c. of McIlvaine's citric acid–phosphate buffer,* $p_H = 7$.

DISCUSSION.

The depolarisation potentials of benzaldehyde have been measured by a number of investigators. Values are recorded in lithium chloride, and in mixtures of lithium chloride with lithium hydroxide or hydrochloric acid (Semerano and de Ponte, *Gazzetta*, 1932, **62**, 991), in ammonium chloride and in hydrochloric acid (Semerano and Chisini, *ibid.*, 1933, **63**, 802, who also examined the influence of nuclear substituents, *o*-, *m*-, *p*-Cl and CH_3, *o*-OH, and *p*-OCH_3, on the potential). Winkel and Proske (*Ber.*, 1936, **69**, 693, 1917; 1938, **71**, 1785) also gave results in ammonium chloride solution for benzaldehyde and for *p*-chloro- and *p*-methoxy-benzaldehyde, and Adkins and Cox (*J. Amer. Chem. Soc.*, 1938, **60**, 1151) for benzaldehyde and its *p*-methoxy-derivative in tetramethylammonium chloride. The method of measurement of the polarograms and the conditions used by these investigators are generally so diverse that no useful purpose would be served in comparing their numerical results with those now obtained. The most complete investigation of the polarographic waves given by benzaldehyde was conducted by Tokuoka (*loc. cit.*), but detailed potential measurements were not recorded. Tokuoka's work is now fully confirmed.

A quantitative study of the electroreduction of benzaldehyde under different experimental conditions was made by Law (J., 1906, **89**, 1512; 1521; 1907, **91**, 748). He isolated hydro- and *iso*hydro-benzoin from an alkaline medium, and benzyl alcohol, stilbene, and benzene from an acid medium. The earlier workers employing the dropping-mercury cathode dealt only with the first wave of the reduction of benzaldehyde, and considered that hydrobenzoin was the final reduction product. Semerano and de Ponte (*loc. cit.*) assume that in acid solution the reduction is by primarily deposited hydrogen (compare Haber, *Z. physikal. Chem.*, 1900, **32**, 193):

$$H^+ + e \longrightarrow H;\ 2Ph{\cdot}CHO + 2H \longrightarrow Ph{\cdot}CH(OH){\cdot}CH(OH)Ph$$

but that in neutral or alkaline solution the reduction is by alkali metal

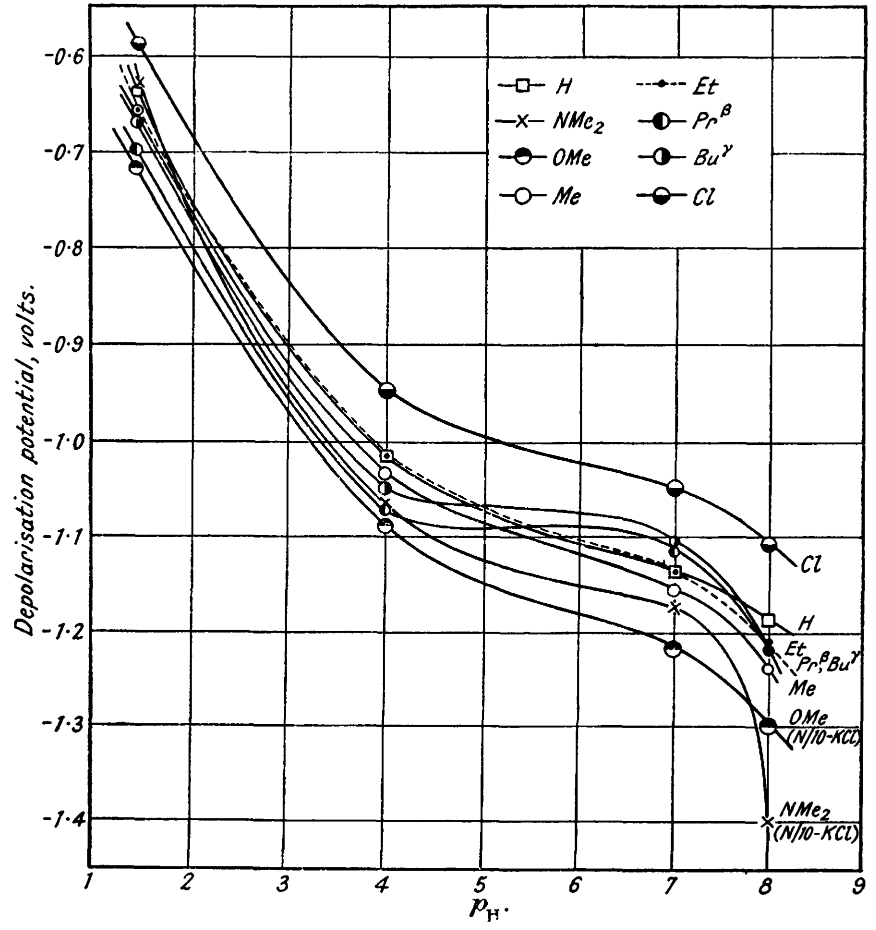
$$Li^+ + e \longrightarrow Li;\ 2Ph{\cdot}CHO + 2Li + 2H_2O \longrightarrow Ph{\cdot}CH(OH){\cdot}CH(OH)Ph + 2LiOH$$

The more complete work of Tokuoka (*loc. cit.*) assumes that the first wave corresponds to reduction of benzaldehyde by primarily deposited hydrogen to a radical, which may then yield hydrobenzoin :

$$\mathrm{H^+} + e \longrightarrow \mathrm{H};\quad \mathrm{H} + \mathrm{Ph{\cdot}CHO} \longrightarrow \mathrm{Ph{\cdot}\overset{|}{C}H(OH)}$$

He considered that the second stage led to benzyl alcohol. Since it took place in neutral and alkaline media, and in tetramethylammonium salts, it does not necessarily involve the deposition of hydrions or of alkali metal, a conclusion confirmed by our new data.

FIG. 3.



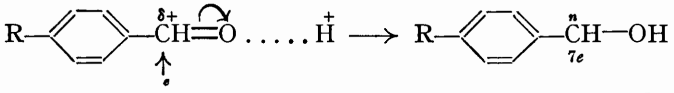
Depolarisation potentials of p-$\mathrm{R{\cdot}C_6H_4{\cdot}CHO}$ *at various values of* p_{H}.

These confirm that the electrolytic reduction of the benzaldehydes at a dropping-mercury cathode takes place in two stages. The first stage, which occurs in acid and neutral solutions, requires one faraday and one atom of hydrogen per molecule of aldehyde. The second stage requires a further one faraday per mol. and this occurs not only in acid and neutral, but also in alkaline media.

It was originally hoped that the reaction would involve one of the simplest types of direct irreversible addition to the carbonyl bond, *viz.*, the addition of hydrogen, but inspection of the depolarisation potentials given in Table II indicates that no simple interpretation of the data is likely to be satisfactory. A possible clue to the complexity emerges from a study of the form of the first-stage depolarisation potential-p_{H} curves plotted in Fig. 3.

Previous evidence (cf. Davies and Evans, *loc. cit.*, and references there cited) suggests that the electrolytic reduction of carbonyl compounds is facilitated (*i.e.*, the potential is made less negative) by electron recession from the seat of addition. This conclusion is further substantiated by two of the curves in Fig. 3. At all values of p_H the depolarisation potentials of *p*-chlorobenzaldehyde ($-I$ effect of chlorine) are uniformly smaller, and those of *p*-methoxybenzaldehyde ($+T$ effect of OMe group) are uniformly larger, than those of unsubstituted benzaldehyde itself. A more complicated result is found in the case of the *p*-alkyl-substituted benzaldehydes. The curves for the Pr^{β} and the Bu^{γ} derivative lie below that of benzaldehyde in the acid region up to about p_H 5, at which point they cross the benzaldehyde curve and lie above it until round about the neutral point. At about p_H 7·5 they again cross the curve of the unsubstituted parent, and in a medium of p_H 8 they possess larger depolarisation potentials than does benzaldehyde itself; *i.e.*, the order of the depolarisation potentials of the *p*-alkylbenzaldehydes amongst themselves and relative to unsubstituted benzaldehyde depends on the p_H of the medium. Such behaviour recalls the alteration of the position of the 2 : 4-dinitro-substituent in the relative velocities of reaction between pyridine and substituted benzyl bromides with change in the character of the medium (Baker and Nathan, J., 1935, 1841), and is usually indicative of a mechanism which involves two factors of opposite polar requirements, either of which may be of dominating importance according to the experimental conditions. On this basis the following mechanism of the electrolytic reduction is tentatively suggested: it differs rather from earlier suggestions of other workers (briefly noted above) and even from the ideas put forward by Davies and Evans (*loc. cit.*).

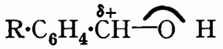
The general over-all mechanism of the first-stage reduction may be represented thus:



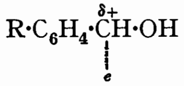
The two factors of opposite polar requirements are: (1) polarisation $\overset{\curvearrowright}{C{=}O}$ of the carbonyl group and the supplementary attachment of a proton from the medium (facilitated by an accession of electrons); (2) attraction of an electron from the cathode (facilitated by recession of electrons from carbonyl carbon). Superimposed upon these requirements will be the variable operation of the polarisation and polarisability effects of the *p*-substituent according to the polar requirements of the actual process involved in the measurement of the depolarisation potential under any particular reaction conditions. An attempt has been made to effect a qualitative analysis and superimposition of these variable factors on the same lines as those previously applied to the prototropy of the methyleneazomethine system and the acid-catalysed prototropy of phenyl alkyl ketones (Baker, *loc. cit.*). For this purpose the depolarisation potential may be regarded as a measure of the activation energy of the reaction, *i.e.*, the difference in energy levels between the requisite ground and activated states of those entities actually involved in the first stage of the electrolytic reduction. The purely arbitrary units employed to represent the magnitudes of electron-release are based on those previously used in the discussion of the dipole moments of alkylbenzenes (*loc. cit.*). Three types of reaction conditions are considered: (1) in strongly acid, (2) in neutral, and (3) in slightly alkaline media.

Case 1. *In acid medium* p_H 1·4. In the presence of high concentrations of hydrions it is suggested that proton addition to the carbonyl group occurs rapidly and reversibly and that it precedes the attachment of the complex (I) to the cathode and the subsequent withdrawal of an electron. If the observed depolarisation potential is concerned with the later stage the above complex would represent the ground state of the reacting entity. Its

(I.)



$R{\cdot}C_6H_4{\cdot}\overset{\delta+}{C}H\overset{\frown}{-O}\ H$



$R{\cdot}C_6H_4{\cdot}\underset{\overset{|}{e}}{\overset{\delta+}{C}}H{\cdot}OH$

(II.)

ease of formation and stability would be increased by electron accession from the *p*-alkyl substituent, especially by the tautomeric mechanism, and hence in assigning the arbitrary energy levels the inductve effect has been slightly, and the tautomeric effect substantially, increased (Table IV). The activated complex through which actual withdrawal of an electron from the cathode occurs would then be of the type (II). The main polar effect of the *p*-substituent would be its ability to increase or decrease the positive charge on the carbonyl carbon. Since the withdrawal of an electron from the cathode would be hindered by electron-accession to the side chain, it is presumed that both the inductive and especially the tautomeric electron-release effects of alkyl substituents would be reduced in the activated complex. Arbitrary values, but qualitatively of correct relative magnitudes, are tabulated in Table IV. The differences in the last column are a measure of the change in the magnitude of the depolarisation potential relative to that of unsubstituted benzaldehyde, taken as a reference standard. A positive sign represents an increase and a negative sign a decrease in the depolarisation potential. The values arbitrarily assigned to Cl and OMe are based on the known strong $- I$, $+ T$ effect of the former and the weak $- I$, strong $+ T$ effect of the latter.

TABLE IV.

Relative energy levels in the ground and activated states in the electrolytic reduction of $R{\cdot}C_6H_4{\cdot}CHO$ in acid medium.

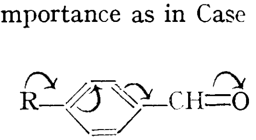
	Ground state.			Activated state.			Diff.
R.	$+I$.	$+T$.	Total (E_g).	$+I$.	$+T$.	Total (E_a).	($E_g - E_a$).
Cl	−170	+70	−100	−100	+45	−55	−45
Me	10	60	70	7	35	42	+28
Et	52	40	92	38	24	62	+30
Pr^β	78	20	98	55	11	66	+32
Bu^γ	98	0	98	70	0	70	+28
OMe	−7	100	93	−3	50	47	+46

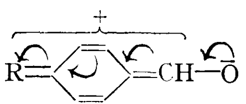
The order of increasing depolarisation potential thus predicted would be

p-Cl $<$ H $<$ Me $=$ $Bu^\gamma \approx$ Et $<$ Pr^β $<$ OMe, whereas the observed order is
p-Cl $<$ H $<$ Me $\approx$ $Bu^\gamma \approx$ Et $<$ Pr^β $<$ OMe.

Case 2. *In a medium approaching neutrality.* As the concentration of hydrions is reduced, proton-catalysis of the carbonyl group polarisation will be rendered increasingly difficult, and a stage may be reached when the depolarisation potential will be determined by the attraction of the polarised aldehyde molecule to the cathode and abstraction therefrom of an electron *prior* to the subsequent addition of a proton, which might need to be abstracted from a neutral solvent molecule by the negatively charged ion first produced. On this assumption the ground state would be the ordinary aldehyde molecule (III). The stabilising effect of both the $+ I$ and the $+ T$ effect of the alkyl group R should be of the same relative importance as in Case 1 but of smaller magnitudes owing to the decreased

(III.)





(IV.)

polarisation of the carbonyl group in the absence of proton catalysis. The activated molecule would be one in which the electron distribution approaches that represented by the structure (IV), and the polar effect of R should again be restricted to its stabilising effect on the positive charge The magnitude of the inductive component would probably remain almost unchanged, but a greater reduction of the tautomeric component (than that assumed in Case 1) would be anticipated because of the opposing $+ T$ effect of the negative charge on the oxygen, which, in this case, has not been neutralised by proton addition. The arbitrary values assigned to each effect and the resultant effect on the depolarisation potentials are tabulated in Table V.

The order of increasing depolarisation potential would thus be

p-Cl $<$ Bu^γ $<$ Pr^β $<$ H $\approx$ Et $<$ Me $<$ OMe : the experimental order is
p-Cl $<$ Bu^γ $<$ Pr^β $<$ H $=$ Et $<$ Me $<$ OMe.

Case 3. *In slightly alkaline or neutral salt solution.* In alkaline media the hydrion concentration will have been reduced almost to zero and thus this case represents the limit to which the conditions depicted in Case 2 approach. The ground and the activated states would thus be the same as in Case 2, and the general magnitudes of the inductive and tautomeric effects should also be similar but probably further reduced owing to the complete removal of proton catalysis of the polarisation of the carbonyl group. Such further reductions have been assumed in assigning the arbitrary values given in Table VI.

TABLE V.

Relative energy levels in the ground and the activated state in the electrolytic reduction of $R{\cdot}C_6H_4{\cdot}CHO$ in neutral medium.

	Ground state.			Activated state.			
R.	$+I$.	$+T$.	Total.	$+I$.	$+T$.	Total.	Diff.
Cl	-160	$+60$	-100	-100	$+42$	-58	-42
Me	6	45	51	7	30	37	$+14$
Et	30	30	60	38	20	58	$+2$
Pr^{β}	47	15	62	55	10	65	-3
Bu^{γ}	60	0	60	70	0	70	-10
OMe	-6	75	69	-3	45	42	$+37$

TABLE VI.

Relative energy levels in the ground and activated states in the electrolytic reduction of $R{\cdot}C_6H_4{\cdot}CHO$ in alkaline medium.

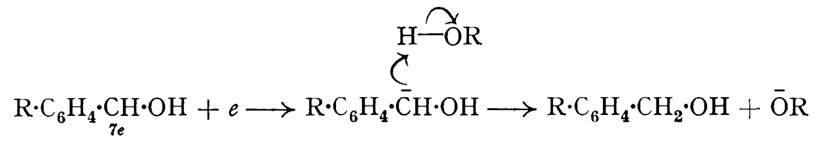
	Ground state.			Activated state.			
R.	$+I$.	$+T$.	Total.	$+I$.	$+T$.	Total.	Diff.
Cl	-160	$+50$	-110	-90	$+30$	-60	-50
Me	6	40	46	5	20	25	$+21$
Et	30	26	56	27	14	41	$+15$
Pr^{β}	47	13	60	39	7	46	$+14$
Bu^{γ}	60	0	60	47	0	47	$+13$
OMe	-6	$+70$	64	-3	35	32	$+32$

This predicts an order of increasing depolarisation potentials

p-Cl $<$ H $<$ $Bu^{\gamma} \approx Pr^{\beta} \approx$ Et $<$ Me $<$ OMe : the experimental order is
p-Cl $<$ H $<$ $Bu^{\gamma} = Pr^{\beta} =$ Et $<$ Me $<$ OMe.

The position of *p*-dimethylaminobenzaldehyde in these series has intentionally been omitted from the above discussion since the ionogenic character of the NMe_2 group further complicates the position. In strongly acid media incipient salt formation will convert it into an electron-attracting substituent $-\overset{\delta+}{N}Me_2 \ldots . H$. In agreement with this the depolarisation potential of *p*-dimethylaminobenzaldehyde in the medium of p_H 1·4 lies between those of the *p*-chloro-derivative and unsubstituted benzaldehyde. With successive reduction in the acidity of the medium the group will alter its character and exhibit the usual electron-release effects of a free $-NMe_2$ group, and the strong $+T$ effect of tervalent nitrogen will increase the depolarisation potential. Fig. 3 shows that the curve for *p*-dimethylaminobenzaldehyde crosses that of benzaldehyde itself at about p_H 2·5 (but still lies above that of the *p*-Me compound until p_H 7·5), but in alkaline medium (p_H 8) it has the largest depolarisation potential of all the derivatives examined, in agreement with the usual order of increasing $+T$ effect : $CR_3 \ll OMe < NMe_2$.

Second-stage Reduction of the Aldehyde.—The product of the second-stage reduction is almost certainly the corresponding benzyl alcohol. Hydrobenzoin is stated (Semerano and Chisini, *Gazzetta*, 1936, **66**, 510) not to be reducible at a dropping-mercury cathode, and it is thus improbable that it is the intermediate product of the first stage of the reduction of benzaldehyde. The mechanism already suggested requires the neutral radical $R{\cdot}C_6H_4{\cdot}\overset{\odot}{C}H{\cdot}OH$ as the initial product : its further reduction to benzyl alcohol would follow by the abstraction of a second electron from the cathode to give a negatively charged ion which, by withdrawal of a proton from the medium, would afford benzyl alcohol:

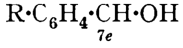


$$R{\cdot}C_6H_4{\cdot}\underset{7e}{CH}{\cdot}OH + e \longrightarrow R{\cdot}C_6H_4{\cdot}\bar{C}H{\cdot}OH \longrightarrow R{\cdot}C_6H_4{\cdot}CH_2{\cdot}OH + \bar{O}R$$

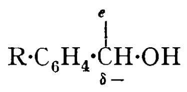
The second wave is observed at p_H 4, but at certain values of p_H (*e.g.*, p_H 7) the depolarisation potentials of both stages might be at the same voltage, and thus a single wave, but of twice the height of the first stage wave, is found.

The ground state (V) and the activated state (VI) for this process are of the same types as in Case 1, except that the carbon at the seat of reaction is either neutral or negatively charged instead of carrying a small positive charge. The respective contributions of the

(V.)



$$R{\cdot}C_6H_4{\cdot}\underset{7e}{CH}{\cdot}OH$$



$$R{\cdot}C_6H_4{\cdot}\underset{\delta-}{\overset{e}{CH}}{\cdot}OH$$

(VI.)

inductive and tautomeric effects of R should thus bear the same ratio to each other as in Case 1 but will all be somewhat reduced because of the absence of the $\delta +$ charge on the side chain. The arbitrary values assigned in Table VII are computed on this basis.

TABLE VII.

Relative energy levels in the ground and the activated state in the (second-stage) electrolytic reduction of $R{\cdot}C_6H_4{\cdot}\underset{7e}{CH}{\cdot}OH$.

	Ground state.			Activated state.			
R.	$+I$.	$+T$.	Total.	$+I$.	$+T$.	Total.	Diff.
Cl	−150	+50	−100	−90	+43	−47	−53
Me	7	40	47	5	32	37	+10
Et	38	26	64	25	22	47	+17
Pr^{β}	55	13	68	40	10	50	+18
Bu^{γ}	70	0	70	50	0	50	+20
OMe	−6	+80	74	−2	+46	44	+30

The predicted order of depolarisation potentials for the second stage of the reduction is thus $Cl < H < Me < Et < Pr^{\beta} < Bu^{\gamma} < OMe$, in agreement with that observed experimentally in neutral-salt solution.

It is evident, therefore, that over the whole range of p_H 1·4—8 the experimental results may be explained on the basis of the suggested mechanism of electrolytic reduction combined with certain arbitrary assumptions concerning the relative magnitudes and importance of the polarisation and polarisability effects of the *p*-substituent. Except that such assumptions adhere rigidly to the correct *relative* order of magnitudes of such polar effects amongst the substituent groups themselves, no *numerical* significance is, of course, attached to the actual values used.

EXPERIMENTAL.

Preparation of Materials.—Benzaldehyde. A pure sample, free from benzoic acid (Messrs. British Drug Houses, Ltd.), was again purified through its bisulphite derivative, and the product was repeatedly fractionally distilled in a vacuum to give, finally, a specimen of b. p. 73°/21 mm. All operations involving the free aldehyde were effected in an atmosphere of carbon dioxide.

p-*Methylbenzaldehyde.* A commercial sample similarly purified had b. p. 98°/24 mm.

p-*Ethylbenzaldehyde.* *p*-Ethylbenzyl chloride (36 g.), b. p. 95—99°/13 mm., prepared by Sommelet's method (*Compt. rend.*, 1913, **157**, 445), was oxidised by refluxing with an equimolecular proportion of hexamethylenetetramine in 800 c.c. of 60% alcohol on the steam-bath for 2 hours (*idem, ibid.*, p. 852), a current of carbon dioxide being passed through the solution all the time. After removal of the alcohol by distillation, the mixture was steam-distilled (carbon dioxide stream), the distillate was extracted with ether and washed with sodium bicarbonate solution. The aldehyde obtained from the dried ethereal extract was purified, first through its bisulphite derivative and then through its semicarbazone (m.p. 205°), being regenerated from the latter by steam distillation with aqueous oxalic acid and finally fractionated under reduced pressure (current of nitrogen) to give the pure aldehyde, b. p. 64·2°/1·2 mm.

p-iso*Propylbenzaldehyde.* This was isolated as its bisulphite derivative from the fraction of cumin oil, b. p. >200°, and the aldehyde so obtained was twice purified through its semicarbazone, m. p. 114·5°, and finally distilled to give a pure sample, b. p. 120°/23 mm.

p-tert.-*Butylbenzaldehyde.* *p-tert.*-Butylbenzyl bromide, b. p. 93—95°/1 mm., prepared as described by Baker and Nathan (J., 1935, 1840), was oxidised by the hexamethylenetetramine method, and the aldehyde so obtained was purified through its semicarbazone, m. p. 200°, as in the case of the *p*-ethyl derivative. Fractional distillation in nitrogen gave a pure sample, b. p. 80°/0·9 mm.

In all cases the pure aldehydes were redistilled under reduced pressure in an atmosphere of nitrogen, and the distillate collected in a small bulb in an all-glass apparatus. This was then filled with nitrogen at atmospheric pressure, and the sample immediately sealed off. These sealed samples were opened immediately before the polarographic measurements, and at once dissolved in the media to make the solutions used. The sample of *p-iso*propylbenzaldehyde became slightly yellow before use, but nevertheless gave a polarogram identical with that of an absolutely colourless sample obtained from it by redistillation in a vacuum.

p-*Dimethylaminobenzaldehyde.* This was a newly-opened specimen of B.D.H. " AnalaR " grade.

p-*Methoxybenzaldehyde.* A purchased sample was repeatedly washed with aqueous sodium carbonate solution and water, dried over sodium sulphate, and twice distilled in a vacuum, b. p. 126°/12 mm.

p-*Chlorobenzaldehyde.* A purchased sample was purified through its semicarbazone, fractionated in a vacuum in a current of nitrogen, and sealed under nitrogen until the measurements were taken.

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