

POLAROGRAPHIC REDUCTION
OF ALDEHYDES AND KETONES. XVI.*
IONIZATION OF PHTHALIMIDE

A. RYVOLOVÁ-KEJHAROVÁ and P. ZUMAN**

*J. Heyrovský Institute of Polarography,
Czechoslovak Academy of Sciences, Prague 1*

Dedicated to the 65th anniversary of the late Academician R. Brdička.

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In accordance with observed pH-dependence of wave-heights and half-wave potentials the reduction scheme of phthalimide is proposed: Protonated form of phthalimide (*I*) is reduced in one two-electron step to oxyphthalimidine (*III*). Unionized form of *I* undergoes reduction in two one-electron steps. Radical anion formed in the first step accepts proton and dimerizes to give a pinacol. Unionized molecule of *I* is reduced even at $\text{pH} > 10$, where the phthalimide anion predominates. Intersection of $E_{1/2}$ -pH plots for the first one-electron wave at $\text{pH} 9.7$ is in good agreement with reported $\text{p}K_2$ 9.8. Adsorption phenomena complicating behaviour at $\text{pH} 4-7$ can be avoided when 50% ethanolic solutions are studied.

Most electrochemical reductions of organic compounds are accompanied by a proton transfer, as in the course of the reduction process either a hydrogenation of a multiple bond or a nucleophilic substitution by hydrogen takes place. The acid-base equilibrium can be either preceding the electrode process proper, interposed between two electron transfers or subsequent to the potential determining step. Realization of the role of acid-base equilibria led to the use of buffered systems in organic polarography in aqueous media. The role of this equilibria is one of the reasons which make interpretation of processes following the first electron uptake in non-aqueous media (which we are unable to buffer) more complex.

In systems in which the acidity during electrolysis can be controlled by buffering it is possible from changes in polarographic current-voltage curves with pH to make deductions on participation of acid-base equilibria in the electroreduction and on their position relative to the electrode process proper. The presence and type of the acid-base equilibria was postulated from observed changes either in the wave-heights¹⁻⁵ or in half-wave potentials⁴⁻⁸. Even when the importance to follow both wave-heights and half-wave potentials of a given system was recognized in the early stages of development of organic polarography, the general importance of simultaneous discussion of pH-dependence of both wave-heights and half-wave potentials have been stressed only recently⁹. It has been pointed out⁹ that such discussion enables distinguishing between some

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** Present address: Department of Chemistry, Clarkson College of Technology, Potsdam, N. Y., USA.

reaction schemes which cannot be distinguished *e.g.* by studying the change in limiting currents only.

One of such systems is the reduction of phthalimide, for which originally only an overall scheme was suggested¹⁰⁻¹². A detailed investigation of the pH-dependence of limiting currents¹³ indicated the possibility of a proton uptake either prior to or following the first electron transfer. The interpretation based on interposed proton transfer was preferred¹³ and generally accepted^{4,5,14}.

Comparison of changes due to pH in wave-heights with those in the half-wave potentials lead to the proposal of a reduction scheme which involves protonation preceding the first electron uptake. This scheme is the subject of the present paper together with controlled potential electrolysis experiments. Further more, the polarographic behaviour of phthalimide was compared with that of its N-methyl derivative. For the latter type of compounds it was only stated^{11,14} that the morphology of the waves is essentially the same as for the parent unsubstituted compound, but a more detailed discussion of the pH-dependence was not offered.

EXPERIMENTAL

Apparatus

Polarographic curves were recorded by means of a polarograph LP 60 (Laboratorní přístroje, Prague) in connection with a pen-recorder EZ 2 and by means of a photographically recording polarograph LP 55 (from the same manufacturer) with a galvanometer of a sensitivity $2 \cdot 13 \cdot 10^{-9}$ A/mm. Polarographic electrolysis was carried out in a Kalousek cell with a separated saturated calomel electrode (s.c.e.) and an H-cell according to Manoušek with an s.c.e. separated by an saturated KCl bridge¹⁵. All values of half-wave potentials are expressed against s.c.e. The capillary used had an out-flow velocity of $m = 1.34$ mg/s at the height of mercury column $h = 60$ cm. Drop-time was regulated by means of an automatic detachment device (Tesla, Prague). pH-Values of investigated solutions were measured using a pH-meter PHM 4 (Radiometer, Denmark) in connection with a glass electrode G 200 B.

Substances and Solutions

Phthalimide was a commercial product (Spolek pro chemickou a hutní, Prague) m.p. 238°C. N-methylphthalimide (m.p. 133°C) was prepared by Dr O. Exner, J. Heyrovský Institute of Polarography, Prague. Stock solutions of electroactive compounds were prepared 0.02M or 0.005M by dissolving the weighted amount of the substance in 96% ethanol.

Buffers and supporting electrolytes were prepared from Analar Grade chemicals. Phosphate buffers pH 5—8 were prepared in such a way that concentration of one component (either monopotassium or disodium phosphate) was kept constant and pH changed by variation of the concentration of the second component. Ionic strength was kept constant by addition of a sodium chloride solution.

Measuring Procedures

Polarography. Solutions for polarography were prepared by addition of 0.4 ml, 0.5 ml or 2.5 ml of the stock solution to 4.6 ml, 4.5 ml or 2.5 ml of a buffer with ionic strength kept con-

stant. Resulting ethanol concentrations were 8%, 10% or 50%. Oxygen was removed by a nitrogen stream. Polarographic curves were recorded within 3 minutes after mixing the solutions, in alkaline solutions, at $\text{pH} > 9$, within 1 minute. In particular for N-methylphthalimide it was necessary to extrapolate the wave-height to $t = 0$ to make up for the decrease of waves caused by hydrolysis.

Cyclic voltametry. Current-voltage curves of a solution of 10^{-2}M phthalimide in Britton-Robinson buffer $\text{pH} 7.5$ containing 50% ethanol obtained by means of a hanging mercury drop electrode were four times repeated. Second and further curves were shifted by some 60 mV to more negative potentials when compared with the first curve. This shift was taken into consideration in selection of the applied voltage for electrolysis at the mercury pool electrode.

Controlled potential electrolysis with a mercury pool electrode. Preparative electrolysis of phthalimide was carried out in a cell according to Lingane¹⁶ constructed by J. Holubek, Research Institute of Natural Drugs, Prague. In this cell the cathode was a stirred mercury pool electrode, anode a silver chloride electrode in saturated potassium chloride solution. Potential of the working cathode was measured potentiometrically against a third electrode, an s.c.e.

To study the reduction in acidic media, 30 ml of a saturated solution in 1M-HCl containing 50% ethanol (Sample I) were deaerated by a stream of nitrogen which was gently swept over the solution surface during the electrolysis. Potential was kept at -1.0 V which corresponds to the limiting current of the two-electron wave A (*cf.* Results). Decrease of phthalimide concentration in the course of electrolysis was controlled polarographically on samples taken from the reduction mixture. The colour of the solution changed during electrolysis first into grey, then in a yellowish. The electrolysis was completed after seven hours. The reduced solution was neutralized by addition of ammonia, extracted into ether and dried over magnesium sulphate. Ether was distilled off at reduced pressure. From the resulting yellow oily residue, overnight at 0°C , white crystals separated (m.p. 169°C). Recrystallization from water gave crystals of different appearance (m.p. 108°C).

Reduction of phthalimide in neutral media was carried out in 1M-LiCl containing 50% ethanol (Sample II). This solution gave two one-electron waves on polarographic curves. The preparative electroreduction was carried out at -1.1 V corresponding to the limiting current of the first one-electron wave A'. In the course of electrolysis the reduced solution turned first turbid and yellow-brown, later became clear and colourless. Polarographic control revealed that after nine hours the reduction was practically complete. The electrolysed solution was extracted by ether, the ether solution dried, the solvent distilled off and resulting yellow crystals (m.p. 239°C) isolated.

Alternatively a cell according to Manoušek¹⁵ was used, where the cathode was a mercury pool at the bottom of the cell connected with a mercury reservoir, the anode a separated s.c.e.

Reduction of 10^{-3}M phthalimide in Britton-Robinson buffer $\text{pH} 7.5$ containing 50% ethanol (Sample III) was carried out in 1 ml of the solution, both at a potential corresponding to the limiting current of wave A' (-1.22 V , s.c.e.) and at potential corresponding to that of wave B (-1.53 V). The reduction was monitored polarographically and was found completed within 2 hours. U. v. spectra of the reduced solution were recorded and its reactivity towards periodate oxidation was tested polarographically¹⁷.

To 0.8 ml of the acetate buffer $\text{pH} 4.7$ 0.1 ml of the solution after electrolysis was added so that the final concentration was $1 \cdot 10^{-4}\text{M}$ phthalimide and 5% ethanol. After purging by argon the zero line was recorded, the cell protected from light and 0.1 ml of $1 \cdot 10^{-3}\text{M-KIO}_4$ was added, argon briefly introduced and at a constant potential $E = 0\text{ V}$ (s.c.e.) the decrease of the periodic acid wave with time was followed. As periodic acid under these conditions reacts with traces of reducing agents and dropped off mercury present in the polarographic cell, a comparison with blank was essential. The behaviour of the product of the one-electron reduction in wave A' was therefore compared with behaviour of the pure buffer solution containing 5% of ethanol, with solution

of phthalimide before electrolysis and with solution obtained by electrolysis at the limiting current of the two-electron wave B. The decrease in these three solutions was reproducible and identical. Decrease in the presence of the one-electron reduction product was significantly greater.

Controlled potential electrolysis with the dropping mercury electrode. When dropping mercury electrode was used, 0.5 to 1.0 ml of the solution containing 5 to 8 · 10⁻⁴M phthalimide was placed in a cell designed by Manoušek¹⁵. Inert gas was swept over the surface of the solution during the electrolysis, carried out for 6 to 20 hours. After chosen intervals polarographic curves were recorded and logarithm of the current was plotted as a function of time. The plots were linear and the slope corresponded to the number of electrons transferred, when the electrolysis was carried out at the limiting current of the two-electron wave A at -1.05 V in acetate buffer pH 3.8 containing 8% ethanol or at the limiting current of both one-electron wave A' at -1.15 V or two-electron wave B at -1.40 V in a phosphate buffer pH 7.3.

RESULTS

Polarography of Phthalimide (I)

As it has been reported¹³, phthalimide is reduced in buffered solutions of pH 2-4 at the dropping mercury electrode in a wave A which corresponds to a two-electron reduction step. The height of this wave remains unchanged at pH < 5, but its slope

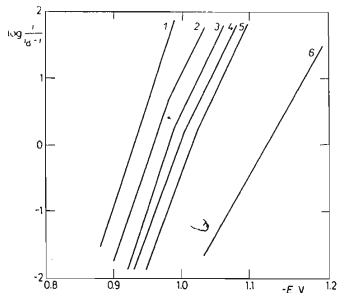


FIG. 1

Change of the Logarithmic Analysis of Phthalimide Waves with pH and Ethanol Concentration

4 · 10⁻⁴M phthalimide, acetate buffer, $\mu = 0.16$. 1-5: 8% ethanol; 6 50% ethanol. pH: 1 4.55; 2 4.8; 3 5.1; 4 5.4; 5 5.7; 6 5.8.

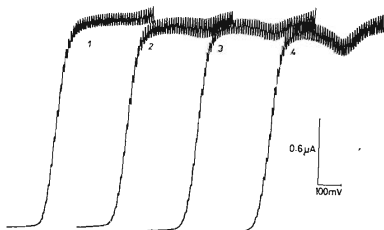


FIG. 2

Effect of Buffer Concentration on Shapes of Phthalimide Waves

4 · 10⁻⁴M phthalimide, acetate buffer pH 5.4, 8% ethanol. Concentration of buffer components: Acetic acid: 1 0.032M; 2 0.024M; 3 0.016M; 4 0.008M; Sodium acetate: 1 0.16M; 2 0.12M; 3 0.08M; 4 0.04M. From -0.8 V, S.C.E.

varies: Whereas at $\text{pH} < 4$ the slope of the logarithmic analysis corresponds to 0.030 V, at $\text{pH} > 5.8$ it corresponds to 0.050 V. In the intermediate range the logarithmic analysis can be approximated by two linear portions with slopes of 0.030 and 0.050 V, the ratio of which changes with pH (Fig. 1).

At $\text{pH} > 5$ the height of the wave A decreases with increasing pH in the shape of a dissociation curve (Fig. 4, ref.¹³) until it reaches 50% of its original height and is then denoted A'. Simultaneously a new wave B is formed at more negative potentials, the total height of waves A and B remaining constant. At $\text{pH} > 8$ the reduction of phthalimide takes place in two one-electron steps A' and B (Fig. 1, ref.¹³).

At pH 5 to 5.7, in the initial stage of the dissociation curve, the lowering of wave A is more marked at lower buffer concentration (Fig. 2). With dilution of the buffer of pH 5.4 the decrease of current is more pronounced at potential some 200 mV more negative than the half-wave potential. This dependence of the current decrease on potential results in a dip (trough) on the limiting current (Fig. 2).

In this pH -region the shape of the polarographic wave depends also on the nature of the components used for buffer preparation (Fig. 3), whereas for pH 6–8, where phosphate buffers were used, the height of wave A was found independent of concentration and composition of the buffer. The shape of the pH -dependence in phosphate buffers prepared with concentration of either the acid or the base buffer com-

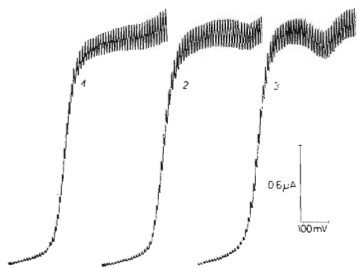


FIG. 3

Effect of Nature of Buffer on Shapes of Phthalimide Waves

$4 \cdot 10^{-4}\text{M}$ phthalimide, 8% ethanol. 1 0.05M citrate buffer pH 5.4; 2 0.05M acetate buffer pH 5.5; 3 0.05M phosphate buffer pH 5.65. From -0.8 V, s.c.e.

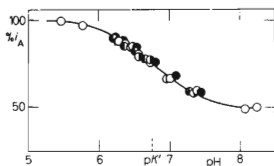


FIG. 4

Polarographic Dissociation Curve of Phthalimide Obtained at Various Buffer Concentration

$4 \cdot 10^{-4}\text{M}$ phthalimide, 8% ethanol, $\mu = 0.24$, $t_1 = 3$ s. Small circles: acetate buffer; large circles: 0.04M phosphate buffer; full points: 0.032M phosphate buffer; halved circles 0.024M and 0.016M phosphate buffers.

ponent constant is practically unaffected by the type of the buffer (Fig. 4). The polarographic dissociation curve corresponds to pK' 6.75.

Change in ionic strength due to an addition of a neutral salt to a buffered solution of phthalimide results in the elimination of the dip on the limiting current of wave A in acetate buffers and an increase of this limiting current in phosphate buffers, but the latter effect is due to a pH change. If the effect on change of pH is taken into account, the shape and the position of the dissociation curve in phosphate buffers is independent (Fig. 5) of ionic strength.

Increase in ethanol concentration in phosphate buffers pH 6.75 results in a decrease of the over-all wave-height ($i_A + i_B$, Fig. 6), in elimination of the dip on the limiting current of wave A, in the change in the ratio $i_A : i_B$ in favour of wave B and in shifts of half-wave potentials of both waves to more negative values* (Table I). The observed decrease of i_A relative to $i_A + i_B$ is greater than corresponds to the pH increase (corresponding to 0.33 pH, as measured by glass electrode standardized against aqueous buffers) caused by the increase in ethanol concentration from 8 to 32%.

Due to a higher solubility of buffer components, it is possible to extend the ethanol concentration in acetate buffers up to 50%. At such concentration the dip on the limiting current is no longer observed (Fig. 7), and dissociation curve is shifted to lower pH-values. For $4 \cdot 10^{-4} M$ to $1 \cdot 10^{-3} M$ phthalimide pK'_1 6.3, for $2.5 \cdot 10^{-3} M$ phthalimide, pK'_1 6.2 were found. Logarithmic analysis of wave A at pH 5.8 gives in the presence of 50% ethanol a linear plot with a slope of 0.057 V (Fig. 1, curve 6). The plot of the pH-dependence of half-wave potentials (Fig. 8)

TABLE I

Effect of Ethanol Concentration on Wave-Heights and Half-Wave Potentials of Phthalimide $4 \cdot 10^{-4} M$ phthalimide, $\mu = 0.24$.

M-KH ₂ PO ₄ 0.08		M-Na ₂ HPO ₄ 0.04		M-KH ₂ PO ₄ 0.04		M-Na ₂ HPO ₄ 0.04					
% eth	pH	$i_A, \mu A$	$i_A + i_B$ μA	$-E_{1/2}^A$ V	$-E_{1/2}^B$ V	% eth	pH	$i_A, \mu A$	$i_A + i_B$ μA	$-E_{1/2}^A$ V	$-E_{1/2}^B$ V
8	6.48	1.75	2.0	1.05	1.29	8	6.75	1.63	2.08	1.04	1.27
16	6.6	1.5	1.88	1.07	1.29	16	6.89	1.29	1.91	1.08	1.29
24	6.72	1.22	1.74	1.09	1.29	24	7.05	1.05	1.77	1.09	1.29
32	6.83	1.02	1.61	1.11	1.30	32	7.18	0.92	1.63	1.11	1.30

* This shift is not caused by a pH-change, since over the pH-range (6.5–9) in which the pH can change due to ethanol addition, the half wave potential of wave A is pH-independent (Fig. 8.)

in solutions containing 8% ethanol and $5 \cdot 10^{-4} \text{M}$ phthalimide shows that the half-wave potentials of wave B are pH-independent. For wave A in solutions of simple buffers containing successively hydrochloric acid, citrate, acetate and borate this

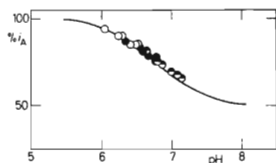


FIG. 5

Effect of Ionic Strength on Polarographic Dissociation Curve of Phthalimide

$4 \cdot 10^{-4} \text{M}$ phthalimide, 8% ethanol, $t_1 = 3 \text{ s}$
 $0.04 \text{M-Na}_2\text{HPO}_4$, conc. of KH_2PO_4 ○ 0.08M;
 ● 0.04; ◐ 0.02. Ionic strength is changed by adding NaCl. $\mu = 0.2; 0.24; 0.3; 0.4; 0.5; 0.84$. (pH changes with increasing ionic strength to lower values).

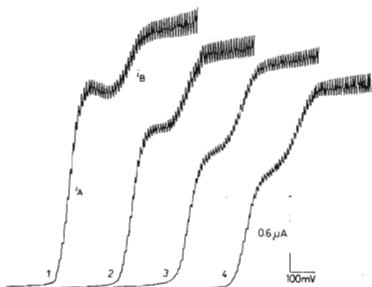


FIG. 6

Effect of Ethanol Concentration on Heights of Phthalimide Waves

$4 \cdot 10^{-4} \text{M}$ phthalimide, $0.04 \text{M-KH}_2\text{PO}_4$, $0.04 \text{M-Na}_2\text{HPO}_4$, $\mu = 0.24$. Ethanol concentration and pH-value (measured with glass electrode standardized against aqueous buffers): 1 8%, 6.75; 2 16%, 6.89; 3 24%, 7.05; 4 32%, 7.18. From -0.8 V , s.c.e., $t_1 = 3 \text{ s}$.

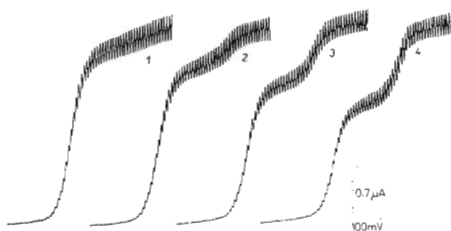


FIG. 7

pH-Dependence of Phthalimide Waves in Presence of 50% Ethanol

$1 \cdot 10^{-3} \text{M}$ phthalimide, 0.08M acetate buffer, pH (measured as in Fig. 6): 1 5.9; 2 6.2; 3 6.5; 4 6.9. From -0.9 V , s.c.e., $t_1 = 3 \text{ s}$.

dependence shows three linear portions: two where the slope can be approximated as 0.058 V/pH and one, between $\text{pH } 6.75$ and 9.7 , pH-independent. Shifts of index potentials $E_{1/4}$ and $E_{3/4}$ are parallel up to $\text{pH } 4$ and divergent at higher pH-values (Table II). The two intersections on the $E_{1/2} - \text{pH}$ plot (Fig. 8) correspond to polarographic $\text{p}K_1'' 6.75$ and to the equilibrium constant $\text{p}K_2 9.7$.

In 50% ethanol the half-wave potentials are shifted to more negative values and in the pH-independent range at $\text{pH } 6.2$ the half-wave potential of wave A' is -1.15 V and that of wave B is -1.39 V (S.C.E.).

The effect of phthalimide concentration on the shape of polarographic curves depends on pH and ethanol concentration at which this effect is investigated. In solutions containing ethanol in concentrations of 8–10% at pH about 5 the wave A shows at concentration up to $8 \cdot 10^{-4} \text{ M}$ a flat limiting current. Only at higher phthalimide concentrations the dip, indicating the separation of two waves (Fig. 9) appears on the limiting current. In solutions containing 8–10% of ethanol the height of wave A at $\text{pH } 6$ to 7 is linearly proportional to phthalimide concentration up to $8 \cdot 10^{-4} \text{ M}$

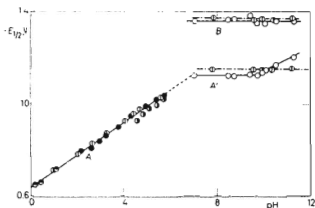


FIG. 8

pH-Dependence of Half-Wave Potentials (S.C.E.) of Phthalimide (full) and N-Methylphthalimide (dot-and-dashed) in Simple Buffers

$5 \cdot 10^{-4} \text{ M}$ phthalimide derivative, 8% ethanol solutions: ● hydrochloric acid; ● citrate buffer; ○ borate buffer; ● acetate buffer. ○ N-Methylphthalimide in the same buffer solutions.

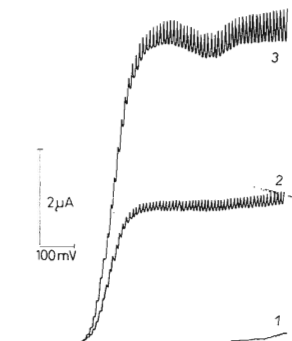


FIG. 9

Dependence of Wave Shape on Phthalimide Concentration

0.12 M phosphate buffer $\text{pH } 5.2$, 8% ethanol; $\mu = 0.24$, $t_1 = 3 \text{ s}$, phthalimide concentration: 1 0; 2 $6 \cdot 10^{-4} \text{ M}$; 3 $1.4 \cdot 10^{-3} \text{ M}$. From -0.7 V , S.C.E.

and shows deviations at higher concentrations (Fig. 10, curve 2 and 3). Consequently also the value of the ratio $i_A : (i_A + i_B)$ remains unchanged up to $8 \cdot 10^{-4}M$ and decreases only at higher concentrations. In solutions containing 50% ethanol the deviations of the $i - C$ plot from linearity are observed only for concentrations higher than $1.5 \cdot 10^{-3}M$. Even under conditions where the wave i_A shows deviations from the linear $i_A - c$ plot, the total wave-height $i_A + i_B$ is always a strictly linear function of concentration (Fig. 10, curve 1). At $pH > 8$ both waves A' and B are a simple linear function of concentration up to $3 \cdot 10^{-3}M$ and the ratio $i_A/i_B = 1 : 1$ remains concentration independent.

As a consequence of the aforementioned concentration dependence of wave A in 8% ethanolic solutions, the polarographic dissociation curve is shifted with increasing phthalimide concentration towards lower pH-values. In phosphate buffer of constant ionic strength $\mu = 0.24$ and 8% ethanol at phthalimide concentration $4 \cdot 10^{-4}M$ pK'_1 6.75; at $8 \cdot 10^{-4}M$ pK'_1 6.6 and at $1.6 \cdot 10^{-3}M$ pK'_1 6.45. In 50% ethanol the pK' -value is virtually concentration independent. In 8% ethanol at pH about 6 the wave A becomes less steep at higher phthalimide concentration. The half-wave potential of wave A is shifted by about 20 mV to more negative potentials with a tenfold increase in phthalimide concentration.

When in solutions containing 8% ethanol the index potentials $E_{1/4}$ and $E_{3/4}$ were measured as a function of phthalimide concentration at $i_A/4$ and $3i_A/4$, $E_{1/4}$ is found concentration independent, whereas $E_{3/4}$ is shifted with increasing phthalimide concentration to more negative potentials: For example, at $4 \cdot 10^{-4}M$ phthalimide $E_{3/4}$ is -1.02 V and at $1.6 \cdot 10^{-3}M$ the potential $E_{3/4}$ is -1.04 V (S.C.E.).

TABLE II
pH-Dependence of Index Potentials of Phthalimide
 $5 \cdot 10^{-4}M$ phthalimide, 8% ethanol.

Solutions	pH	$-E_{1/4}$, V	$-E_{3/4}$, V
HCl	0.15	0.63	0.66
	0.4	0.66	0.685
	1.05	0.705	0.73
Citrate buffer	2.0	0.76	0.79
	2.6	0.8	0.83
	3.0	0.84	0.87
	3.9	0.9	0.93
	4.3	0.93	0.975
	4.8	0.96	1.015
	5.4	1.005	1.055

Polarography of *N*-Methylphthalimide (II)

The *N*-methylphthalimide shows waves *A* and *B* similar to that of the unsubstituted parent compound. The wave *A* decreases in the shape of a dissociation curve until it reaches 50% of its original value. But contrary to the unsubstituted phthalimide, the shape of the polarographic dissociation curve even at low (8%) ethanol concentration is not affected by concentration of the methyl derivative. Only small changes of the inflexion point pK' with concentration were observed.

Another difference between the methyl derivative *II* and parent compound *I* is shown by the pH-dependence of the half-wave potentials. In acidic media half-wave potentials of waves *A* of *I* and *II* are so close that they practically overlap (Fig. 8). At pH 6 to 9 waves *A'* and *B* of *I* and its methyl derivative *II* (Fig. 8, dashed line) are similar and parallel. At pH > 9, where for *I* shift in half wave potentials of *A'* were observed, for methyl derivative *II* both waves *A'* and *B* remain pH-independent at -1.15 V and -1.37 V.

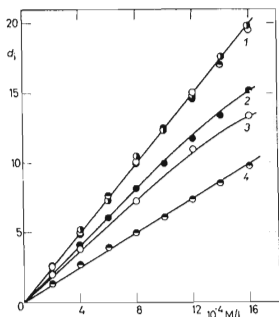


FIG. 10

Concentration Dependence of Phthalimide Waves at Varying pH

8% ethanol, μ 0.24, phosphate buffer
pH: ● 5.2; ● 6.48; ○ 6.75; ● 8.1.

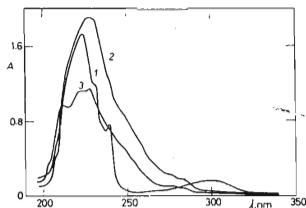


FIG. 11

Electronic Spectra of Phthalimide and of Products of its Reduction at a Mercury Pool Electrode

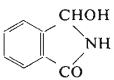
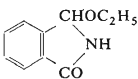
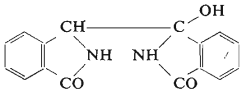
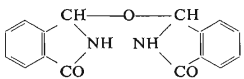
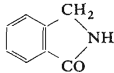
Britton-Robinson buffer pH 7.5, 50% ethanol, d 0.2 cm, $1.25 \cdot 10^{-4}$ M phthalimide before electrolysis; 2 product of electrolysis of $1 \cdot 10^{-3}$ M phthalimide at -1.22 V (s.c.e.) corresponding to the limiting current of one-electron wave *A'*; 3 product of electrolysis of $5 \cdot 10^{-4}$ M phthalimide at -1.53 V (s.c.e.) corresponding to the limiting current of the two-electron process in wave *B*.

Controlled Potential Electrolysis

Preparative electrolysis indicated that the reduction products of phthalimide are reactive, easily undergo subsequent changes and are stable only under narrowly defined conditions. This is in agreement with reports in the literature¹⁸⁻²³ and reflected by the variety of reported products (Table III).

TABLE III

Reduction Products of Phthalimide Reported in the Literature

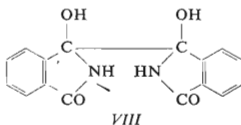
No	Attributed structure	M.p., °C	Author	Ref.
III	 Oxyphthalimidine	171-2	Reisert	18
		178	Dunct	22
		105	Sakurai	19
IV	 Ethoxyphthalimidine	108	Dunct	22
V	 Oxyphthalimidine dimer	240 ^a	Reisert	18
		171 ^b	Sakurai	19
VI	 Bis-oxyphthalimidine anhydride	240	Sakurai	19
VII	 Phthalimidine	149	Sakurai	19

^a Results by boiling compound III in glacial acetic acid; ^b by treatment with glacial acetic acid of V results VI.

The product isolated from the mercury pool electrolysis at the potential corresponding to a two-electron reduction (*A*) in acidic media can be attributed to oxyphthalimidine *III*, the observed m.p. (169°C) being in agreement with data by Reissert¹⁸ and Dunet²² (Table III). This compound undergoes hydrolysis to form the compound of m.p. 108°C which is according to Dunet²² ethoxyphthalimidine *IV*, that can be formed from oxyphthalimidine *III* in presence of ethanol. This compound was seemingly identical with that isolated by Sakurai^{19,20} who attributed it structure *III* and has shown the reversibility of the hydrolysis process, when in glacial acetic acid the compound with m.p. 171°C was recovered. The same type of reduction product can be assumed to be formed in the two-electron reduction in wave *B*.

UV absorption spectra (Fig. 11) show a decrease of the absorbance corresponding to the conjugate carbonyl groupings in the region of 300 nm, when electrolysis was carried out at -1.53 V at pH 7.5. Absorption at 275 nm can be attributed to one conjugated carbonyl group as compared with two groups in *I*.

The product of the one-electron reduction in unbuffered media (m.p. 239°C) is probably identical with the compound obtained by Reissert¹⁸. This compound shows an absorption at 275 nm which can be attributed to benzoyl grouping and an increased absorption at 225 nm (Fig. 11). From the reactivity of the reduction product in periodic acid oxidation and analogy with other carbonyl compounds²⁴, it can be assumed that the radical generated at -1.22 V at pH 7.5 will dimerize and form a pinacol *VIII* rather than *V*.



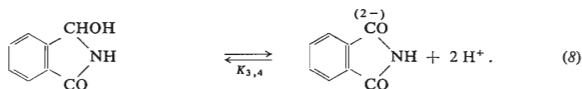
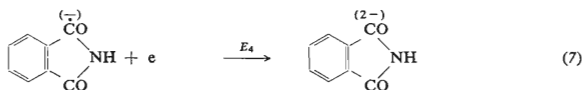
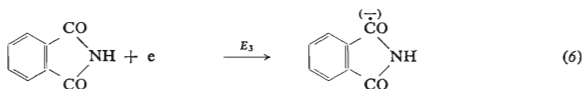
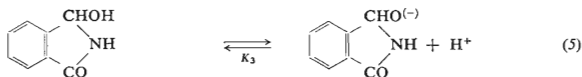
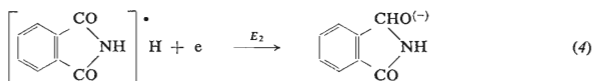
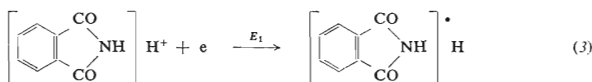
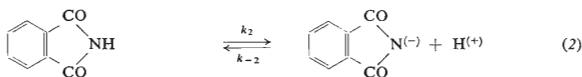
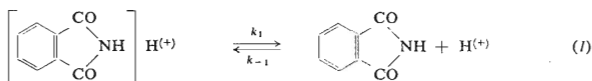
The structure of reduction products is being further investigated.

DISCUSSION

Changes of heights of waves *A*, *A'* and *B*, shifts of the half-wave potentials and isolated products are in agreement with the reduction Scheme (1)–(8) (p. 1031).

At pH 0–5 phthalimide exists in the solution predominantly in the unprotonated form, but the protonation is rapidly established and the protonated form is electroactive in one-electron uptake (3). Unprotonated form is transported to the electrode surface by diffusion. The equilibrium perturbed by the reduction of the protonated form is rapidly reestablished. Reduction of the protonated form produces in step (3) a radical. Formation of a single two-electron wave indicates that potential E_2 of the reduction of this radical in step (4) is either comparable or more positive than potential

of the first electron uptake E_1 . Because the acid-base equilibrium (1) is precedent to the potential determining step (3), the half-wave potential of the wave A in this pH-range, at $\text{pH} < (\text{p}K' - 1)$ is shifted to more negative potentials with increasing pH by 0.058 V/pH. Protonation (5) takes place as a consecutive reaction.



At pH 5–7 unprotonated form of phthalimide is still transported by diffusion to the electrode surface and undergoes there protonation, but as the rate of protona-

tion decreases with increasing pH, not all of the phthalimide is transformed into protonated form. As the rate of the protonation decreases so does wave A. The part of phthalimide which cannot be protonated is reduced in two steps, (6) and (7). Because there is no separation of waves A and A', it must be concluded that in this pH-range (pH 5–7) the potential E_1 of step (3) differs so little from potential E_3 of step (6) that the difference is not sufficient for formation of separate waves but their presence is indicated by logarithmic analysis. The reduction of the radical anion in step (7) takes place, nevertheless, at considerably more negative potential E_4 than that of the radical (E_2). Therefore the second one-electron uptake takes place in wave B at potential E_4 . With increasing pH the proportion of phthalimide which is reduced *via* path (6), (7) as compared with path (1), (3), (4) increases and so does wave B.

At pH 7–9.5 phthalimide exists in the bulk of the solution predominantly in unprotonated form and is reduced in the same form in steps (6) and (7). The half-wave potentials of the two one-electron waves A' and B in this pH-range are pH-independent and this is in agreement with path (6), (7) as none of these reactions involves antecedent proton transfer. The dianion formed accepts two protons in step (8), but as this reaction takes place subsequent to the irreversible step (7), this proton transfer does not affect the half-wave potentials.

At pH > 10 considerable part of the phthalimide is present in the solution as anion, because of the shift of the equilibrium (2) to the right hand side. Because, nevertheless, the establishment of the equilibrium (2) is fast and because uncharged phthalimide molecule takes up the first electron in step (6) at more positive potentials than the reduction of the conjugate base-anion would occur, reduction in wave still corresponds to the reduction of the unprotonated phthalimide. The compound is transported from the bulk of the solution predominantly by diffusion of the anion which is at the electrode surface rapidly converted into electroactive molecule. In the sequence (2), (6), (7) acid-base equilibrium (2) is preceding electron uptake (6) and therefore potential of wave A' shifts again to more negative potentials. Reduction of the radical anion in wave B does not involve antecedent acid-base reaction and therefore its half-wave potential remains pH-independent.

In 8% ethanolic solutions the polarographic values of pK'_1 6.75 from pH-dependence of wave heights and pK''_1 6.75 from the shifts of half-wave potentials of wave A were in good agreement. Similarly, the intersect an $E_{1/2}$ -pH plot at pH 9.7 corresponding to pK_2 value of reaction (2) is in good agreement with the value $pK_2 = 9.80$ reported in the literature²⁵.

The above scheme is further supported by the fact that N-methylphthalimide (II) which can be protonated as in reaction (1) but cannot undergo dissociation as in (2) shows a decrease of wave A and formation of wave B, but at pH > 9 shows no change in half-wave potential of wave A' with pH. The same reduction scheme applies also to N-substituted maleinimides²⁶, the half-wave potentials of which at pH > pK'_1 are also pH-independent.

The general scheme has been found to be at low ethanol concentration (8%) somewhat more complicated in the range between pH 4 and 7. As the increase in ethanol concentration to 50% results in removal of the dip on the limiting current of wave A, in elimination of the irregularities in the shape of wave A as indicated by logarithmic analysis, extension of the linear increase of the wave A with increasing concentration over the whole studied concentration range and furthermore makes the dissociation curves concentration independent, it can be deduced that the observed irregularities are due to adsorption phenomena. Decrease of wave i_A with increasing ethanol concentration indicates that surface concentration of phthalimide is decreased. It is thus possible to deduce that the adsorption phenomena are caused by adsorption of the protonated form of phthalimide. The adsorption of protonated phthalimide which increases concentration of the electroactive form, can result in increased concentration of an adsorbed proton donor and can also result in blocking of the surface to further reduction process (at higher phthalimide concentration). The dip observed on the limiting current can be explained by potential dependence of the surface concentration³. The elimination of the dip by increasing ionic strength is in agreement with this explanation. Observation of more pronounced adsorption perturbations in acetate than in phosphate buffers can be interpreted by less strong adsorption of phthalimide in the presence of bivalent phosphate anions. Some observations, *e.g.* the change in logarithmic analysis (Fig. 1) indicate that the electrode process can be also affected by adsorption of the radical formed in reaction (3). Absence of adsorption effects in the reduction of N-methyl derivative II even in 8% ethanolic solutions indicates strong dependence of adsorptivity on structure.

Because the pK -value of the protonation (I) is not accessible, and because the presence of dips on limiting current, effect of ethanol and difference between pK_1 and pK'_1 greater than 6 pK -units indicate the surface character of protonation, no attempts have been made to use treatments¹⁻⁵ for antecedent protonations to calculate the value of k_{-1} .

Behaviour of phthalimide in solutions containing 50% ethanol is uncomplicated and follows strictly scheme (1)–(8). The studied system thus contributes to the principle that when the goal of a study of organic electrode processes is the establishment of the reduction path rather than investigation of adsorption peculiarities, it is useful to carry out investigation under such conditions (concentration of the electroactive substance and solvent composition) that the adsorption effects are eliminated or at least minimized.

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