3. *Polarographic Behaviour of Iodo-compounds. Part I.*

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

Organic iodo-compounds are reducible at the dropping-mercury cathode, hydrogen replacing the iodine which appears as the iodide ion. The half-wave potentials are independent of pH in the case of most non-ionizable compounds, but reduction of such compounds as acids and amines is pH dependent. The reduction is found to be a two-electron process, the general equation being :

$$RI + 2e + H^+ = RH + I^-$$

We record in this paper some polarographic studies, also the cathodic reduction on a larger scale, of some iodo-compounds, mainly aromatic, including iodobenzene. When the greater part of our work was completed there appeared an abstract, and subsequently the original account, of similar work on halogeno-compounds and iodobenzene itself (von Stackelberg and Stracke, *Z. Elektrochem.*, 1949, **53**, 118). Some of the Germans' conclusions are substantially the same as ours, but the compounds we used were usually different and our objectives were not quite the same.

In 1935 Brdička (*J. Gen. Physiol.*, 1935, **19**, 843) followed the hydrolysis of iodoacetic acid by observing the decrease in the height of the polarographic wave of the acid, attributing it to the elimination of iodine according to the equation : $CH_2I{\cdot}CO_2H + H^+ + 2e = CH_3{\cdot}CO_2H + I^-$. Proske (*Angew. Chem.*, 1943, **56**, 24) studied the polarographic reduction of halogeno-ketones and similar compounds, but was only concerned with the influence of the halogen on the half-wave potentials of the reduction of the keto-group. Lingane, Gardner, Swain, and Fields (*J. Amer. Chem. Soc.*, 1943, **65**, 1348) reported the reduction of iodophenylacridine in neutral and alkaline media in a two-electron step. In 1946 the reductions of iodofuchson (Stromberg and Reims, *J. Gen. Chem. Russia*, 1946, **16**, 1731) and of di-iodotyrosine and thyroxine (Simpson and Traill, *Biochem. J.*, 1946, **40**, 116) were reported. The first attempt to understand the mechanism of the polarographic reduction of halogenated organic compounds was made by Pasternak and von Halban (*Helv. Chim. Acta*, 1946, **29**, 190) who found that the half-wave potentials of ω-bromoacetophenone did not move to more positive values as the buffer medium was changed from alkali to acid, and they were led to assume that the mechanism was a direct electron addition and not a hydrogenation. But in the same year Keller, Hochweber, and von Halban (*Helv. Chim. Acta*, 1946, 29, 760), in a paper on the reduction of a series of chlorinated compounds, concluded that only the halogens bound to the aliphatic part of the compound were reducible at the dropping cathode. As this was not in agreement with the work of other investigators, we considered a study of the polarographic behaviour of iodo-compounds, especially wherein the iodine is bound to an aromatic carbon, would be of interest and importance.

All the compounds we examined proved to be reducible at the dropping-mercury cathode. The wave-heights for the compounds showed that two electrons were involved in the reduction, calculations being made by means of the Ilkovic equation : $n = i_d/605D^{\frac{1}{2}}cm^{\frac{2}{3}}t^{\frac{1}{6}}$, where n is the number of electrons involved, i_d the diffusion current in microampères, D the diffusion coefficient in cm.^{2} sec.$^{-1}$, c the concentration of the reducible substance in millimoles per litre, m the quantity of mercury dropping per second in mg., and t the drop-time in seconds. The diffusion coefficients were calculated indirectly from the diffusion coefficient of one of the substances, *i.e.*, *o*-iodobenzoic acid, by means of the Northrop–Anson formula : $D_1/D_2 = \sqrt{M_2/M_1}$, M_1 and M_2 being the molecular weights of the substance and the acid, respectively (Northrop and Anson, *J. Gen. Physiol.*, 1929, **12**, 543). The diffusion coefficient of the acid itself was obtained from its equivalent conductivity by means of the Nernst equation : $D = 2{\cdot}67 \times 10^{-7}\ \lambda_0/2$cm.^{2} sec.$^{-1}$ (Askenary and Meyer, *Ber.*, 1893, **26**, 1354), and has the value $0{\cdot}854 \times 10^{-5}$ cm.^{2} sec.$^{-1}$. We also found that two electrons were involved in the reductions when large-scale operations were carried out in an apparatus similar to that described by Lingane and co-workers (*loc. cit.*). The amount of electricity required for the reduction of a sample was always in agreement with the theoretical value calculated for a two-electron process, *e.g.*, for the reduction of one gram of *o*-iodobenzoic acid to benzoic acid 784 coulombs were needed, whilst the theoretical value would be 780 coulombs where two electrons were involved. The reduction products were identified and we found in each case that the iodine had been replaced by hydrogen, and the iodine split off in the form of the iodide ion. The latter was estimated, and about 70% of the expected amount was usually found in the cathode vessel. Some iodide was also found in the anode vessel, and this must be due to inter-diffusion. No hydrolysis of the iodo-group occurred under our experimental conditions, except in the case of iodoacetic acid. The heights of the polarographic waves of the aromatic iodides did not decrease after storage even in the alkaline buffers and other supporting electrolytes, and the reduction products never showed traces of phenolic hydroxyl groups when tested with ferric chloride. Our investigations seem to show that the polarographic waves of these compounds are due to the total reaction: $RI + 2e + H^+ = RH + I^-$, suggested by **Brdička** (*loc. cit.*) for iodoacetic acid.

The wave-heights were proportional to the concentrations of the solutions, but the slopes of the waves were found to be less steep than would be expected for two-electron reductions. The usual logarithmic plots ($\log \frac{i}{i_d+i}$ against potential, E,) were found to be of the order of 0·09 v. per log. unit unstead of the theoretical value, 0·03 v. Both the half-wave potentials and the wave-slopes proved to be very sensitive to experimental conditions, *e.g.*, to the ionic strength, the alcoholic content of the solution, and the nature of the cations of the supporting electrolyte. In some cases a slight shift of the half-wave potential to more negative values was observed when the concentration of the solution was increased. However, by keeping all experimental conditions rigorously constant from one run to another, we could reproduce both wave-height and half-wave potential very well. We have mentioned that Pasternak and von Halban (*loc. cit.*) noticed that the half-wave potential of certain halogenated compounds was independent of the pH of the supporting electrolyte, a fact also discerned by von Stackelberg and Strake (*loc. cit.*). Our experiments seemed to show that although this might be true for one series of iodo-compounds such as the iodo-derivatives of hydrocarbons, it was not the case for such substances as the iodobenzoic acids and the iodoanilines. It has been shown by Laitinen and Wawzonek (*J. Amer. Chem. Soc.*, 1942, **64**, 1765, 2365; 1946, **68**, 2541) that the half-wave potentials of the unsaturated hydrocarbons do not shift with the pH of the solution. The authors suggest that the reduction of the double bond takes place according to the general reaction, $[R] + 2e + 2H^+ = [RH_2]$, which is made up of the several part reactions: (1) $[R] + e = [R]^-$, (2) $[R]^- + e = [R]^{--}$, and (3) $[R]^{--} + 2H_2O = [RH_2] + 2OH^-$, (where $[R] = R'CH{:}CHR''$). The first step, *i.e.*, addition of the electron, is the potential-determining step. However, the half-wave potentials of maleic and fumaric acids *do* shift with the pH (Vopicka, *Coll. Czeck. Chem. Comm.*, 1936, **8**, 349) showing that hydrogen ions play an important part in the reduction of these compounds, although the reducible group is again the double bond as in the previously mentioned compounds. The situation is complicated because the pH of the solution has also a great effect on the proportion of ions and molecules present. It is possible that double bonds may be reduced by two different mechanisms.

We have noticed a similar behaviour in the case of the iodo-compounds. The general equation, $RI + 2e + H^+ = RH + I^-$, may be compounded in the case of pH-independent reductions, of the following steps: (1) $RI + e = RI^-$, (2) $RI^- = R + I^-$, (3) $R + e = R^-$, (4) $R^- + H_2O = RH + OH^-$, the addition of the electron being the potential-determining step. We have listed in the table the half-wave potentials at 25° of a number of iodo-compounds in M/100-tetraethylammonium bromide as supporting electrolyte. The solutions contained 66% by volume of ethanol and 1/3 millimol./litre of the reducible compound. Potentials are referred to the saturated calomel electrode (S.C.E.) as zero.

The differences in the potentials for different compounds and isomers are very interesting, and something may be deduced from them without departing greatly from current theories. Maccoll (*Nature*, 1949, **163**, 178) has shown that with some hydrocarbons polarographic reductions proceed at potentials determined by the energy of the first unoccupied molecular orbital. If we assume that the addition of the electron in the case of iodo-compounds occurs at the first unoccupied orbital of the bond which is subsequently broken, it should occur with greater ease the lower the electron density at that bond (Wheland and Pauling, *J. Amer. Chem. Soc.*, 1935, **57**, 2086). It is easy to understand why the electron adds on more easily to *m*-iodotoluene (1·613 v.; not greatly different from iodobenzene, 1·616 v.) than to the *o*- and *p*-derivatives (1·656 v. and 1·660 v.). Substitution of the methyl group in the benzene ring produces by hyperconjugation a greater electron density in the *o*- and *p*-positions than in the *m*-. The electrophilic reagent, iodine, goes more readily to the *o*- or *p*-positions. *But the reverse of this, removal of the iodine by polarographic reduction, goes more readily from the* m-*position.*

The greater ease with which α-iodonaphthalene is reduced (1·506 v.) compared with β-iodonaphthalene (1·560 v.) is not quite so easy to explain, but it may be compared to the reactivity of sodium with naphthalene, where the sodium adds on more readily in the α-position. Here the electron comes from the sodium atom.

The half-wave potential for *p*-iodonitrobenzene (1·71 v.) seems anomalous, because the nitro-group should decrease the electron density least at the *m*-position, and the potential for the *p*-derivative should be comparable with or lower than that of iodobenzene. We found, however, that *p*-iodonitrobenzene had two half-wave potentials: the first one is due to the reduction of the nitro-group, and the second to the iodine. We are dealing, then, at this second potential with the reduction, not of the nitro-compound, but of *p*-iodoaniline, which itself has a half-wave potential of this order (1·716 v.), and this is quite understandable, as the amino-group by its resonance properties enhances the electron density at the *p*-position. However, both these iodo-compounds show a pH dependence which we have yet to investigate further.

Half-wave potentials (in volts) in M/100-*tetraethylammonium bromide*; 66% *ethanol*; *concentrations* 1/3 *millimol./litre*; *temp.* 25°. *Potentials are referred to the saturated calomel electrode.*

Iodobenzene	−1·616	α-Iodonaphthalene	−1·506	2-Iodo-1 : 4-dimethoxy-benzene	−1·446
m-Iodotoluene	−1·613	β-Iodonaphthalene	−1·560	*p*-Iodonitrobenzene	−1·710
o-Iodotoluene	−1·656	4-Iodoacenaphthene	−1·620	*p*-Iodoaniline	−1·716
p-Iodotoluene	−1·660				

The iodobenzoic acids, iodoacetic acid, and *o*- and *p*-iodoaniline were also investigated, and were found to have half-wave potentials dependent on the pH of the solution. *o*-Iodobenzoic acid gives two steps (1·04 v. and 1·60 v.) in N/10-potassium chloride, and also two steps (1·14 v. and 1·60 v.) in tetraethylammonium bromide and 66% alcohol, the sum of the two wave-heights being, in each case, proportional to the concentration of the acid. In buffered solutions the two steps are not obtainable in one polarogram, as the hydrogen decomposition in acid buffers precedes the second step, whilst in the alkaline buffers only the second step is present. In buffers from pH 1·12 to pH 12·5 the measurable half-wave potentials were shifting from 1·00 v. to 1·64 v.

m-Iodobenzoic acid gives only a very wide wave in potassium chloride solution and in tetraethylammonium bromide. The separation of the two waves was not possible. The reduction of the *m*-acid in acid buffers starts at somewhat lower potentials than the hydrogen discharge, but it is very close to it from the point of view of the measurement, which is rendered very difficult. In alkaline buffers the half-wave potential is 1·605 v.

p-Iodobenzoic acid never reduces at potentials lower than those of the hydrogen discharge. Only in alkaline buffers is a definitive half-wave (1·58 v.) obtained.

The half-wave potentials of iodoacetic acid shift from 0·17 v. to 0·67 v. when the pH is increased from 1·12 to 12·5.

The iodoanilines show maxima in acid buffers, but in alkaline buffers and in tetraethylammonium bromide no maxima were obtained.

These pH-dependent iodo-compounds, on account of their ionization and difference in properties of the molecule and the ion, are being investigated in greater detail.

EXPERIMENTAL.

The polarographic apparatus was of the manually controlled, conventional design. The dropping cell was connected by an agar-saturated potassium chloride bridge to a saturated calomel electrode, prepared from pure mercury, calomel, and potassium chloride (supplied by Leeds and Northrop). The cell and electrode were contained in a thermostat at 25° ± 0·1°. Purified hydrogen was bubbled through the solutions to remove dissolved oxygen. The characteristics of the capillary were: m = 0·9166 mg., t = 5·44 seconds. The 50-ohm coil resistance galvanometer was shunted and calibrated with a standard microammeter in series.

Buffers: pH 1·2 to 5·3, were made from N/5 hydrochloric acid and N/5-sodium acetate; pH 5·3 to 8·20, from N/5-potassium dihydrogen phosphate and N/5-disodium hydrogen phosphate; pH 8·2 to 12·6, from N/5-sodium hydroxide, N/5-sodium chloride, and N/5-glycine.

The iodo-compounds used had all been carefully purified by recrystallization and vacuum sublimation by the group of workers engaged on spectroscopic studies of these compounds.

We are indebted to Dr. B. Breyer for helpful discussion. We gratefully acknowledge financial assistance from the Commonwealth Science Grant to this University.

PHYSICO-CHEMICAL LABORATORIES,
UNIVERSITY OF SYDNEY, N.S.W., AUSTRALIA.

[*Received, July* 10*th*, 1950.]