771. *Polarographic Behaviour of Iodo-compounds. Part II.**

By (Mrs.) E. Gergely and T. Iredale.

The polarographic reduction potentials ($E_{\frac{1}{2}}$) of the iodobenzoic acids, iodoacetic acid, iodoanilines, and iodophenols in various media and buffers of controlled pH, have been investigated. All of these compounds have half-wave potentials dependent on pH, and tentative explanations have been given of their behaviour. The possible part played by hydrogen bonding in the *ortho*-derivatives has been indicated. The influence of iodine on the reduction potentials of nitro and other neighbouring groups in the benzene ring is discussed, as well as the relationship of $E_{\frac{1}{2}}$ to " positive halogen."

We recorded in a previous communication (*J.*, 1951, 13) * that organic iodine is reducible at the dropping-mercury cathode by two different mechanisms. The iodo-hydrocarbons give half-wave potentials independent of hydrogen-ion concentration, whilst the ionizable compounds, such as iodoacetic acid, the iodobenzoic acids, iodoanilines, and iodophenols, have values of $E_{\frac{1}{2}}$ dependent on pH. The shift of the half-wave potential with pH cannot be attributed to dissociation equilibrium only. The greater part of this paper is concerned with these pH-dependent reductions.

Results.

Iodobenzoic Acids.—*o*-Iodobenzoic acid when reduced at a concentration of M/2500 in N/10-potassium chloride containing 5% ethanol gave a very wide wave from $-1{\cdot}00$ to $-1{\cdot}70$ v [all potentials are referred to the Standard Calomel Electrode (S.C.E.)]. When N/10-sodium hydroxide was added only one wave was obtained, having $E_{\frac{1}{2}} = -1{\cdot}6$ v. In weaker solutions (M/5000), however, two waves could be distinguished, the smaller one having $E_{\frac{1}{2}} = -1{\cdot}04$, the larger, $E_{\frac{1}{2}} = -1{\cdot}60$ v (Fig. 1). When reduction took place in M/100-tetraethylammonium bromide and 50% ethanol, two waves were again obtained, having $E_{\frac{1}{2}} = -1{\cdot}14$ and $-1{\cdot}60$ v. The first wave, however, was considerably higher than in the 5% ethanol plus potassium chloride supporting electrolyte. When the alcohol concentration was increased to 66%, the first wave continued to increase at the expense of the second wave. The sum total of both wave heights was constant, and therefore must be proportional to the total concentration of acid (Fig. 2). These experiments indicate, as Brdička (*Coll. Czech. Chem. Comm.*, 1947, **12**, 212) suggests for the reduction of pyruvic acid, that the first wave originates in the reduction of the undissociated acid molecules, the second wave in the reduction of the ions. This explains why increasing alcohol concentration augments the height of the first wave by shifting the dissociation equilibrium in the direction of the undissociated acid molecules. The wide wave obtained in potassium chloride solution could be explained by assuming that, after the reduction of the undissociated molecules present in the drop (electrode) area, the equilibrium is restored by recombination of hydrogen ions with acid anions. When reducing the *ortho*-acid in buffers, we could never obtain two waves in one polarogram, as in the acid buffers (pH 4—5) where the presence of both undissociated acid and ion is expected, the reduction of the ion is preceded by the decomposition of the buffer. The step heights of the waves obtained show that when the pH is less than 3 the acid is present largely in the associated state; from pH 3 to pH 5 the step-height decreases, showing that the measured wave is the reduction of undissociated acid only; in the range pH 5—7 the wave is probably due to reduction of both acid and ions; and when pH is greater than 9, the wave obtained is due to reduction of the ion only (Fig. 3). The half-wave potential of the undissociated acid appears, therefore, to shift with the pH, whereas that of the ion appears to be independent of pH.

The diffusion currents measured in acid media were about 15% larger than those measured in alkaline media. As the wave height does not decrease after the acid has been in alkaline buffers for a considerable time, this difference cannot be attributed to hydrolysis of the iodine to give the iodide ion.

m-Iodobenzoic acid was also reduced in one large step in N/10-potassium chloride or N/10-tetraethylammonium bromide and 5% ethanol. Separation of the two waves could not be achieved. In buffers the reduction follows a similar course to that of the *ortho*-acid.

p-Iodobenzoic acid was reduced in N/10-potassium chloride in a step which did not show double-wave character, the slope of the wave being the same as with the other iodo-compounds. In buffers

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* Part I, *J.*, 1951, 13.

FIG. 1.

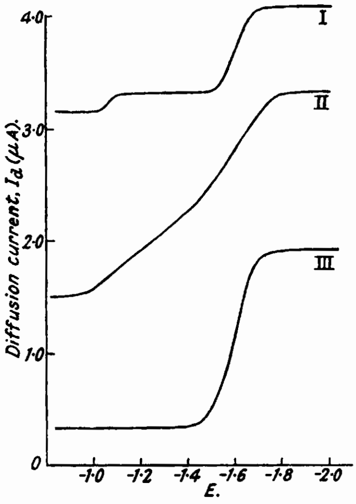


FIG. 2.

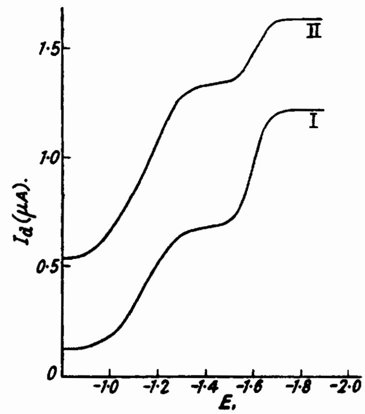


FIG. 1.

I. M/5000-o-*Iodobenzoic acid in* N/10-KCl–5% *ethanol.*
II. M/2500-o-*Iodobenzoic acid in* N/10-KCl–5% *ethanol.*
III. M/2600-o-*Iodobenzoic acid in* N/10-KCl–5% *ethanol and* N/100-NaOH.

FIG. 2.

I. M/3000-o-*Iodobenzoic acid in* M/100-*tetraethylammonium bromide*–50% *ethanol.*
II. M/3000-o-*Iodobenzoic acid in* M/100-*tetraethylammonium bromide*–66% *ethanol.*

FIG. 3.

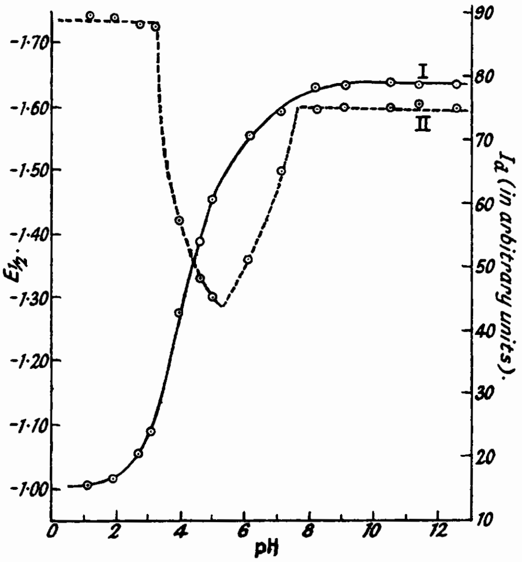


FIG. 4.

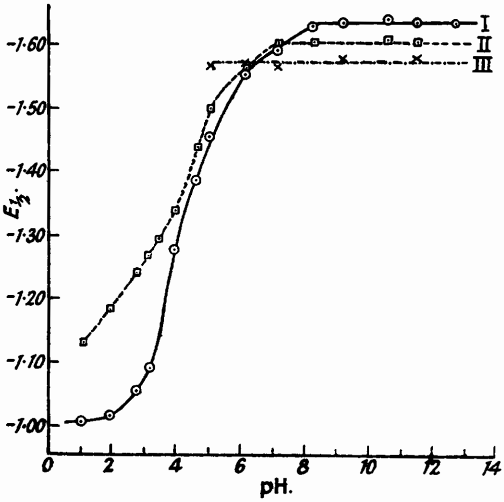


FIG. 3.

I. *Half-wave potential against* pH *for* o-*iodobenzoic acid.*
II. *Diffusion current of the measurable step.*

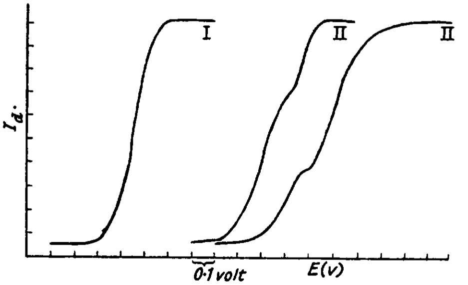
FIG. 4.

I. o-*Iodobenzoic acid.* II. m-*Iodobenzoic acid.* III. p-*Iodobenzoic acid* the wave occurred only when the pH exceeded 5; as in the more acid regions the buffer decomposition preceded the reduction of the acid.

The order of increasing ease of reduction of the undissociated acid is *ortho* > *meta* > *para*, and of the acid anion *para* > *meta* > *ortho* (Fig. 4).

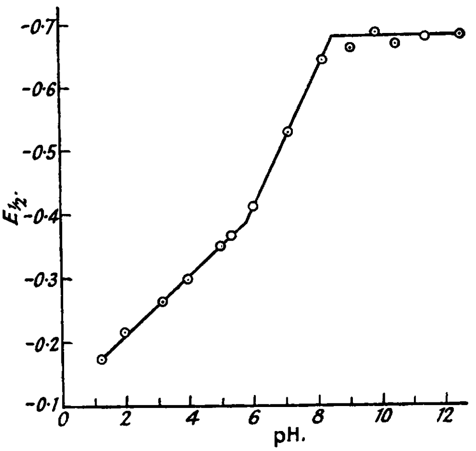
Iodoacetic Acid.—When reduced in N/10-potassium chloride this gave a wide wave which spread over a range of 0·5 v ($E_{\frac{1}{2}}$ = 0·32 v). If the solution was made alkaline, a usual wave was obtained ($E_{\frac{1}{2}}$ = 0·65 v). Determination of the value of $E_{\frac{1}{2}}$ in buffers shows that it varies from 0·17 to 0·68 v in the pH range 1·12—12·5.

FIG. 5.



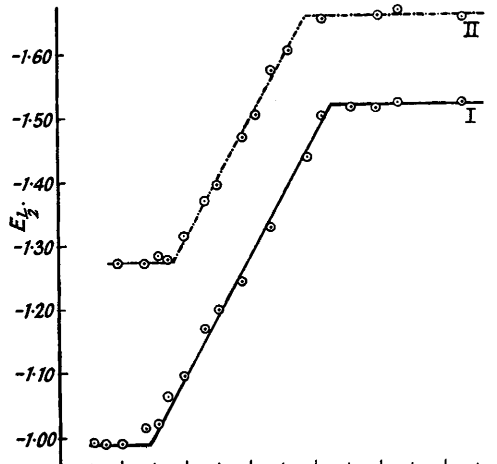
I. *Polarogram of iodoacetic acid in buffers of* pH<6.
II. *Polarograms of iodoacetic acid in buffers of* pH>6.

FIG. 6.



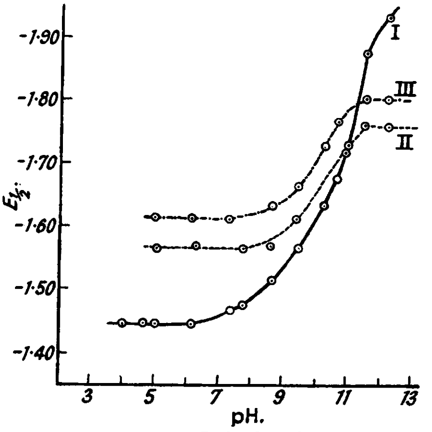
Plot of half-wave potential against pH *for* M/2500-*iodoacetic acid.*

FIG. 7.



I. *Half-wave potentials of* M/2500-o-*iodoaniline.*
II. *Half-wave potentials of* M/2500-p-*iodoaniline.*

FIG. 8.



I. o-*Iodophenol.*
II. m-*Iodophenol.*
III. p-*Iodophenol.*

The waves obtained in acid buffers up to pH 6 are the usual ones with logarithmic plots of the order of 0·08 v per log $i/(i_d - i)$ unit. When pH is greater than 6 the waves are extremely wide and are apparently composed of two waves with very poor separation (Fig. 5). The half-wave potential increases linearly with pH up to pH 5·5 with a slope of 0·045 v/pH, and above pH 5·5 the slope is more pronounced (0·085 v/pH). When pH > 9 the over-all half-wave potential does not change, but the double character of the waves is still observed (Fig. 6). The step-height corresponding to a two-electron reduction is in alkaline media about 5—10% lower than in acid media.

Iodoanilines.—In N/5-potassium chloride no sign of double-wave character was observed. The half-wave potentials in this medium are approximately equal to those in a buffer of pH 7. The horizontal lines obtained in the $E_{\frac{1}{2}}$/pH plot up to pH ~ 3 most probably represent the reduction of the odoanilinium ion, and the horizontal lines in the alkaline region the reduction of the iodoaniline molecule (Fig. 7). The potential change in the intermediate pH region should be related in some way to the $IR{\cdot}NH_3^+ \rightleftharpoons IR{\cdot}NH_2 + H^+$ equilibrium. However, the relation is not very clear, as the waves obtained in buffers of pH 4—7 are narrow, and do not spread to either acid or alkaline potentials, and cannot be due to superposition of two waves. The diffusion currents measured were, within the experimental error, the same throughout the whole pH range. The iodoanilines, however, show maxima in the acid region, which are suppressed by addition of gelatin.

Iodophenols.—The reduction waves in N/5-potassium chloride are wide and might be composed of two elements. The straight line in Fig. 8 in the pH 4—7 region is the reduction of the iodophenol molecule. The upward trend from pH 8—12 is probably related to the equilibrium $IR{\cdot}OH \rightleftharpoons IR{\cdot}O^- + H^+$. The straight line at pH ~ 11—12 is probably the reduction of the iodophenoxide ion. The curve for *o*-iodophenol tends to a constant final potential, which, however, cannot be reached within the measurable pH and potential ranges.

DISCUSSION.

General.—The reduction of iodo-compounds at the dropping-mercury cathode is a process requiring two electrons, as previously calculated with the aid of the Ilkovic equation (*J.*, 1951, 13). The reduction product is always the compound which results from the replacement of iodine by hydrogen, but it may arise from two different mechanisms. When the half-wave potential is independent of the pH the suggested mechanism is :

$$RI + 2e + H_2O = RH + I^- + OH^- \quad \ldots\ldots\ldots \quad (1)$$

When it is dependent on pH the mechanism may be :

$$RI + e + H^+ = RH^+ + I^- \quad \ldots\ldots\ldots \quad (2)$$

followed by :

$$RH^+ + e = RH \quad \ldots\ldots\ldots \quad (3)$$

Whether the two electrons add on at the same time or not cannot be decided from the $E_{\frac{1}{2}}$–log $i/(i_d - i)$ plot, this reduction being irreversible. The slopes of the logarithmic plots are of the order 0·09 v, which does not agree with the requirements for the reversible, one-electron process (0·06 v), or the two-electron process (0·03 v).

It is apparent that all the iodo-compounds having half-wave potentials dependent on pH contain groups undergoing electrolytic dissociation, whilst the pH-independent ones are non-electrolytes. Similarly it has been found that the double-bond of unsaturated hydrocarbons can be reduced at potentials independent of the pH (Laitinen and Wawzonek, *J. Amer. Chem. Soc.*, 1942, **64**, 1765, 2365; 1946, **68**, 2541), but in the case of the double-bond reduction of fumaric and maleic acids, the half-wave potential shifts with pH (Vopicka, *Coll. Czech. Chem. Comm.*, 1936, **8**, 349).

In attempting to attribute the half-wave potential dependence on pH entirely to the electrolytic dissociation of the molecule, we make the fairly obvious assumption that the reduction of the undissociated acid is easier and requires less potential than the reduction of the negatively charged anion, where the reducing electron has to overcome the electrostatic repulsion of the ion. It is to be expected also that the positively charged iodoanilinium ion should be more readily reduced than the neutral molecule.

If dissociation, however, were the only factor affecting the half-wave potential $E_{\frac{1}{2}}$, we should expect to obtain in the acid regions the more or less pH-independent reduction waves of the undissociated iodo-acids or iodoanilinium ion, and in the alkaline region, the reduction waves of the dissociated acid anions, or undissociated iodoanilines. In the pH region around pH = p*K*, we should expect to get two separate waves, each having pH-independent half-wave potentials.

In the extreme acid and alkali regions, the half-wave potentials are independent of pH in the case of *o*-iodobenzoic acid, the iodoanilines, and *m*- and *p*-iodophenols. If measurements could be carried out in the more alkaline region, the same results might be expected for *m*-iodobenzoic acid and *o*-iodophenol. Iodoacetic acid, however, has a pH-independent $E_{\frac{1}{2}}$ in the alkaline regions only, whilst in the acid regions a regular shift of 0·045 v per pH unit is observed. In the intermediate region two independent waves are not shown.

If the values of $E_{\frac{1}{2}}$ of the pH-independent compounds [iodobenzene, −1·62 v; *o*-, *m*-, and *p*-iodotoluene, −1·66, −1·61, −1·66 v, respectively (*J.*, 1951, 15); iodoethane, −1·67 v; iodomethane, −1·63 v (von Stackelberg and Strecke, *Z. Elektrochem.*, 1949, **53**, 118)] are compared with the values of $E_{\frac{1}{2}}$ of the pH-dependent compounds in acid buffers [*o*-iodobenzoic acid, −1·00 v; *o*-iodoaniline, −1·00 v; *m*-iodobenzoic acid, −1·13 v; *p*-iodoaniline, −1·28 v, etc.], it would seem that some interaction with hydrogen ions renders the reduction easier. In the alkaline buffers the $E_{\frac{1}{2}} \sim -1{\cdot}6$ v of all the pH-dependent compounds are of the same order as those of the pH-independent compounds. There may be some balancing-out factor, which we have yet to discover, which makes the agreement fortuitous.*

For the iodoanilines, iodophenols, and iodoacetic acid at pH 5—8 we find $\mathrm{d}E_{\frac{1}{2}}/\mathrm{dpH} \sim 0{\cdot}085$—$0{\cdot}09$ v. According to von Stackelberg (*Z. Elektrochem.*, 1939, **45**, 466) for irreversible organic reductions where dissociation equilibria are involved:

$$\mathrm{d}E_{\frac{1}{2}}/\mathrm{dpH} = 0{\cdot}058(n_{\mathrm{ox.}} - n_{\mathrm{red.}})/v \text{ volts}$$

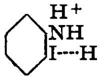
where v = number of electrons involved; $n_{\mathrm{ox.}}$ = number of oxidized reactants; and $n_{\mathrm{red.}}$ = number of reduced reactants.

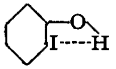
Consider the reduction equation for an iodo-acid when pH > pK:

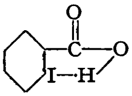
$$\mathrm{IR{\cdot}CO_2^- + 3H^+ + 2}e \longrightarrow \mathrm{HR{\cdot}CO_2H + HI}$$

here $n_{\mathrm{ox.}}$ is 4 and $n_{\mathrm{red.}}$ is 1; if it is assumed that hydrogen iodide does not affect the redox system the above equation beomes $\mathrm{d}E_{\frac{1}{2}}/\mathrm{dpH} = (4 - 1)0{\cdot}058/2 = 0{\cdot}087$ v/pH, which is in agreement with experiment.

In the alkaline regions the half-wave potential does not continue to move to more negative values with increasing pH, and the half-wave potentials are of the same order as those of the pH-independent reductions of iodo-hydrocarbons. When the hydrogen-ion concentration decreases to a limiting value, apparently mechanism (1), attributed to the pH-independent reductions, is the easier one. In the extreme acid regions with the iodophenols and iodoanilines (iodoanilinium ion), the hydrogen-ion concentration seems to be great enough to make the reduction potential independent of pH. It is, however, possible also that intramolecular hydrogen bonding might be a contributing factor, as the half-wave potentials of the *ortho*-derivatives are lower than those of the *para*-derivatives, although from electron-density considerations they might be expected to be approximately the same. The extremely low half-wave potential for iodoacetic acid, however, is not easy to explain on grounds similar to these.







Previous work has demonstrated the existence of hydrogen bonding in *ortho*-derivatives. In their investigation of the polarographic reduction of *o*- and *p*-nitrophenols, Astle and McConnell (*J. Amer. Chem. Soc.*, 1943, **65**, 35) attribute the lower half-wave potential of the *o*-compound to hydrogen bonding between the hydroxyl and the nitro-group. In their study of the electric moments of the *ortho*-halogenated phenols, Anziloth and Curran (*J. Amer. Chem. Soc.*, 1943, **65**, 620) conclude that 85—90% of the molecules have the hydroxyl group in the *cis*-position relative to halogen, owing to intramolecular bonding. The order of the bond strengths is H . . . . F > H . . . . . Cl > H . . . . . Br. The corresponding iodo-compound was not studied, but we may assume that some hydrogen bonding does exist in this case also. Some evidence of hydrogen bonding with iodine was also found from infra-red measurements on iodophenol (Wulf, Liddel, and Hendricks, *J. Amer. Chem. Soc.*, 1936, **58**, 2287).

The Influence of Iodine on Polarographic Reduction Potentials of Neighbouring Groups.—We reported in our previous paper (*J.*, 1951, 13) that the half-wave potential of combined iodine exhibits a shift to less negative potentials when electrophilic groups, and to more negative potentials when nucleophilic groups, are introduced into the same benzene ring; *e.g.*, the half-wave potential of undissociated *o*-iodobenzoic acid in tetraethylammonium bromide is −1·14 v, whilst that of *o*-iodotoluene is about −1·66 v, of *p*-iodoaniline −1·72 v, of *p*-iodophenol −1·71 v, etc., the first being lower, the others higher, than the half-wave potential of unsubstituted iodobenzene, −1·62 v, in the same medium. These results may be correlated with the Pauling–Wheland (*J. Amer. Chem. Soc.*, 1935, **57**, 2086) theory of electron densities, it being assumed that if the substituent causes by induction or resonance a greater electron density at the carbon atom where the iodine is bonded, the replacement of the iodine during the reduction will need more energy (greater negative potential) than that required for the reduction of iodobenzene, whilst if the substituent produces a lower electron density in the carbon–iodine region, the reduction will occur at a lower negative potential.

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* This comparison is not made under quite the same conditions, as the $E_{\frac{1}{2}}$ values of the pH-independent compounds were measured in solutions containing 66% ethanol or 70% butanol, and would have approximately 0·06 v lower negative values in 5% ethanol solutions of which the buffers were made.

The halogens are electrophilic, but direct to *ortho* and *para* substitution. Iodine, as well as the other halogens, usually causes " red shift " in the absorption spectra of aromatic compounds, and behaves as " positive halogen " in certain organic reactions, especially if attached to a double-bonded carbon atom (Robertson and Waters, *J.*, 1947, 492; Atherton and Todd, *J.*, 1947, 674; Muirhead, *Annals App. Biol.*, 1949, **36**, 250). Our investigations with the iodonitrobenzenes and tetraiodopyrrole seem to agree with these facts. We have reduced these compounds at the dropping cathode in solution in M/100-tetraethylammonium bromide and 66% ethanol at a concentration of 1/3 millimol./l. Nitrobenzene gives one wave in this medium due to the reduction of the nitro-group. The iodonitrobenzenes give two waves, the first due to the reduction of the nitro-group, the second to replacement of the iodine :

Compound.	$E_{\frac{1}{2}}$ for the nitro-group.
Nitrobenzene	−0·935 v
o-Iodo-nitrobenzene	−0·816
m- ,,	−0·757
p- ,,	−0·780

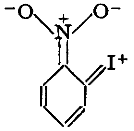
Tetraiodopyrrole is reduced in four steps; the $E_{\frac{1}{2}}$ for iodine of each step being : first step −0·74 v, second −0·90 v, third −1·10 v, fourth −1·60 v (there was poor separation for first three steps). The reduction potential of the monoiodopyrrole (−1·60 v) is thus of the order of the reduction potential of iodobenzene (−1·62 v).

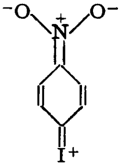
The comparative ease of the first reduction (−0·74 v) indicates the positive nature of the iodine when four iodine atoms are attached directly to the ring.

These results show that the presence of iodine attached directly to the ring enhances the reduction of the other reducible group, whether it is a nitro-group or another iodine. The order of increasing ease of reduction is :

m- > *p*- > *o*-iodonitrobenzene > nitrobenzene.

The iodine lowers the reduction potential of the nitro-groups in all positions in the ring because of its electron-attracting character. The electron deficiency all around the ring seems to be partly counterbalanced by a contribution of resonance structures such as those shown :





affecting only the *ortho*- and the *para*-positions. The lowest reduction potential for the *meta*-derivative is thus understandable.

It is interesting to compare these results with those obtained when chlorine is the modifying substituent. The following are the values of $E_{\frac{1}{2}}$ for the reduction of the nitro-group in the chloronitrobenzenes : *o*- −0·866 v, *m*- −0·830 v, *p*- −0·930 v.

The influence of chlorine is evidently less pronounced than that of iodine, and the order of increasing ease of reduction is different : *m*- > *o*- > *p*-chloro-compound > nitrobenzene.

The influence of chlorine on the reduction potential of the iodo-group itself shows itself more strongly : *o*- −1·34 v, *m*- −1·45 v, *p*-chloroiodobenzene −1·54 v, all of which are less than the $E_{\frac{1}{2}}$ for iodobenzene (1·62 v).

These differences are connected in some quantitative way with the electron-density differences in the specific groups, and theoretical work is being undertaken to discover this relation.

EXPERIMENTAL.

Details of the experimental apparatus and technique were described previously (*J.*, 1951, **13**). The dropping-potentials were checked with the aid of the third electrode described by Lingane and Kolthoff (*J. Amer. Chem. Soc.*, 1939, **61**, 825). Chemicals used, with the exception of iodopyrrole, were purified by the group of workers engaged on their spectroscopy. Details will appear in forthcoming publications. The tetraiodopyrrole used was a May and Baker product (Found : N, 2·8. Calc. : N, 2·5%).

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