Cathodic Reduction of Phthalimide Systems in Nonaqueous Solutions

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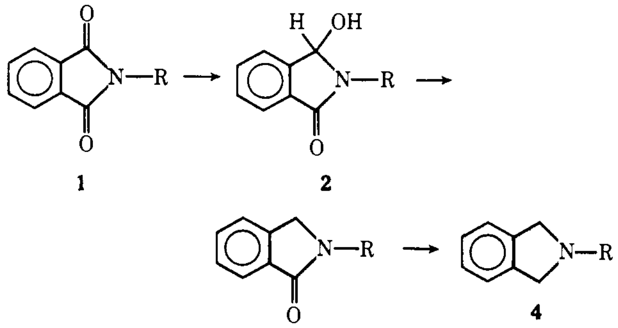
Abstract: Electrochemical reduction of phthalimide derivatives in *N,N*-dimethylformamide (DMF) with tetraethylammonium perchlorate (TEAP) as supporting electrolyte leads to products which can be accounted for on the basis of opening of the phthalimide ring. Mechanistic evidence based on cyclic voltammetric and chronoamperometric measurements indicates that reduction at potentials corresponding to an initial two-electron process yields a product that is consumed in a slow follow-up chemical reaction which is apparently dianion protonation. The postulation of the intermediacy of *o*-formylbenzamides in the reduction process accounts for the major products: *o*-hydroxymethylbenzamides and phthalide. The synthetic utility of this reaction is hampered due to the further reducibility of the major products at cathode potentials employed.

The electrolytic reduction of phthalimide systems has been investigated on several previous occasions. As early as 1913 Hope and Lankshear described the preparation of isoindolines **4** from phthalimides.[1] In later work it was found that various intermediate reduction products such as hydroxyphthalimidines **2** and phthalimidines **3** could be isolated in this reduction process as a function of the cathode material.[2,3] Isoindoline formation was also supported in the later work of Allen and Ocampo.[4,5]



1 **2** **3** **4**

The previous work was primarily conducted in aqueous acid solution. These reductions appear to follow the reduction of phthalimide compounds with tin and hydrochloric acid.[6] In these cases reduction proceeds through the hydroxyphthalimidine and stops with phthalimidine. Sodium borohydride reduction also proceeds through the hydroxyphthalimidine but further reduction occurs which leads to ring-opened products.[7]

With the exception of an electron spin resonance (esr) investigation of the radical anions of a series of phthalic acid derivatives, there has been no report of the electrochemistry of these compounds in nonaqueous media.[8] The present article reports on studies in our laboratory of the nonaqueous electrochemistry of these compounds. These studies indicate that electrochemical reduction of compounds of the phthalimide type in *N,N*-dimethylformamide (DMF) leads to products similar to those obtained by sodium borohydride reduction.[7] Electroanalytical studies combined with product analyses have allowed us to postulate a mechanism for this reaction.

Electroanalytical Studies

The compounds investigated are shown in Table I along with their reduction half-peak potentials as measured by cyclic voltammetry. All measurements in this study were made in anhydrous *N,N*-dimethylformamide (DMF) with tetraethylammonium perchlorate (TEAP) as supporting electrolyte. The working electrode was either a mercury-plated platinum button or a hanging mercury drop. The mercury-plated platinum button generally offered better reproducibility than the hanging mercury drop. A platinum button electrode was utilized in several instances to ensure that the electrochemical behavior observed was not specific to mercury cathodes. Solvent decomposition on platinum, however, precluded investigation of the secondary cathodic processes of the pthalimides investigated.

N-Substituted Phthalimides. The electrochemical behavior of the phthalimides is relatively uncomplicated with the exception of phthalimide itself which will be discussed later. Figure 1 shows a cyclic polarogram of *N*-methylphthalimide in DMF. In the time period of cyclic voltammetry (*ca.* 0.5 min) the phthalimide system is reversibly reduced to the radical anion at −1.37 V *vs.* sce and then to the dianion at −2.16 V. Radical anion formation in the electrolytic reduction of phthalimides has been previously shown by Sioda and Koski[8] and verified by us.[9] The chronoamperometric data for these compounds are given in Table II. With the exception of a slight difference in the reduction potentials, the electrochemistry of the *N*-methyl- and *N*-phenylphthalimides was identical.

The stability of the anion radical and dianion of *N*-methyl- and *N*-phenylphthalimide was investigated by cyclic voltammetry. Figure 2 shows the cyclic voltammetry of *N*-phenylphthalimide with the potential scan

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(1) E. Hope and F. Lankshear, *Proc. Chem. Soc.*, **29**, 224 (1913).

(2) B. Sakurai, *Bull. Chem. Soc. Jap.*, **5**, 184 (1930).

(3) E. W. Cook and W. G. France, *J. Phys. Chem.*, **36**, 2383 (1932).

(4) M. J. Allen and J. Ocampo, *J. Electrochem. Soc.*, 103, 452 (1956).

(5) M. J. Allen and J. Ocampo, *ibid.*, 103, 682 (1956).

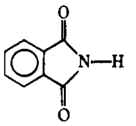
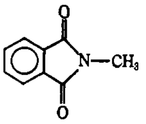
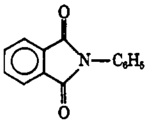
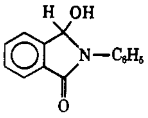
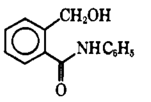
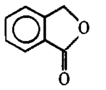
(6) C. Graebe and A. Pictet, *Justus Liebigs Ann. Chem.*, **247**, 302 (1888).

(7) Z. Horii, C. Iwata, and Y. Tamura, *J. Org. Chem.*, **26**, 2273 (1961).

(8) R. E. Sioda and W. S. Koski, *J. Amer. Chem. Soc.*, **89**, 475 (1967).

(9) We are grateful to Professor Theodore Kuwana of Case-Western Reserve University for assistance with esr measurements.

Table I. Phthalimide and Related Compounds Studied and Reduction Potentials[a]

No.	Compound	Structure	$E_{p/2}(1)$[b]	$E_{p/2}(2)$
I	Phthalimide		−1.45	(−1.76), (−1.99), (−2.14), −2.29[c]
II	*N*-Methylphthalimide		−1.37	−2.16
III	*N*-Phenylphthalimide		−1.31	−2.09
IV	*N*-Phenyl-3-hydroxy-phthalimidine		−2.01	
V	*o*-Hydroxymethyl-benzanilide		−1.98	
VI	Phthalide		−2.11	

[a] 0.1 *M* TEAP in DMF at a mercury-plated platinum button electrode. [b] Half-peak potential of first electron transfer process *vs.* sce. [c] Phthalimide exhibits several poorly resolved reduction processes that occur at the approximate potentials in parentheses.

held and reversed at a potential negative of the first (curve A) and second (curve B) electrode processes. This method of establishing the stability of the products formed at the electrode surface has been discussed previously.[10] The potential is increased sufficiently negative of the electrode process in question so that a diffusion-controlled reaction results and the current is allowed to decay to a constant value. Reversal of the potential scan and observation of the reverse process, in this case the anodic process, gives an indication of the stability of the products of the reaction. Curve A of Figure 2 shows the cyclic polarogram that results when the potential scan is stopped at a point midway between the two reduction processes (−1.71 V). The current decays to a constant value and subsequent reversal of the potential scan gives rise to reoxidation of the radical anion of *N*-phenylphthalimide to the parent phthalimide. The ratio of the anodic and cathodic peak currents is unity within experimental error which shows that the anion radical is considerably stable. When the same experiment is performed with the potential scan terminated past the second cathodic process (−2.42 V), reversal of the po-

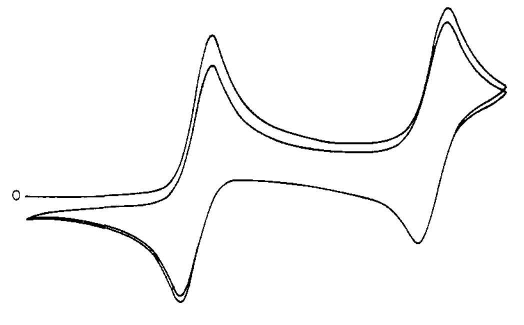


Figure 1. Cyclic voltammetry of *N*-methylphthalimide (II) in DMF with 0.1 *M* TEAP at a Hg-plated Pt button electrode, scan rate = 6 V/min.

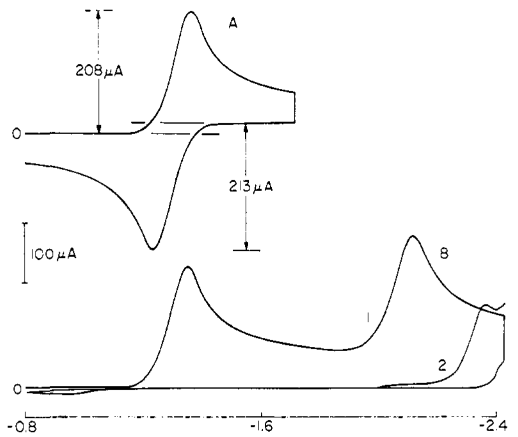


Figure 2. Cyclic voltammetry of *N*-phenylphthalimide (III) in DMF with 0.1 *M* TEAP at a Hg-plated Pt button electrode, scan rate = 6 V/min: curve A, potential scan terminated at *ca.* −1.7 V, held until current reached steady state and then reversed in the anodic direction; curve B, same as curve A except potential scan terminated at *ca.* −2.4 V. The first (1) and second (2) cycles are shown. See text for details.

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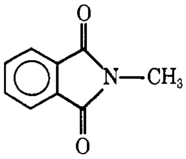
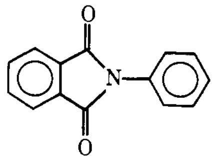
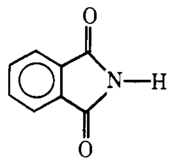
(10) R. F. Nelson, D. W. Leedy, E. T. Seo, and R. N. Adams, *Z. Anal. Chem.*, **224**, 184 (1967).

Table II. Chronoamperometric Data for Phthalimides

						
Time, sec	$it^{1/2}(1)$[a]	$it^{1/2}(2)$[b]	$it^{1/2}(1)$	$it^{1/2}(2)$	$it^{1/2}(1)$	$it^{1/2}(2)$
1.5	46.80	89.15	34.50	70.15	23.90	89.40
2.0	46.50	88.65	34.60	69.00	24.10	91.85
2.5	46.15	88.35	34.75	68.85	24.20	93.00
3.0	46.25	88.15	34.75	68.50	24.25	93.50
3.5	46.20	87.65	35.00	67.50	24.35	95.50
4.0	46.10	87.65	35.00	67.50	24.55	96.00
4.5	46.75	87.65	35.25	66.00	24.95	97.50
5.0	46.85	87.85	35.25	66.00	24.60	97.50
5.5	46.90	88.35	35.50	65.75	24.70	97.50
6.0	47.10	88.50	35.50	64.50	24.65	99.00
6.5	47.40	88.50	35.75	64.00	24.90	100.0
7.0	47.65	89.00	35.75	64.00	24.90	101.00
7.5	47.85	89.10	35.90	64.00	24.90	101.50
8.0	48.30	89.50	36.00	64.00	25.20	102.00
8.5	48.40	90.00	36.10	64.00	25.25	102.00
9.0	48.75	90.50	36.05	63.50	25.35	102.00
9.5	49.00	90.00	36.10	62.75	25.50	102.00
10.0	49.40	91.00	36.40	62.00	25.50	102.00
$[it^{1/2}/C]_{(av)}$[c]	47.42	89.03	35.42	66.24	24.75	97.58
Ratio[d]	1.88		1.87		3.94	

[a] $it^{1/2}(1)$ in μA sec$^{1/2}$ for the first cathodic wave. [b] Same for second cathodic wave. [c] $it^{1/2}/C$ in μA sec$^{1/2}$/mM. [d] Ratio = $[it^{1/2}(2)/it^{1/2}(1)]$.

tential scan shows no evidence of reoxidation of the dianion (curve B, Figure 2). Continuation of the anodic sweep to −0.8 V and reversal in the cathodic direction shows that a new material has been formed which is reducible at *ca.* −2.36 V. The *N*-phenylphthalimide dianion is seen to be very unstable under these conditions and is quite obviously consumed in a chemical reaction subsequent to electron transfer.

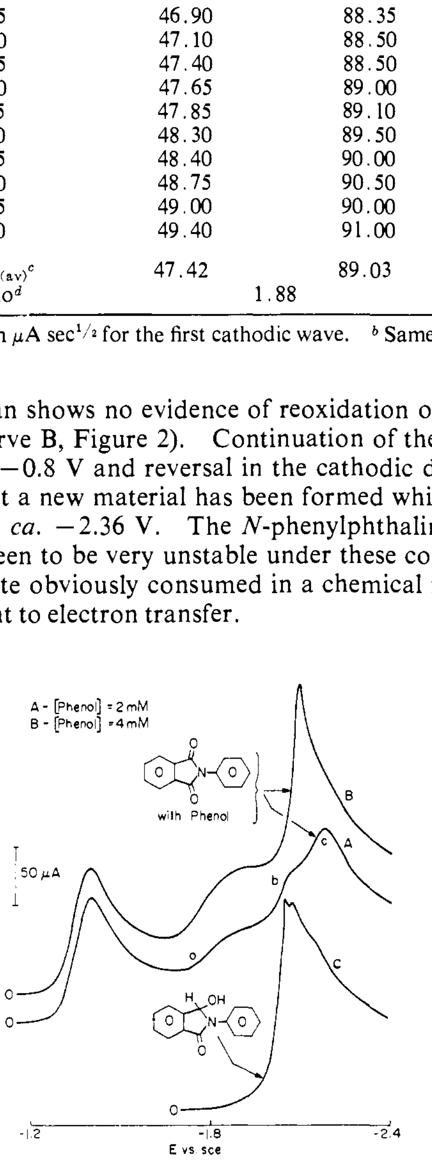


Figure 3. Linear sweep voltammetry of *N*-phenylphthalimide in the presence of phenol (curves A and B). Curve C shows linear sweep voltammetry of *N*-phenyl-3-hydroxyphthalimidine (IV). See text for details.

The decomposition of the dianion of *N*-phenylphthalimide was found to be a first-order reaction in this medium. The case of an electron transfer reaction followed by a homogeneous first-order chemical reaction has been treated theoretically for cyclic voltammetry by Nicholson and Shain.[11,12] Analysis of the cyclic voltammetry of *N*-phenylphthalimide as a function of the rate of potential scan adheres well to the above theory. The rate of the decomposition reaction is 5.4×10^{-2} sec^{-1}.

The results of these experiments suggested that the *N*-phenylphthalimide dianion was being protonated by the reaction medium. This is in analogy with the observed behavior of aromatic hydrocarbons[13] and aromatic azo compounds.[14] This hypothesis was investigated further by briefly examining the voltammetry of *N*-phenylphthalimide in the presence of phenol as a proton source. Figure 3 summarizes these data. When phenol is added to the solution the anodic current corresponding to the dianion completely disappears as would be expected if protonation were involved in the decomposition reaction. Furthermore, two additional cathodic waves appear between the original waves (a and b, Figure 3). Both of these new waves increase as a function of increasing phenol concentration. The initial reduction process (anion formation) is not affected by the presence of phenol up to a phenol–phthalimide ratio of 10:1. These data can be interpreted in the following manner.[15] The radical anion is in equilibrium with the protonated radical anion. The protonated anion is then reduced at lower potentials than the anion. The fact that the initial reduction process is unaffected by the presence of a proton source leads us to believe that protonation of the radical anion immediately precedes electron transfer. The reduction of the protonated anion is wave a of curve A, Figure 3.

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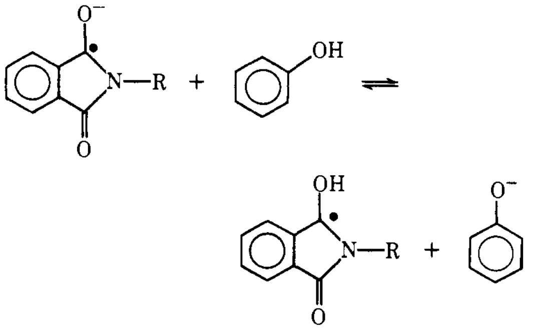
(11) R. S. Nicholson and I. Shain, *Anal. Chem.*, **36**, 706 (1964).

(12) R. S. Nicholson, *ibid.*, **38**, 1406 (1966).

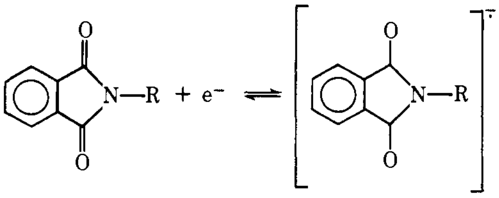
(13) M. E. Peover in "Electroanalytical Chemistry," Vol. II, A. J. Bard, Ed., Marcel Dekker, New York, N. Y., 1967, Chapter 1.

(14) J. L. Sadler and A. J. Bard, *J. Amer. Chem. Soc.*, **90**, 1979 (1968).

(15) P. H. Given and M. E. Peover, *J. Chem. Soc.*, 385 (1960).


(1)

As is expected from eq 1, an increase in the phenol concentration results in an increase in the height of wave a at the expense of the height of wave c which is the original wave corresponding to the reduction of the anion to the dianion. The new wave b increases with increasing phenol concentration. This rather sharp wave is very characteristic of the reduction wave observed for N-phenyl-3-hydroxyphthalimidine. Curve C of Figure 3 shows that the hydroxyphthalimidine might very well be a reduction product of N-phenylphthalimide under conditions where a proton source is available. A reasonable mechanism which is consistent with the above discussion can be written as eq 2–8 where HS denotes any proton source. The keto–enol tautomerism of eq 5, 6, and 7 is an interesting aspect of this reaction. The 1,4-dihydroxy reduction products of 2-phenylindandione-1,3 and anthraquinone are known to undergo this type of tautomeric equilibrium.[16,17] The phthalimide dianion upon protonation could then tautomerize (eq 5 and 6). Alternatively, the dianion could fully protonate and then undergo tautomerization. Electrolysis of N-phenylphthalimide in the presence of acetic anhydride in an attempt to trap any transient anionic intermediates resulted in isolation of only acetylated derivatives of the product of the overall reduction process. The new cathodic wave seen on the second scan of curve B, Figure 2, may be the reduction process corresponding to further reduction of the anion (eq 7).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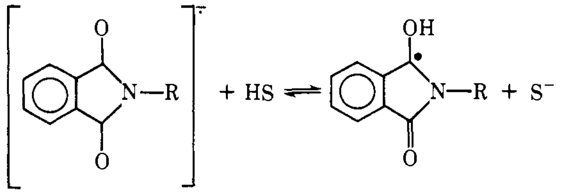
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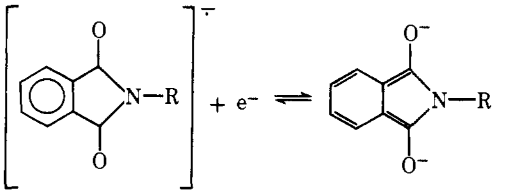
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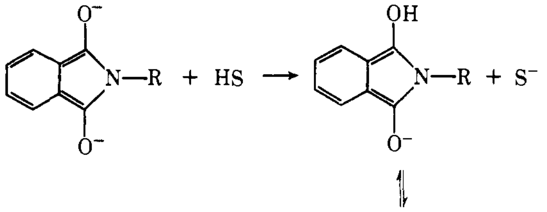
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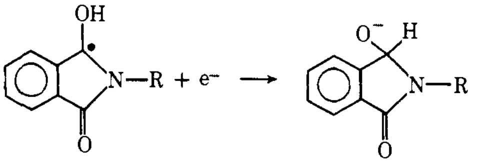
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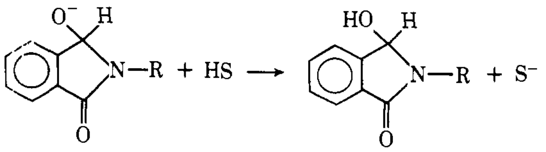
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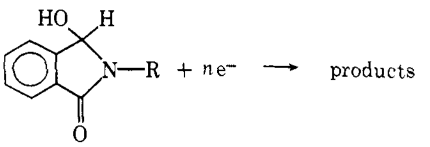
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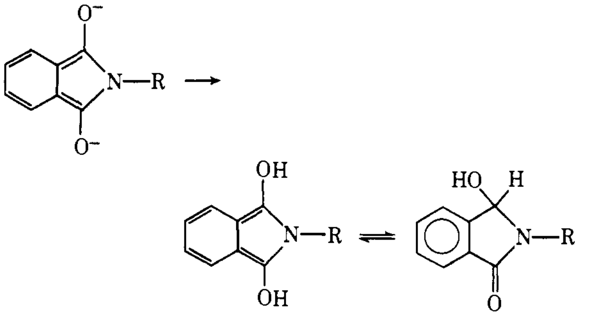
(9)

Phthalimide. The electrochemistry of phthalimide is complicated due to the acidity of the nitrogen proton ($pK_a = 6.96$).[18] Thus, the electrochemical characteristics of phthalimide resemble those of the substituted compounds in the presence of an added proton source. The complex nature of the reduction of phthalimide is seen in the cyclic polarogram shown in Figure 4. Five cathodic processes are evident. The initial reduction has been shown to produce the phthalimide anion.[8,19] By analogy to the N-methyl and N-phenyl compounds, wave 4 which occurs at *ca.* -2.14 V involves reduction of the anion to the dianion. The cathodic wave 5 and the corresponding anodic wave 6 arise from a reduction product of phthalimide. The basis for this assignment is as follows. The cyclic polarogram for this system is curve A of Figure 4. Reversal of the potential scan at -2.44 V results in the observation of only a single anodic wave. If, before reversal, the potential is held at -2.44 V and then a cyclic polarogram is run, only waves 5 and 6 are observed. This is seen as curve B, Figure 4. Previous work has shown that the phthalimide anion reacts with phthalimide to produce several forms of the radical anion.[8,19] The free radical **5** and the enolic form of the anion **6**

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[16] I. K. Tutane and Ya. P. Stradyn, *Elektrokhimiya*, **4**, 352 (1968).

[17] (a) A. D. Broadbent and E. F. Sommermann, *J. Chem. Soc. B*, 1144 (1968); (b) K. Bredereck, F. Sommermann, and M. Diamantoglou, *Chem. Ber.*, **102**, 1053 (1969).

[18] J. K. Wood, *J. Chem. Soc.*, **89**, 1831 (1906).

[19] P. H. Rieger, Ph.D. Thesis, Columbia University, New York, N. Y., 1961.

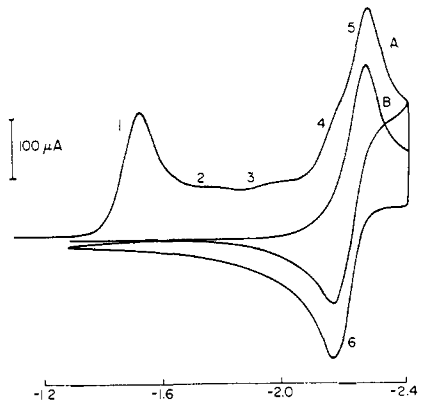
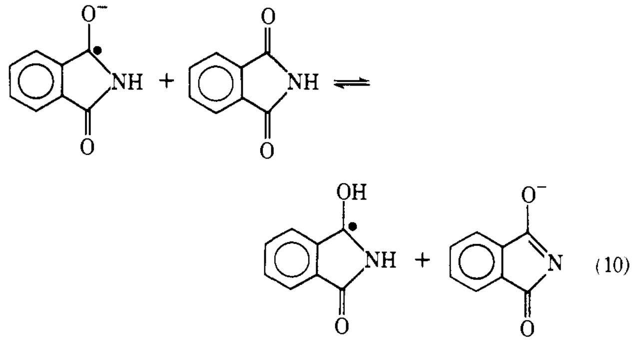


Figure 4. Cyclic voltammetry of phthalimide (1) in DMF with 0.1 *M* TEAP at a Hg-plated Pt button electrode. Curve A shows one cycle with reversal at *ca.* −2.4 V. Curve B shows two cycles with potential scan held at *ca.* −2.4 V after the initial cathodic sweep. See text for details.

have been observed by these workers by their esr spectra. Waves 2 and 3 of Figure 4 are undoubtedly accounted for as the reduction of **5** and **6**. The reduction processes 2, 3, and 4 quite obviously lead to the same product which is further reduced at wave 5.



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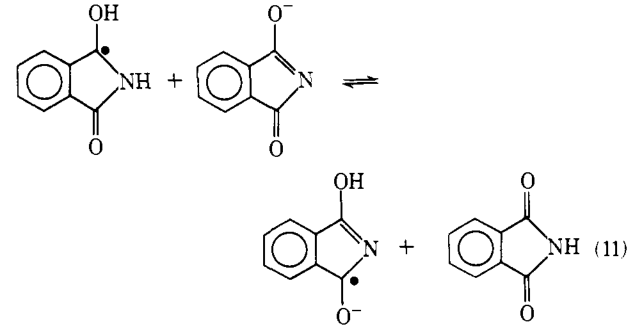
(10)



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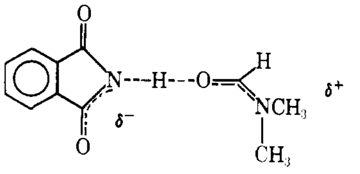
(11)

Although this interpretation of the reduction mechanism of phthalimide is consistent with the electrochemical data and the products isolated (see Product Studies) a rigorous kinetic analysis has not been accomplished to verify our conclusions. There is little doubt that the initial cathodic reduction process corresponds to radical anion formation as has been discussed previously. However, the fact that the $it^{1/2}/C$ constant obtained for phthalimide (Table II) is considerably lower than for the *N*-methyl or *N*-phenyl derivatives deserves comment. The constancy of the $it^{1/2}$ values for the first reduction process indicates that the electron transfer reaction which results in radical anion formation is a diffusion-controlled process. This phenomenon is not particular to the Hg-plated Pt button electrode. The data shown in Table III indicate similar results for Pt and the dropping mercury electrode (dme). It is not unreasonable to suggest that the high relative acidity of phthalimide leads to greater solvation by DMF and an effective decrease in the diffusion coefficient. The considerably more negative reduction potential of phthalimide with respect to the *N*-methyl and *N*-phenyl compounds is consistent with this hypothesis and suggests that solvation may induce some anionic character to the phthalimide system by structures such as **7**.

Table III. Relative Phthalimide Diffusion Currents[a]

Compound	Hg-plated Pt[b]	Pt[b]	DME[c]
Phthalimide	1.0	1.0	1.0
N-Methyl-phthalimide	1.82	1.74	1.64
N-Phenyl-phthalimide	1.36	1.52	1.13

[a] 0.1 *M* TEAP in DMF. [b] Ratio of chronoamperometric constants of N-substituted phthalimide to phthalimide. [c] Ratio of diffusion currents obtained by dropping mercury polarography.



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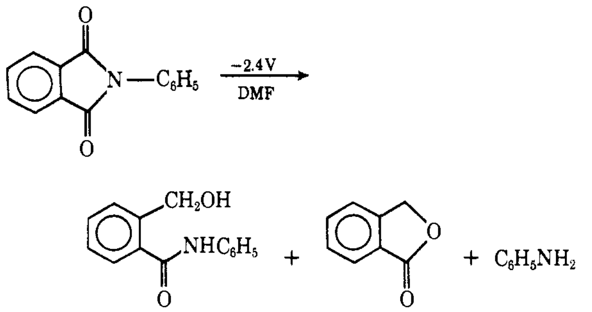
The net result of the phthalimide acidity is that the increased proton availability assists electron transfer. Therefore, on chronoamperometric time scales of *ca.* 10 sec, reduction of phthalimide at −2.6 V results in a four-electron process (Table II), whereas a two-electron process is observed with the N-substituted derivatives.

Phthalimide Related Compounds. *N*-Phenyl-3-hydroxyphthalimidine, *o*-hydroxymethylbenzanilide, and phthalide were included in this study because of their involvement in the overall electrochemistry of *N*-phenylphthalimide. These compounds all exhibit only one reduction wave by cyclic voltammetry under these conditions. The half-peak potentials for these reductions are given in Table I. The hydroxyphthalimidine and the benzanilide show no oxidation wave corresponding to reoxidation of the products of the reduction. Phthalide does show some reoxidation current which decreases as a function of decreasing scan rate. The products of these reactions were not investigated in this study.

Product Studies

Previous studies have shown that electrolytic reduction of phthalimides in nonaqueous solvents at potentials beyond the first reduction process leads to stable solutions of the corresponding anion radicals.[8,19] In the present study we have characterized the products formed at potentials past the second reduction process. Electrolyses were carried out under controlled potential conditions in a divided compartment cell at a mercury pool electrode. Typical electrolyses and isolation techniques are given in the Experimental Section.

***N*-Phenylphthalimide.** Electrolytic reduction of *N*-phenylphthalimide at −2.4 V *vs.* sce resulted in the isolation of *o*-hydroxymethylbenzanilide, phthalide, and aniline. Electrolysis of the *N*-phenyl compound with an equimolar concentration of phenol as a proton source resulted in an increase in the yield of benzanilide and a decrease in phthalide. In an attempt to trap any transient anionic intermediates, electrolyses were conducted in the presence of acetic anhydride.[20] These experiments yielded an oily material which could not be crystallized. The nmr spectrum in DMSO-d_6 of this material was identical with that of *O*-acetyl-*o*-hydroxymethylbenzanilide (**8**) prepared by acetylation of *o*-hydroxymethylbenzanilide.



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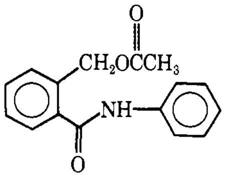

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Phthalimide. Reduction of phthalimide at −2,6 V produced phthalide in 60% yield. The products and yields of these reactions are summarized in Table IV.

Table IV. Nonaqueous Electrolytic Reduction of Phthalimides[a]

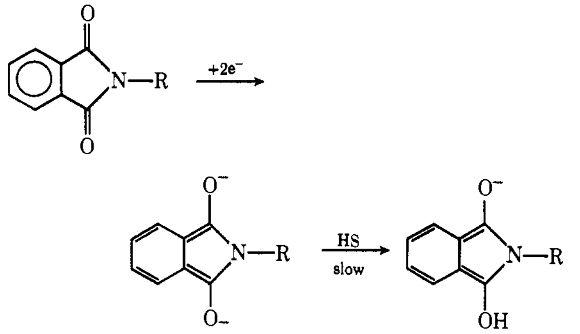
Reactants	Product(s)	Yield, %
Phthalimide	Phthalide	60
N-Phenylphthalimide	*o*-Hydroxymethyl-benzanilide	15
	Phthalide	35
N-Phenylphthalimide and phenol	*o*-Hydroxymethyl-benzanilide	34
	Phthalide	19
N-Phenylphthalimide and acetic anhydride	*O*-Acetyl-*o*-hydroxy-methylbenzanilide	67

[a] All reductions were in DMF with 0.1 *M* TEAP as supporting electrolyte. For cathode potentials, see text.

Discussion

The intermediacy of free radicals and radical ions in electrolytic reductions of phthalimides has been well documented. This discussion will therefore be restricted to cathode potentials cathodic of the second electron transfer process of the various phthalimides (see Table I). Our particular interest in this reduction was concerned with *N*-arylphthalimides and therefore the emphasis has been placed on the elucidation of the mechanism and products of the reduction of *N*-phenylphthalimide. The experimental results clearly suggest the following mechanism.

The initially formed dianion reacts slowly with the solvent or electrolyte producing a protonated species. We would like to suggest on the basis of the cyclic voltammetry that tautomerization and rapid further protonation produces 3-hydroxyphthalimidine at this point. The electroanalytical data show that the hydroxy compound is reducible at these potentials. It is reasonable to assume that this compound is in equilibrium with the open aldehyde.[21]



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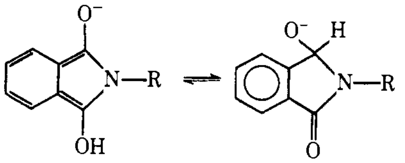

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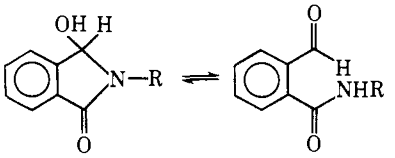

(15)

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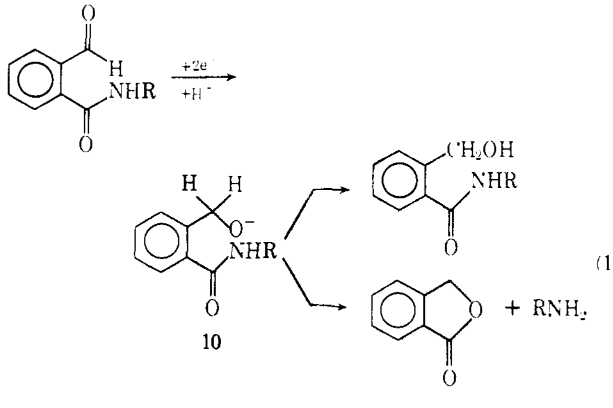
The aldehydes of the phthalic acid series are known to reduce at low potentials.[22] Reduction of the *o*-formylbenzamide **9** would lead to an intermediate **10** which would either protonate to form *o*-hydroxymethylbenzamide or cyclize with subsequent formation of phthalide



(16)

Equation 16 is consistent with the effect phenol has on the final product distribution. As would be expected from this mechanism, electrolysis of *N*-phenylphthalimide in the presence of a proton source leads to an increase in the protonated product, *o*-hydroxymethylbenzanilide and a decrease in phthalide (Table III).

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(20) P. H. Given, M. F. Peover, and J. Schoen, *J. Chem. Soc.*, 2674 (1958).

(21) T. C. Bruice and S. Benkovic, "Bioorganic Mechanisms," W. A. Benjamin, New York, N. Y., 1966.

(22) L. Holleck and H. Marsen, *Z. Elektrochem.*, 57, 944 (1953).

The results of the reactions in the presence of acetic anhydride provide some interesting data for speculation. It is not possible to say for certain whether or not the predominant product isolated, *O*-acetyl-*o*-hydroxymethylbenzanilide, results from reaction with *o*-hydroxymethylbenzanilide or with the anionic intermediate **10**. However, the fact that no aniline or phthalide was observed in the reaction is indication that the reaction of acetic anhydride with **10** is faster than intramolecular cyclization and also provides evidence for the existence of **10** as an intermediate.

In the case of the phthalimide reduction, we were not able to isolate any material corresponding to *o*-hydroxymethylbenzamide. This is not surprising since this material is known to expel rapidly ammonia and close to phthalide upon heating,[23] a necessary requisite for solvent removal under our conditions.

Experimental Section

Solvent and Electrolyte. Purification of DMF was accomplished in the following manner. Reagent grade DMF (Matheson Coleman and Bell) was stirred over CaH_2 for at least 2 days prior to distillation. The solvent was then twice distilled under reduced pressure through a 3-ft packed column of glass beads. The first distillation was from CaH_2 and the final distillation was from phthalic anhydride. The temperature of the distillation never exceeded 90° to avoid decomposition. Tetraethylammonium perchlorate (TEAP) was prepared from tetraethylammonium hydroxide and perchloric acid, recrystallized from water, and dried in a vacuum oven at 100° for several days. All electrolysis solutions contained 0.1 *M* TEAP.

Apparatus. Electroanalytical measurements were made on a conventional multipurpose instrument utilizing operational amplifier circuitry.[24] A Hewlett-Packard Model 7030A X-Y recorder was used for recording cyclic voltammetric and chronoamperometric data. The three-electrode cell used for these measurements was of conventional design. A Luggin capillary was used in conjunction with the aqueous saturated calomel electrode (sce). A Beckman platinum button electrode, no. 39273, was plated with mercury and utilized as the working electrode. This electrode had a geometric area of *ca.* 0.22 cm². Reproducibility of the surface of this electrode was excellent and measurements were reproducible within 0.5%. All solutions were purged with nitrogen which was prepurified by conventional methods and presaturated with DMF. Solutions were kept under a blanket of nitrogen while measurements were being made.

For controlled potential electrolyses, an instrument based on Kepco power supplies was utilized. This instrument consists of a combination of Kepco KS 120-5M and OPS 100-0.2 power supplies. The cell used for the product studies contained approximately 200 ml of solvent in the cathode compartment and 100 ml in the anode compartment. A mercury pool electrode of ring-shaped design to avoid undue potential drop was used and had an area of *ca.* 20 cm². Argon was continuously bubbled through the solution during the course of the reaction and stirring was accomplished by a mechanical stirrer.

Chemicals. *N*-Phenylphthalimide, *N*-methylphthalimide, and phthalimide were Eastman White Label. These compounds were recrystallized from ethanol and their melting points agreed with those in the literature. *N*-Phenyl-3-hydroxyphthalimidine was prepared by reduction of *N*-phenylphthalimide with sodium borohydride and recrystallized from ethanol.[7] Phthalide was Eastman technical quality, which was purified by sublimation, mp 72–73°. *o*-Hydroxymethylbenzanilide was prepared electrolytically from *N*-phenylphthalimide as described below.

O-Acetyl-*o*-hydroxymethylbenzanilide was prepared in the following manner. *o*-Hydroxymethylbenzanilide (0.4 g) was dissolved in 10 ml of dry pyridine, 1 ml of acetic anhydride was added, and the mixture was allowed to stir at room temperature for 1 hr. Removal of excess acetic anhydride and pyridine yielded a crystalline residue which was recrystallized from benzene before yielding colorless, fluffy needles, mp 104–105°.

Anal. Calcd for $C_{16}H_{15}NO_3$: C, 71.3; H, 5.58; N, 5.21. Found: C, 71.2; H, 5.55; N, 5.1.

Electrolyses. Typical electrolyses are summarized below.

Electrochemical Reduction of *N*-Phenylphthalimide. A solution of 3 g of *N*-phenylphthalimide and 10 g of TEAP in 200 ml of DMF was electrolyzed at a cathode potential of −2.4 V. The anode compartment contained 100 ml of DMF and 5 g of TEAP. The electrolysis was discontinued after the current decayed to 10% of the initial value. The solution changed from initially clear to green, to yellow, and finally to red. Integration of the current–time curves indicated that from 3.5 to 4.0 electrons were transferred per mole of phthalimide. The solution was transferred to a 500-ml round-bottomed flask and evaporated on a rotary evaporator. Upon heating the red solution immediately turned yellow-brown. The residue was dissolved in 75 ml of absolute alcohol. Addition of ether precipitated the TEAP. Evaporation of the filtrate yielded an oily residue which was stirred with 100 ml of water. The resultant milky solution was extracted with eight 50-ml portions of ether. Removal of the ether left 1.65 g of residue which was a mixture of starting material and *o*-hydroxymethylbenzanilide. Recrystallization from benzene yielded 0.38 g of the benzanilide, mp 143–144°.

Anal. Calcd for $C_{14}H_{13}NO_2$: C, 73.99; H, 5.77; N, 6.16; O, 14.08. Found: C, 73.96; H, 5.71; N, 6.06; O, 14.03.

The water was removed from the aqueous layer above and the residue was dissolved in 100 ml of benzene. Aniline was isolated by extraction with three 100-ml portions of 1 *M* HCl. After neutralization with 50% NaOH and extraction with benzene, 0.55 g of aniline was found. The benzene layer from which the aniline was extracted was dried with Na_2SO_4 and the benzene removed which resulted in the isolation of 0.74 g of phthalide, mp 73°.

Electrochemical Reduction of *N*-Phenylphthalimide in the Presence of Phenol. Phthalimide (2 g), 0.84 g of phenol, and 10 g of TEAP in 200 ml of DMF was electrolyzed for 4.5 hr at −2.4 V. Evaporation of the DMF yielded a brown residue. Upon addition of 125 ml of H_2O, 0.53 g of *o*-hydroxymethylbenzanilide precipitated. After filtering, the filtrate was adjusted to pH 13 with 1 *M* NaOH and 0.122 g of aniline was extracted with seven 50-ml portions of benzene. The pH of the aqueous layer was lowered to 7 with concentrated $HClO_4$ and 0.684 g of phenol was extracted with five 50-ml portions of benzene. Subsequent adjustment of the remaining aqueous solution to pH 1 and extraction with benzene yielded 0.45 g of *N*-phenylphthalimide and 0.18 g of phthalide.

Electrochemical Reduction of *N*-Phenylphthalimide in the Presence of Acetic Anhydride. *N*-Phenylphthalimide (3 g), 10 ml of acetic anhydride, and 10 g of TEAP was electrolyzed for 5 hr at −2.4 V. Evaporation of the DMF left a dark brown oily residue. This residue was dissolved in 100 ml of 1 *M* $NaHCO_3$ and extracted with ether. Removal of the ether left a yellow oil (1.9 g) which could not be crystallized.

The structure of this material was assigned to *O*-acetyl-*o*-hydroxymethylbenzanilide by comparison of the nmr spectrum with the authentic compound (see Product Studies).

Electrochemical Reduction of Phthalimide. Phthalimide (3 g) and 10 g of TEAP in 200 ml of DMF were electrolyzed at a cathode potential of −2.45 V for 6 hr. The anode compartment contained 5 g of TEAP in 100 ml of DMF. The residue obtained upon removal of the DMF was dissolved in 150 ml of H_2O and adjusted to pH 1 with $HClO_4$. Extraction with five 50-ml portions of benzene yielded 1.66 g of phthalide.

Acknowledgment. We wish to thank Dr. G. P. Rizzi for the preparation of *N*-phenyl-3-hydroxyphthalimidine and *O*-acetyl-*o*-hydroxymethylbenzanilide. We wish also to thank Professor A. J. Bard and Dr. S. W. Feldberg for their helpful suggestions. The technical assistance of Mr. Reinhold A. Lampe is gratefully acknowledged.

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(23) A. Reissert, *Ber.*, 46, 1484 (1913).

(24) We are grateful to Dr. M. D. Hawley of Kansas State University for design of the circuit and to C. W. Gausmann and D. L. Maloney of our Research Instrument Shop for assistance in construction of the instrument.