640. *Polarographic Behaviour of Disubstituted Benzenes: Relation of $E_{\frac{1}{2}}$'s to Electron Densities and Activation Energies for Electrophilic Substitution.*

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The polarographic half-wave potentials ($E_{\frac{1}{2}}$) of a number of substituted nitrobenzenes, benzaldehydes, and iodobenzenes have been measured under comparable conditions, and have been correlated with (*a*) electron densities in *o*-, *m*-, and *p*-positions, and (*b*) polarization energies defining the orientating properties of substituents. General agreement was found, and some notable exceptions, *e.g.*, $E_{\frac{1}{2}}$'s for *ortho*-compounds, have been explained by hydrogen-bonding (chelation). The high *para*-yields for anionoid ($-E$) substituents are predicted exceedingly well by $E_{\frac{1}{2}}$ results.

We have investigated the polarographic reduction of a number of *o*-, *m*-, and *p*-disubstituted benzenes, and found variations in the reduction potential ($E_{\frac{1}{2}}$) in each series of *o*-, *m*-, and *p*-derivatives, which appeared to be related to certain properties of the molecule and to the influence one substituent had on the other, one of the substituents being the reducible group. We have already shown (*J.*, 1951, 13) that, whereas the reduction potential of iodobenzene is $-1{\cdot}650$ v (compared with the standard calomel electrode), the $E_{\frac{1}{2}}$'s of *o*-, *m*-, and *p*-iodotoluene are respectively $-1{\cdot}683$, $-1{\cdot}660$, and $-1{\cdot}685$ v. As in every case it is the iodo-group which is being reduced, we assume that the methyl group *o*- or *p*- to the iodine makes the reduction more difficult. This behaviour is explicable if we consider those cases where the methyl group shows its favourable influences on electrophilic substitution in positions *ortho* and *para* to it. Evidently the reduction is the very reverse of this, and involves the *addition* of an electron to the reducible group, and so the methyl group opposes this in the *o*- and the *p*-position.

Although the mechanism of reduction varies a little from molecule to molecule in the number of electrons finally involved, and sometimes shows dependence on the pH of the medium and sometimes does not, we believe in the correctness of our basic assumption, namely, that the relevant step in the process is the addition of an electron to the molecule and that $E_{\frac{1}{2}}$ is a measure of the energy required for this addition. Whether the electron goes into the next higher orbital of the ring itself or into an orbital of the reducible group is not directly ascertainable from any of our results. But $E_{\frac{1}{2}}$ must be proportional to the activation energy necessary to overcome some potential barrier.

Our results might therefore be expected to show some relation (*a*) to electron densities at positions in the ring *ortho*, *meta*, and *para* to some group (Pauling and Wheland, *J. Amer. Chem. Soc.*, 1935, **57**, 2086; Ploquin, *Mem. Soc. Chim. France*, 1948, 640), or (*b*) to activation energies for substitution of hydrogen in the ring by the reducible group (Wheland, *J. Amer. Chem. Soc.*, 1942, **64**, 900; Dewar, *J.*, 1949, 463).

(*a*) Calculations of electron densities in disubstituted benzenes are very difficult, and only approximations can be obtained. In comparing our results with such data, we are aware that we are concerned mainly with differences, and that a constant quantity, the electronic property of the reducible group itself, appears in the calculations in a form modified by the *o*-, *m*-, or *p*-substituent. It seems reasonable therefore to use electron-density data obtained for the single, modifying substituents (Pauling and Wheland, *loc. cit.*).

Differences in $E_{\frac{1}{2}}$ for *o*-, *m*-, and *p*-derivatives can be equated, where possible, to differences in electron densities in the *o*-, *m*-, and *p*-positions.

(*b*) In the theoretical treatment initiated by Wheland (*loc. cit.*) and refined by Dewar (*loc. cit.*) the relevant part of the activation energy required for electrophilic substitution is identified with the π electron-energy difference between XPh and the transition complex XPh Y, in other words, with the energy needed to provide an unshared pair of electrons at the point of attack. Dewar has calculated the electron energies for the three types of substituted benzenes: pure inductive, I; anionoid, $-E$; cationoid, $+E$, with varying δ_x values (δ_x being a parameter, positive or negative in sign, which measures the electronegativity or electropositivity of the substituted atom or group in relation to the carbon atom in benzene). The results of his calculations, represented diagrammatically in his paper, account for *o–p* ratios in reaction yields, and also suggest that the activation energy for any electronic type of substituted benzene can exceed the activation energy for benzene itself (as is required for *deactivating* substituents), provided that a sufficiently high, positive θ is assigned to the substituents.

We have tabulated our results under headings corresponding to the different electronic types of substituent. Where $E_{\frac{1}{2}}$ varies with the pH, we have quoted our results under the varying pH conditions. We have selected the low pH region for comparison, because this is the region where $E_{\frac{1}{2}}$–pH curves of substituted and unsubstituted compounds are approximately parallel and show no complication due to change of mechanism, dissociation equilibria, etc. Comparisons are further possible only when other factors such as the medium, ionic strength, etc., are kept constant, and for these reasons we have had to repeat some of the earlier measurements so as to bring them into line with our own results.

TABLE 1. *Influence of the methyl group* ($E_{\frac{1}{2}}$ *in* v).

Reduction of NO_2	$E_{\frac{1}{2}}$ in aq. NEt_4Br	$E_{\frac{1}{2}}$ in buffers of pH : 1·73	2·25	3·16
$PhNO_2$	0·935	0·326	0·366	0·430
o-$C_6H_4Me{\cdot}NO_2$	1·005	0·358	0·390	0·525
m-$C_6H_4Me{\cdot}NO_2$	0·936	0·305	0·338	0·416
p-$C_6H_4Me{\cdot}NO_2$	1·035	0·336	0·366	0·442

Reduction of CHO	$E_{\frac{1}{2}}$ in aq. NEt_4Br	$E_{\frac{1}{2}}$ in buffers of pH : 1·73	2·25	2·59	3·16
Ph·CHO	1·506	1·000	1·022	1·051	1·088
o-$C_6H_4Me{\cdot}CHO$	1·493	0·962	0·990	1·018	1·062
m-$C_6H_4Me{\cdot}CHO$	1·526	1·000	1·030	1·056	1·092
p-$C_6H_4Me{\cdot}CHO$	1·562	1·020	1·050	1·080	1·106

Reduction of I	$E_{\frac{1}{2}}$ in aq. NEt_4Br
PhI	1·650
o-C_6H_4MeI	1·683

Reduction of I	$E_{\frac{1}{2}}$ in aq. NEt_4Br
m-C_6H_4MeI	1·660
p-C_6H_4MeI	1·685

Influence of the Methyl Group.—The methyl group is considered to be an anionoid inductive (—*I*) substituent in Dewar's treatment (*loc. cit.*). It is known to activate the benzene ring for second substitution and to be *op*-orientating. Experiment shows that it leads to a greater degree of *o*-nitration than of *o*-halogenation. Yields (%) obtained by Holleman (*Chem. Reviews*, 1925, **1**, 187) for nitration and bromination of toluene were :

	ortho	*meta*	*para*
Nitration	56	3·1	40·9
Bromination	39·7	—	60·3

The $E_{\frac{1}{2}}$'s of the *o*- and *p*-methyl compounds are more negative than those of the otherwise unsubstituted compounds, in agreement with the *ortho-para*-activating effect of the methyl group. We notice further that $E_{\frac{1}{2}}$ of *o*-nitrotoluene is more negative than that of *p*-nitrotoluene, whereas *o*- and *p*-iodotoluene have almost equal $E_{\frac{1}{2}}$. Formylation of toluene yields mainly *p*-tolualdehyde, and $E_{\frac{1}{2}}$ of this is also the most negative of the aldehyde series; but the very low $E_{\frac{1}{2}}$ observed for the reduction of *o*-tolualdehyde could be the consequence of some hydrogen-bonding between the aldehyde and the *o*-methyl group.

We tried to apply the electron-density calculations of Pauling and Wheland (*loc. cit.*) for inductive substituents. The following equations are given for the electron densities :

$$Q_x = (1 + 0{\cdot}398\delta_1 - 0{\cdot}315\delta_2)e$$

$$Q_{ortho} = (1 - 0{\cdot}158\delta_1 - 0{\cdot}407\delta_2)e$$

$$Q_{meta} = (1 + 0{\cdot}0093\delta_1 - 0{\cdot}259\delta_2)e$$

$$Q_{para} = (1 - 0{\cdot}1028\delta_1 + 0{\cdot}019\delta_2)e$$

The reduction potentials (v) of the iodotoluenes in relation to iodobenzene are :

	$E_{\frac{1}{2}}$	Relative to PhI
Iodobenzene	−1·650	
o-Iodotoluene	−1·683	−0·033
m-Iodotoluene	−1·660	−0·011
p-Iodotoluene	−1·685	−0·035

If we take the electron density of the unsubstituted iodobenzene to be unity, the differences in $E_{\frac{1}{2}}$ may be considered to be the electron-density differences caused by the substituent in the iodotoluenes :

$$Q_{ortho} = (1 + 0{\cdot}033)e = (1 - 0{\cdot}158\delta_1 + 0{\cdot}407\delta_2)e$$

$$Q_{meta} = (1 + 0{\cdot}011)e = (1 + 0{\cdot}0093\delta_1 - 0{\cdot}259\delta_2)e$$

from which $\delta_1 = -0{\cdot}352$ and $\delta_2 = -0{\cdot}055$.

Substituting these values in the equation for Q_{para}, we obtain for $Q_{para} = (1 + 0{\cdot}035)e$ in agreement with the experimental results.

In Dewar's treatment for (*I*) substituents, the activation energy for negative δ_x values show the decreasing order which corresponds to the increasing order of $E_{\frac{1}{2}}$'s, Unsubst. > *meta* > *para* > *ortho*; the greater the spread, the more negative is δ_x.

The polarographic $E_{\frac{1}{2}}$'s follow this order, but the methyl group must be assigned a more negative δ_x value in conjunction with the nitro-group than with the iodo-group in order to account for its effect on $E_{\frac{1}{2}}$ of the *o*-nitro-group being more pronounced than that on $E_{\frac{1}{2}}$ of the *o*-iodo-group. As the parameter δ_x stands for the electron affinity of the group relative to the electron affinity of the benzene-carbon atom, the numerical value of the negative δ_x is the measure of its electron-releasing power. It is not unreasonable to account for it as such, and to assume that it should release electrons more readily in presence of the very electronegative nitro-group than in presence of the less electronegative iodo-group.

We can see that the polarographic results can be brought into agreement with both the electron-density and polarization-energy treatments. This is not astonishing, as it is known (Sandorfy, Vroeland, Yvan, Chalvet, and Daudel, *Mem. Soc. Chim. France*, 1950, 304) that the two kinds of treatment lead to very similar conclusions for inductive substituents.

Influence of —E *Substituents.*—Nitration is directed by all —*E* substituents to a greater extent in the *p*- than in the *o*-position, the $\frac{1}{2}$*o*–*p* ratios (Dewar, *loc. cit.*) never exceeding unity. This ratio increases in the series Cl, Br, I. The $\frac{1}{2}$*o*–*p* ratio of the nitrodiphenyls is highest of all (0·56). A similar trend can be observed when these substituents affect $E_{\frac{1}{2}}$ of the nitro-group. $E_{\frac{1}{2}}$ of the nitro-group *para* to the activating methoxy-, amino,- and hydroxy-groups is more negative than $E_{\frac{1}{2}}$ for unsubstituted nitrobenzene, and also more negative than $E_{\frac{1}{2}}$ for the *ortho*-disposition, in agreement with the low $\frac{1}{2}$*o*–*p* ratios.

The activating substituents hardly affect $E_{\frac{1}{2}}$ when they are *meta* to the reducible group, but $E_{\frac{1}{2}}$ of *o*-nitrophenol is less negative than that of *m*-nitrophenol, in spite of the *ortho*-yields, being higher than the *meta*-yields when phenol is nitrated.

The deactivating halogens,* and also the phenyl group, lower $E_{\frac{1}{2}}$ of the NO_2 reduction in all positions, but most for the *meta*-position, in agreement with their *op*-directing properties. The increasing $\frac{1}{2}$*o*–*p* ratios (Dewar, *loc. cit.*) in the series Cl, Br, I are reflected in the $E_{\frac{1}{2}}$'s : $p < o$ for iodo- and bromo-nitrobenzene, but $o < p$ for the chloronitrobenzenes. $E_{\frac{1}{2}}$ of 2-nitrodiphenyl is more negative than that of the 4-isomer, in accord with their relatively high $\frac{1}{2}$*o*–*p* ratio.

The overall $E_{\frac{1}{2}}$-lowering produced by the halogens is in the order Cl < Br < I, the reverse of the order of their deactivating influence.

Direct introduction of the CHO group into the substituted benzene ring, when it can be done, and into diphenyl, by the Gattermann–Koch reaction, yield *para*-products exclusively. The $E_{\frac{1}{2}}$'s of all *para*-substituted benzaldehydes are the most negative.

Iodination of aniline, halogeno-benzenes, and diphenyl yield *para*-products almost exclusively, but a large amount of *o*-iodophenol is obtained. The $E_{\frac{1}{2}}$'s of all —*E* substituted iodobenzenes are in the order $o < m < p$. Hydroxy- and amino-groups when *para* to iodine make its reduction more difficult than it is in iodobenzene.

The lower $E_{\frac{1}{2}}$'s of the *o*-halogeno-iodobenzenes and benzaldehydes, compared with the

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* The oft-quoted statement that iodobenzene is nitrated more readily than benzene is surely incorrect. We have repeated the experiment, by a method similar to that of Ingold and Bird (*J.*, 1938, 918), using the polarographic method to estimate the nitrobenzene (NB) and iodonitrobenzene formed (INB) and have found the ratio of the yields INB/NB to be 0·17—0·22.

m-isomers, seem to be in contradiction to the orientating properties of the halogens in their reactions, the *o*-isomer generally being formed in second largest quantities. It must be remembered that halogenations and formylation have to be carried out in the presence of catalysts, and the ratio of isomers formed is influenced by the catalyst. For instance, bromination of bromobenzene at 55° with aluminium chloride as carrier gives 8·3% of *ortho*-, 30·1% of *meta*-, and 61·6% of *para*-isomer (Richter, "Text-Book of Organic Chemistry," 1951, p. 408, John Wiley and Sons, Inc., New York), this order being in agreement with the $E_{\frac{1}{2}}$'s.

TABLE 2. *Anionoid* (—E) *substituents* ($E_{\frac{1}{2}}$ *in* v).

(*a*) *Reduction of* NO_2.

	$E_{\frac{1}{2}}$ in aq.	$E_{\frac{1}{2}}$ in buffers of pH :				$E_{\frac{1}{2}}$ in aq.	$E_{\frac{1}{2}}$ in buffers of pH :		
	NEt_4Br	1·73	2·25	3·16		NEt_4Br	1·73	2·25	3·16
$Ph\cdot NO_2$	0·935	0·326	0·366	0·430	*o*-$NO_2\cdot C_6H_4\cdot OH$	0·990	0·246	0·284	0·362
o-$C_6H_4I\cdot NO_2$	0·816	0·204	0·232	0·306	*m*-$NO_2\cdot C_6H_4\cdot OH$	0·960	0·310	0·350	0·418
m-$C_6H_4I\cdot NO_2$	0·757	0·176	0·214	0·276	*p*-$NO_2\cdot C_6H_4\cdot OH$	1·350	0·408	0·470	0·566
p-$C_6H_4I\cdot NO_2$	0·780	0·194	0·226	0·294	*o*-$NO_2\cdot C_6H_4\cdot NH_2$	1·030	0·372	0·422	0·488
o-$C_6H_4Br\cdot NO_2$	0·860	0·263	0·294	0·396	*m*-$NO_2\cdot C_6H_4\cdot NH_2$	0·935	0·320	0·356	0·422
m-$C_6H_4Br\cdot NO_2$	0·816	0·208	0·238	0·308	*p*-$NO_2\cdot C_6H_4\cdot NH_2$	1·128	0·438	0·476	0·554
p-$C_6H_4Br\cdot NO_2$	0·854	0·230	0·270	0·342	*o*-$C_6H_4Ph\cdot NO_2$	0·928	0·290	0·341	0·412
o-$C_6H_4Cl\cdot NO_2$	0·866	0·256	0·306	0·410	*m*-$C_6H_4Ph\cdot NO_2$	0·844	0·228	0·264	0·348
m-$C_6H_4Cl\cdot NO_2$	0·830	0·222	0·262	0·340	*p*-$C_6H_4Ph\cdot NO_2$	0·854	0·228	0·266	0·342
p-$C_6H_4Cl\cdot NO_2$	0·930	0·292	0·332	0·400					

(*b*) *Reduction of* CHO *group*.

	$E_{\frac{1}{2}}$ in aq.	$E_{\frac{1}{2}}$ in buffers of pH :					$E_{\frac{1}{2}}$ in aq.	$E_{\frac{1}{2}}$ in buffers of pH :			
	NEt_4Br	1·73	2·25	2·59	3·16		NEt_4Br	1·73	2·25	2·59	3·16
$Ph\cdot CHO$	1·506	1·000	1·022	1·051	1·088	*o*-$MeO\cdot C_6H_4\cdot CHO$	1·494	0·960	0·994	1·020	—
o-$C_6H_4I\cdot CHO$	1·248	0·827	0·850	0·876	0·914	*m*-$MeO\cdot C_6H_4\cdot CHO$	1·622	1·080	1·106	1·122	—
m-$C_6H_4I\cdot CHO$	1·390	0·860	0·888	0·912	0·952	*o*-$HO\cdot C_6H_4\cdot CHO$	1·504	1·050	1·070	1·098	1·134
p-$C_6H_4I\cdot CHO$	1·400	0·878	0·912	0·934	0·980	*m*-$HO\cdot C_6H_4\cdot CHO$	1·500	1·008	1·030	1·053	1·098
m-$C_6H_4Br\cdot CHO$	1·358	0·904	0·948	0·986	1·028	*p*-$HO\cdot C_6H_4\cdot CHO$	1·72	1·116	1·146	1·166	1·200
p-$C_6H_4Br\cdot CHO$	1·410	0·918	0·952	0·992	1·032	*o*-$NH_2\cdot C_6H_4\cdot CHO$	—	—	1·030	—	1·090
o-$C_6H_4Cl\cdot CHO$	1·331	0·868	0·895	0·918	0·970	*m*-$NH_2\cdot C_6H_4\cdot CHO$	1·52	0·950	0·974	—	1·030
m-$C_6H_4Cl\cdot CHO$	1·384	0·910	0·950	0·982	1·030	*p*-$NH_2\cdot C_6H_4\cdot CHO$	1·70	1·064	—	—	1·158
p-$C_6H_4Cl\cdot CHO$	1·422	0·952	0·976	1·006	1·050						

(*c*) *Reduction of iodo-group in* $C_6H_4R\cdot I$ *in aq.* NEt_4Br ($E_{\frac{1}{2}}$ *for* PhI = 1·65).

R	*o*-	*m*-	*p*-	R	*o*-	*m*-	*p*-	R	*o*-	*m*-	*p*-
I	1·235	1·38	1·46	Br	1·30	1·43	1·53	Cl	1·34	1·45	1·54
HO	1·49	1·62	1·685	NH_2	1·56	1·66	1·72				
o-C_6H_4PhI			1·48	*m*-C_6H_4PhI			1·56	*p*-C_6H_4PhI			1·585

(*d*) *Relation between* $E_{\frac{1}{2}}$ *and activation* (*polarization*) *energies* (*Dewar*).

Substituent	Reducible group	Relative $E_{\frac{1}{2}}$	Estimated δ_x	Relative activation energies for δ_x
NH_2	NO_2	$m \ll \text{unsubst.} < o < p$	1·3	$m > \text{unsubst.} > o > p$
	CHO	$m < \text{unsubst.} < o < p$	1·4	$m > \text{unsubst.} > o > p$
	I	$o < \text{unsubst.} < m < p$	1·7	$m > o > \text{unsubst.} > p$
HO	NO_2	$o < m < \text{unsubst.} < p$	1·5 (?)	$m > o > \text{unsubst.} > p$
	CHO	$\text{unsubst.} \ll m < o < p$	1·4	$m > \text{unsubst.} > o > p$
	I	$o < m < \text{unsubst.} < p$	1·7	$m > o > \text{unsubst.} > p$
Ph	NO_2	$m \ll p < o < \text{unsubst.}$	1·8	$m > o > p > \text{unsubst.}$
	I	$o < m < p < \text{unsubst.}$	2·2	$o > m > p > \text{unsubst.}$
Cl	NO_2	$m < p < o < \text{unsubst.}$	1·8	$m > o > p > \text{unsubst.}$
	CHO	$o < m < p < \text{unsubst.}$	2·2	$o > m > p > \text{unsubst.}$
	I	$o < m < p < \text{unsubst.}$	2·3	$o > m > p > \text{unsubst.}$
Br	NO_2	$m < p < o < \text{unsubst.}$	1·9	$m > o > p > \text{unsubst.}$
	CHO	$m < p < \text{unsubst.}$	2·2	$m > p > \text{unsubst.}$
	I	$o < m < p < \text{unsubst.}$	2·3	$o > m > p > \text{unsubst.}$
I	NO_2	$m < p < o < \text{unsubst.}$	2·0	$m > o > p > \text{unsubst.}$
	CHO	$o < m < p < \text{unsubst.}$	2·3	$o > m > p > \text{unsubst.}$
	I	$o < m < p < \text{unsubst.}$	2·4	$o > m > p > \text{unsubst.}$

The iodo-phenols and -anilines have $E_{\frac{1}{2}}$'s dependent on pH; the order of ease of reduction is, however, the same as in aq. NEt_4Br over the whole pH scale, apart from the very alkaline pH regions where the phenolic hydroxyl group is dissociated.

The most striking exception to the general parallel between electrophilic substitution and polarographic reduction is the part played by the *o*-hydroxy-group. The $E_{\frac{1}{2}}$'s of *o*-nitro- and *o*-iodo-phenol are the lowest among the isomers, whilst the yields of *ortho*-isomers on nitration and iodination of phenol are fairly high. This is probably caused by hydrogen-bonding of the nitro-group and iodine atom with the *o*-hydroxy-group, which could be responsible for the unexpectedly low $E_{\frac{1}{2}}$'s and perhaps account for the high *ortho*-yields (de la Mare, *J.*, 1949, 2871).

Polarographic results do not agree with calculations of electron densities in the positions *ortho, meta*, and *para* to $-E$ substituents, as these calculations lead either to unity in the case of the *meta*-position (Sandorfy, Vroelant, *et al., locc. cit.*) or to highest electron densities in the *ortho*-positions, exceeding unity even for the halogens (Jaffé, *J. Chem. Phys.*, 1952, **20**, 279). The $E_{\frac{1}{2}}$'s, however, do follow the trend indicated by Dewar's polarization-energy calculations for isomeric substituted benzenes (*loc. cit.*).

We have listed in Table 2*d* the δ_x values by means of which the calculated polarization energies for the substituted benzenes and for benzene (2·54 β) follow best the opposite order of the $E_{\frac{1}{2}}$'s. It will be noticed that the value of δ_x which allows this agreement varies with each substituent in its relation to the reducible group in the molecule. The shift is in the *same sense* as that already shown with respect to the methyl group, *i.e.*, the positive δ_x is *smaller* when the substituent affects the more electronegative nitro-group than when it affects the less electronegative CHO and iodo-group.

The parallel would be better still if the calculated polarization energies for the *meta*-positions were somewhat lower for all δ_x values, a requirement indicated by other experimental evidence and best summarized in the negative sign of Hammett's σ value for the *m*-amino-group.

The order of electronegativity of $-E$ substituents from their effect on $E_{\frac{1}{2}}$ would be $NH_2 < OH < OMe < Ph < Cl < Br < I$.

Influence of +E *Substituents.*—$+E$ Substituents deactivate the benzene ring for a second substitution. They cause nitration to occur mainly in the *meta*-position, but sometimes fairly high yields of *ortho*-compounds are obtained, *e.g.*, *o*-nitrobenzoic acid (18·5%) and ethyl *o*-nitrobenzoate (28·3%) (Hollemann, *loc. cit.*). Yields of *para*-compounds are always the lowest.

TABLE 3. *Cationoid* (+E) *substituents. Reduction of* NO_2.

	$E_{\frac{1}{2}}$ in aq.	$E_{\frac{1}{2}}$ in buffers of pH :		
	NEt_4Br	1·73	2·25	3·16
$Ph{\cdot}NO_2$	0·935	0·326	0·366	0·430
o-$C_6H_4(NO_2)_2$	0·570[1]	0·134[1]	0·168[1]	0·230[1]
m-$C_6H_4(NO_2)_2$ ...	0·684	0·145	0·187	0·266
p-$C_6H_4(NO_2)_2$ ...	0·436	0·082	0·102	0·158
o-$NO_2{\cdot}C_6H_4{\cdot}CHO$	0·690[2]	0·228[2]	0·286[2]	0·346[2]
m-$NO_2{\cdot}C_6H_4{\cdot}CHO$	0·822	0·257	0·296	0·380
p-$NO_2{\cdot}C_6H_4CHO$	0·632	0·174	0·220	0·322
o-$NO_2{\cdot}C_6H_4{\cdot}CO_2Et$	0·826	0·282	0·313	0·400
m-$NO_2{\cdot}C_6H_4{\cdot}CO_2Et$	0·850	0·214	0·264	0·330
p-$NO_2{\cdot}C_6H_4{\cdot}CO_2Et$	0·770	0·166	0·200	0·282
o-$NO_2{\cdot}C_6H_4{\cdot}CO_2H$	0·526[3] 0·968	0·304	0·340	0·420
m-$NO_2{\cdot}C_6H_4{\cdot}CO_2H$	0·440 1·026	0·252	0·294	0·362
p-$NO_2{\cdot}C_6H_4{\cdot}CO_2H$	0·390 0·972	0·186	0·226	0·304

[1] $E_{\frac{1}{2}}$'s of the reduction of the second nitro-group are equal to the $E_{\frac{1}{2}}$'s of the nitroanilines listed in Table 2*a*. [2] $E_{\frac{1}{2}}$'s of the aldehyde group are equal to $E_{\frac{1}{2}}$'s of the amino-aldehydes listed in Table 2*b*. [3] Two waves appear with the unbuffered solutions, believed to be due to reduction of the nitrobenzoic acid molecule and of the nitrobenzoate ion.

$E_{\frac{1}{2}}$ of the nitro-group is lowered by these substituents in all positions. For dinitrobenzenes and nitrobenzaldehydes $E_{\frac{1}{2}}$ follows the order $p < o < m <$ unsubst., which agrees with the orientating effect of nitro- and CHO-groups, but for the nitrobenzoic acids and ethyl nitrobenzoates the order is $p < m < o <$ unsubst. This should indicate highest yields for the *ortho*-compounds; steric hindrance might account for their being low.

The influence of the nitro-group on the polarographic reduction of CHO and iodo-substituents could not be studied as reduction of the nitro-group occurred at a potential lower than that required for reduction of the other two. Nor, for the same reason, could the influence of the CHO group on the reduction of the iodo-group be observed.

Relative values for $E_{\frac{1}{2}}$ for the iodobenzoic acids ($o < m < p <$ unsubst.) (*J.*, 1951,

3502) cannot be compared with results for the iodination of benzoic acid, as the last reaction does not occur at low temperatures. However, bromination of benzoic acid with potassium bromate and hydrogen bromide at 70—80° yields mainly *p*-bromobenzoic acid (Claus and Reh, *Annalen*, 1891, **266**, 206), whereas large yields of *meta*-compounds are generally obtained at high temperatures.

The polarization energies for $+E$ substituents (Dewar, *loc. cit.*) show the order $p > o > m >$ unsubst. for positive δ_x values up to 2·3, and are in the opposite order to the $E_{\frac{1}{2}}$'s of the isomers of dinitrobenzene and nitrobenzaldehyde. But no such parallel is found with the ethyl nitrobenzoates, nitrobenzoic acids, and iodobenzoic acids. Should the polarization energies required for *meta*-substitution be somewhat higher for all δ_x values, the agreement would be preserved with $\delta_x = 1$—1·3 for the nitrobenzoic acids and ethyl nitrobenzoates and with $\delta_x = 2{\cdot}5$ for the iodobenzoic acids. δ_x for CHO would then be about 1·5 and for NO_2 about 1·8, as the overall lowering of $E_{\frac{1}{2}}$ by the substituents shows the order $CO_2H < CO_2Et < CHO < NO_2$, and their electronegativities should increase in the same order. The δ_x that has to be assigned to the carboxyl group when associated with an iodo-substituent is again higher than the δ_x assigned when it is associated with a nitro-group.

We tried to substitute $E_{\frac{1}{2}}$ differences into the Pauling–Wheland formulæ for *inductive* substituents (as described for the iodotoluenes) in the case of the ethyl nitrobenzoates and the nitrobenzoic acids ($E_{\frac{1}{2}}$ values of Page, Smith, and Waller at pH 4 were used; *J. Phys. Chem.*, 1949, **53**, 545), and for both series of compounds agreement was obtained, *i.e.*, δ_1 and δ_2 values obtained from two equations and substituted into the third equation lead to the observed $E_{\frac{1}{2}}$ difference. Values obtained for the nitrobenzoic acids are $\delta_1 = +1{\cdot}13$ and $\delta_2 = +0{\cdot}36$, and for ethyl nitrobenzoates $\delta_1 = +1{\cdot}33$ and $\delta_2 = +0{\cdot}36$.

This procedure is not completely justified, as the Pauling–Wheland equations account for the inductive effect of the substituents only, and the agreement might be a coincidence. It is interesting, however, that the calculated δ_2 values are close to $\frac{1}{3}\delta_1$ in both instances, as has proved most satisfactory for calculations (Dewar and Jaffé, *locc. cit.*), and that the calculated δ_1 values, +1·13 for the carboxy-group and +1·33 for the ethoxycarbonyl group are approximately those which follow from the Dewar diagrams.

Influence of the Nitrogen Atom in Pyridine.—The nitrogen atom deactivates the pyridine ring strongly towards substitution. It favours nitration and sulphonation in the *meta*-position; halogenations have to be carried out at high temperatures, and a number of multisubstituted by-products including 2 : 3- and 2 : 5-halogenopyridines are generally obtained together with the *meta*(3)-product. Direct iodination of pyridine yields an addition product rather than a substitution product.

The iodopyridines have $E_{\frac{1}{2}}$ as follows: 2-, 1·418 v; 3-, 1·387 v; 4-, 1·348 v ($E_{\frac{1}{2}}$ for PhI is 1·650 v). These values suggest that direct iodination of pyridine, if it could be achieved, would occur at position 2 (equivalent to the *ortho*-positions).

No similar order of polarization energies can be found in Dewar's diagram for inductive substituents. It is interesting, however, that this order of $E_{\frac{1}{2}}$'s is similar to the $E_{\frac{1}{2}}$ order of the *misbehaving* $+E$ substituents when affecting the reduction of the nitro-group.

Insofar as this argument has significance, the pyridine-nitrogen atom, the carboxy-group, and the ethoxycarbonyl group would be of the same electronic type.

EXPERIMENTAL

The polarographic apparatus was a manually controlled three-electrode set up as described by Lingane and Kolthoff (*J. Amer. Chem. Soc.*, 1939, **61**, 825).

Buffers were made from sodium acetate, hydrochloric acid, and potassium chloride to 0·2N, in 60% alcohol. The pH was measured with a glass electrode on a Leeds and Northrup pH-meter, model 7663-AI, and controlled on a more accurate hand-made apparatus kindly supplied by Mr. H. J. Gardner. 0·01M-Tetraethylammonium bromide was made from the Eastman Kodak product; the solution contained 66% of alcohol.

The polarographic measurements were carried out at 25·0° ± 0·1°, the temperature being controlled by a thermostat. The solutions were M/3100 with respect to the reducible compound. Potentials were measured against the saturated calomel electrode.

Materials were obtained from our store or prepared by well-known methods and were purified by recrystallization, vacuum-sublimation, or distillation to constant m. p. or b. p. respectively.

Preparation of Iodo-compounds not described elsewhere.—3-*Iododiphenyl.* 3-Aminodiphenyl was diazotized in hydrochloric acid at 5° and treated with potassium iodide. The 3-iododiphenyl was extracted with ether from alkaline solution and, after evaporation of the solvent and recrystallization three times from 50% ethanol, was colourless and had m. p. 25° (Found: C, 51·2; H, 3·5. Calc. for $C_{12}H_9I$: C, 51·45; H, 3·2%).

3-*Iodopyridine.* This was prepared from 3-aminopyridine as described above. Recrystallized from 50% ethanol it had m. p. 52° (Found: C, 29·2; H, 2·0. Calc. for C_5H_4NI: C, 29·3; H, 1·95%).

4-*Iodopyridine.* Small quantities (about 15% yield) of 4-iodopyridine could be prepared as follows. 4-Aminopyridine (2 g.), dissolved in acetic acid (15 c.c.), concentrated sulphuric acid (1·5 c.c.), and water (2 c.c.), was diazotized ($NaNO_2$) at 0° and potassium iodide (excess) added. The mixture was kept at room temperature for a day, then heated on a water-bath of 50° for ½ hr. The solution was made alkaline and the product was extracted with ether. After evaporation of the solvent and recrystallization from 50% ethanol, 4-iodopyridine had m. p. 100° (decomp.) (Found: N, 6·7. Calc. for C_5H_4NI: N, 6·8%).

We gratefully acknowledge financial assistance from the Commonwealth Science grant to this University.

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[*Received, January 26th,* 1953.]